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Geochemical Controls on Shale Groundwaters: Results of Reaction Path Modeling

K. L. Von Damm
A. J. VandenBrook

Environmental Sciences Division
Publication No. 3173

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A05 Microfiche A01

ORNL/TM-10944

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Date Published--March 1989

Prepared for the
Office of Civilian Radioactive Waste Management
(DB 01 04 01 0)

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

CONTENTS

	Page
LIST OF FIGURES	v
LIST OF TABLES	vii
ABSTRACT	ix
INTRODUCTION	1
METHODS	2
RESULTS	4
Modeling of Illitic Shales	5
Modeling of Smectitic Shales	31
DISCUSSION	66
Comparison of Illitic Cases	66
Comparison of Smectitic Cases	70
Comparison of Illitic to Smectitic Cases	71
CONCLUSIONS	73
ACKNOWLEDGMENTS	75
REFERENCES	77
APPENDIX A. MINERAL NAMES AND CHEMICAL FORMULAS	79

LIST OF FIGURES

Figure		Page
1	Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, CH_4 suppression, pyrite present	11
2	Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, CH_4 suppression, pyrite present.	21
3	Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, no CH_4 suppression, graphite replacing pyrite	28
4	Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, no CH_4 suppression, graphite replacing pyrite	35
5	Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) at T = 10.5°C	43
6	Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) to T = 250°C	50
7	Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) at T = 10.5°C	56
8	Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) to T = 250°C	63

LIST OF TABLES

Table		Page
1	Pumpkin Valley Shale Rock and Groundwater Compositions . .	6
2	Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, CH_4 Suppression, Pyrite Present	8
3	Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, no CH_4 Suppression, Pyrite Present	15
4	Reaction of Pumpkin Valley Shale Groundwater and Rock to T = 250°C, CH_4 Suppression, Pyrite Present	18
5	Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, no CH_4 Suppression, Graphite Replacing Pyrite	25
6	Reaction of Pumpkin Valley Shale Groundwater and Rock to T = 250°C, no CH_4 Suppression, Graphite Replacing Pyrite	32
7	Pierre Shale Rock and Bearpaw Shale Groundwater Compositions	38
8	Reaction of Bearpaw Shale Water and Pierre Shale (Schultz et al.) at T = 10.5°C	40
9	Reaction of Bearpaw Shale Water and Pierre Shale (Schultz et al.) to T = 250°C	47
10	Reaction of Bearpaw Shale Water and Pierre Shale (Lee et al.) at T = 10.5°C	53
11	Reaction of Bearpaw Shale Water and Pierre Shale (Lee et al.) to T = 250°C	60
12	Summary Table of Log Molal Concentrations of Dissolved Elements for all Cases Examined, at Termination of Reaction Progress	67
13	Summary Table of Log Moles of Product Minerals for all Cases Examined, at Termination of Reaction Progress	68

ABSTRACT

VON DAMM, K. L., and A. J. VANDENBROOK. 1988. Geochemical controls on shale groundwaters: Results of reaction path modeling. ORNL/TM-10944. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 90 pp.

The EQ3NR/EQ6 geochemical modeling code was used to simulate the reaction of several shale mineralogies with different groundwater compositions in order to elucidate changes that may occur in both the groundwater compositions, and rock mineralogies and compositions under conditions which may be encountered in a high-level radioactive waste repository. Shales with primarily illitic or smectitic compositions were the focus of this study. The reactions were run at the ambient temperatures of the groundwaters and to temperatures as high as 250°C, the approximate temperature maximum expected in a repository. All modeling assumed that equilibrium was achieved and treated the rock and water assemblage as a closed system. Graphite was used as a proxy mineral for organic matter in the shales. The results show that the presence of even a very small amount of a reducing mineral has a large influence on the redox state of the groundwaters, and that either pyrite or graphite provides essentially the same results, with slight differences in dissolved C, Fe and S concentrations. The thermodynamic data base is inadequate at the present time to fully evaluate the speciation of dissolved carbon, due to the paucity of thermodynamic data for organic compounds. In the illitic cases the groundwaters resulting from interaction at elevated temperatures are acid, while the smectitic cases remain alkaline, although the final equilibrium mineral assemblages are quite similar. At lower temperatures most of the groundwaters remain close to neutral or are alkaline, but the final mineralogies appear to be dependent on the starting mineralogies. Of the minerals which may be important for retarding radionuclides, the zeolites form only in the illitic cases, while smectites and muscovite (which may serve as a proxy for illite) form in most cases.

INTRODUCTION

The chemistry of groundwaters in shales is ultimately controlled by reactions occurring between the groundwaters and the enclosing rocks. The composition of the waters may be influenced by (1) whether equilibrium (or a steady-state) exists between some or all of the phases in the rocks and the waters, (2) the kinetics of reactions occurring between the rocks and the waters, (3) the in situ biota, and (4) the temperature and pressure conditions under which the reactions are occurring. In addition the mineralogy of the rocks, both bulk and possible fracture-lining, and the starting composition of the groundwaters, including pH and redox state, may also exert a strong influence on the observed composition of the groundwaters.

Shales may have a wide range in mineralogy and bulk composition (c.f. Lee et al. 1987) and groundwaters from shales also exhibit a wide range in composition (Von Damm 1987). In order to understand how the chemistry of the groundwaters relates to the chemistry and mineralogy of the enclosing rocks it is necessary to understand the geochemical controls which are important in this rock-water system. Shale groundwaters are of particular interest for the following reasons: (1) shale is a rock type under investigation for potentially hosting high-level nuclear waste (HLW) at several sites world wide, and the groundwater composition will strongly influence waste package stability and radionuclide transport, (2) shales often host economically important mineral deposits, and (3) as shales are the most abundant rock type on the continents they may have a profound overall influence on groundwater compositions in general.

One method of elucidating the controls on groundwater compositions is through the use of geochemical modeling codes such as EQ3NR/EQ6 (Wolery 1983). These computer codes allow the equilibrium state of a groundwater with respect to a rock to be evaluated and also permit reaction path modeling where a groundwater can be "reacted" with a rock and the change in composition and mineralogy of the rock-water system

observed as a function of reaction progress (i.e., time or water:rock mass ratio). The effects of changes in parameters such as the temperature at which the reactions occur can also be evaluated, as can differences in mineralogy, and redox state, for example.

One of the objectives of the Sedimentary Rock Program (SERP) is to examine the properties of sedimentary rocks and coexisting groundwaters with respect to the potential of these systems to host HLW. As part of this program shales have been identified as the sedimentary rock with the best properties for this purpose (Croff et al. 1986). Shales have been further subdivided into 4 generic endmember types based on mineralogy (Brookins and Stow 1986): smectitic (e.g., Pierre Shale), illitic (e.g., Pumpkin Valley and Nolichucky Shales), carbonate-rich (e.g., Green River Shale) and carbonaceous (e.g., Chattanooga Shale).

Several previous reports have examined controls on the groundwater composition based on available field data (Von Damm 1987), and some experimental data on shale-water interactions (Von Damm and Johnson 1987). This study reports results obtained through the use of geochemical modeling codes, in particular EQ3NR/EQ6 (Wolery 1983). The objective was to determine how different representative shale mineralogies and groundwater chemistries would be altered by reaction under conditions representative of both a near field (i.e., high temperature) and far field (i.e., low temperature) HLW repository.

METHODS

The results in this study were obtained using the modeling codes EQ3NR/EQ6, EQ3NR revision 90, EQ6 revision 78, and DATA0 (the thermodynamic data base) revision 46 obtained in December 1986 from the Geochemical Modeling Group at Lawrence Livermore National Laboratory. EQ3NR/EQ6 was used because it (1) contains one of the most complete thermodynamic databases, (2) has high temperature options not available in many of the other modeling codes, (3) has high ionic strength options not available in many of the other modeling codes, (4) is the code which is being used for most of the high level radioactive waste repository work, and (5) is being brought into compliance with quality assurance specifications for repository work. All of the following

results were obtained using the standard low ionic strength version of the codes, which uses the Davies equation to calculate activity coefficients for dissolved species. The mineralogies used were based either on work done for SERP (Lee et al. 1987) or previously published data, and the groundwater compositions are from Von Damm (1987 and unpublished data). As data on the redox state was not available for most of the groundwaters two cases were usually examined: (1) assuming the water was in equilibrium with air (oxidizing), and (2) assuming the water contained dissolved sulfide equal to one-thousandth the amount of dissolved sulfate present (reducing). In addition the formation of methane was suppressed in several of the runs. Although methane should form based on equilibrium thermodynamics, in practice little methane is found due to the extremely slow kinetics of this reaction at low temperatures (Stumm and Morgan 1981). Organic matter is an important constituent of many shales. The form of this organic matter is unknown in many cases (Ho and Meyer 1987), and the thermodynamic data are extremely limited for those compounds which have been identified. For these reasons, graphite was used as a proxy for solid organic matter in the shales. The use of graphite, a pure C compound, omits N, S, and O which may comprise part of the organic matter and, due to their incorporation in functional groups, will affect the overall reactivity of the organic matter. The C in "real" organic matter will also, on average, not be quite as reduced as that in graphite. Some of the few aqueous organic carbon complexes for which data are available are those of acetate, and these are included in the data base.

EQ6 also has the option to include kinetics. The kinetics of dissolution are unknown for many mineral phases, especially in a complex system such as a shale. The kinetics may influence the reaction path, but will not affect the final equilibrium assemblage. For this reason very generalized reaction rates were included such that the relative dissolution rates for carbonates:aluminosilicates: sulfides:silicates(quartz) are 100:20:20:1. No attempt was made to assign relative rates to precipitation reactions.

In any model calculations the results are heavily dependent on the quality of the thermodynamic data, as well as the input data. EQ3NR/EQ6 has one of the most complete data bases available, but for most minerals solid solutions are not incorporated although these are known to occur in nature. The examples below are limited to lower ionic strength solutions as the data available for higher ionic strength solutions are limited. The limited amount of organic data present, the poor quality of the thermodynamic data for some minerals and aqueous species, and the possibility that potentially important species may not be represented all contribute to possible errors.

RESULTS

Of the four endmember type shales only two were modeled extensively, illitic (Pumpkin Valley Shale) and smectitic (Pierre Shale). The carbonate-rich type, as typified by the Green River Shale was not modeled due to the large variety of carbonate minerals found in this formation which are not included in the thermodynamic data base. The effects of carbonate minerals can be seen in some of the other cases modeled. Similarly the carbonaceous type, as typified by the Chattanooga Shale, was also not modeled as organic matter is not specifically included in the data base. The generalized effect of organic matter, modeled as graphite, can be seen in several of the other cases that were examined.

Since shales are relatively impermeable compared to most rock types, the water:rock ratio should be relatively low. EQ6 allows rock, defined on the basis of the number of moles of the minerals it contains, to be titrated into a water. In all the cases modeled the assumption was made that 1000 g of rock were added to this, to achieve a final water:rock ratio of 0.1 on a mass basis. The closed system model was used (i.e., all product minerals were available for back reaction. The reaction progress is monitored as a function of the variable "zi." The initial (e.g., 0) and final values of zi (e.g., 1) are arbitrary, but can be related to the water:rock ratio, to obtain a physically meaningful measure of the extent of reaction. The formulas

of all the minerals mentioned below are given in Appendix A, in the form in which they are included in the data base.

In an HLW repository temperatures close to the waste package may reach temperatures as high as 250°C. For this reason several of the model cases were run at this temperature. In these cases the model was constructed so that the temperature was gradually increased as the rock was added, and the final water:rock ratio of 0.1 was achieved at the point the temperature reached 250°C. Other reaction paths could be examined but the final equilibrium assemblage will be the same, regardless of the path.

Modeling of Illitic Shales

In all cases the illitic shale was represented by a nine mineral approximation of the Pumpkin Valley Shale (PVS). This approximation was based on drill core data for this formation obtained on the Oak Ridge Reservation (C. S. Haase, personal communication, 1987) and is shown in Table 1. The groundwater composition used in the model was based on an analysis of groundwaters sampled from a drill hole on the Oak Ridge Reservation in the PVS at a depth of 560 feet (Table 1). Data from several wells, all of which had been sampled several times, were available. This particular analysis was chosen because (1) the ionic strength was low enough to be modeled (several of the waters have extremely high ionic strengths), (2) it was relatively complete, and (3) it has a composition representative of the other lower ionic strength waters sampled from this formation at this location. Although these groundwaters have not been dated, they are thought to be quite old (based on the high ionic strength, low flow rates, and low permeability of the formation), and may be close to equilibrium with the rock formation. The lowest temperature used in the model is the reported temperature for the groundwater at the time of sampling.

Table 1. Pumpkin Valley Shale Rock and Groundwater Compositions

Shale		
Mineral	Moles in ~10000 g	RRR[a]
Albite	1.33	20
Anorthite	0.539	20
Calcite	9.99	100
K-feldspar	1.80	20
Illite	12.8	20
Kaolinite	2.91	20
Quartz	29.1	1
Pyrite (or graphite)	0.834	20
14A-Ripidolite	0.799	20

Groundwater (DM3a-PV)		
Element or Species	Concentration	
pH	5.6	
T	13.5	°C
Na	4.78×10^{-1}	molal
K	1.03×10^{-3}	molal
Mg	1.27×10^{-2}	molal
Ca	3.61×10^{-2}	molal
Sr	1.41×10^{-3}	molal
Fe	7.03×10^{-4}	molal
Mn	6.01×10^{-5}	molal
Al	4.05×10^{-4}	molal
Si	5.27×10^{-5}	molal
F	1.09×10^{-3}	molal
Cl	5.48×10^{-1}	molal
Br	1.68×10^{-3}	molal
SO_4^{2-}	1.61×10^{-2}	molal
C	3.10×10^{-5}	molal

[a]Relative reaction (dissolution) rate.

[b]Collected 15 December 1986 from 560 ft depth. Assumed to be in equilibrium with air, gibbsite and quartz to provide missing data on redox state, Al, and Si concentrations.

Case 1: Reaction of PVS groundwater and rock at T = 13.5°C. This case was run twice, once with (Case 1a) and once without (Case 1b) the formation of CH_4 suppressed. Although the formation of CH_4 is predicted on the basis of thermodynamic equilibrium, it is kinetically unfavorable at these low temperatures. CH_4 was suppressed to evaluate what effect this might have on the carbonate species. If additional carbonate was formed, this could result in a reduction in the dissolved concentration of certain cations, including radionuclides, in solution (e.g., Sr, ^{90}Sr, Ba, Zn, Fe) due to their precipitation as carbonate minerals.

In Case 1a, in which CH_4 was not permitted to form, the groundwater was initially assumed to be in equilibrium with air (i.e., oxic) but reaction with reduced minerals in the starting assemblage quickly lowered the log f_{O_2} from -1.3 to a final value of -81.0 (Table 2, Fig. 1). The pH decreased initially from 5.6 to 3.3 and then increased steadily to an alkaline value of 8.5. The initial decrease in the pH is probably a result of the oxidation of reduced mineral phases, primarily pyrite, which is accompanied by the production of protons. The alkalinity increased as did the total carbonate and total H_2S, while total SO_4^{2-} decreased during the course of the reaction. Ca, C, and Si increased while Al, Br, F, Fe, K, Mg, Mn, Na, S, and Sr decreased in the dissolved phase. The predominant form of C was CH_3COO^-, followed closely by HCO_3^- and the predominant form of S was as HS^- followed closely by $H_2S(aq)$. A small amount of water was produced during the course of the reaction. The final equilibrium mineral assemblage consisted of calcite, 14A-daphnite, fluorite, kaolinite, laumontite, muscovite, paragonite, pyrite, quartz, strontianite, and Reykjanes- and Ca-smectite. In addition, celestite, ordered dolomite, hematite, pyrolusite, and Na-smectite were also stable during the reaction progress. The final water:rock ratio was 0.16, slightly greater than the 0.1 ratio desired. This is due to the saturation of one or more of the reactant minerals prior to the completion of the reaction progress, preventing the total dissolution of these phases.

Table 2a. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, CH_4 Suppression, Pyrite Present.
Log molal concentrations of dissolved elements.

Log zi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Br	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	Si	S	Sr
-999.00	13.5	1.01	3.00	-1.28	1.043	-7.55	-4.51	-1.80	-141.85	-3.39	-2.77	-2.77	-1.44	-0.262	-3.01	-5.51	-4.51	-2.99	-1.89	-4.77	-0.320	-4.28	-1.80	-2.98
-6.00	13.5	1.01	3.49	-4.10	0.975	-6.47	-3.88	-1.80	-136.69	-3.21	-2.77	-2.77	-1.44	-0.262	-2.96	-7.53	-3.88	-2.97	-1.89	-4.33	-0.320	-4.28	-1.80	-2.98
-5.90	13.5	1.01	4.19	-45.70	0.343	-5.68	-3.81	-1.80	-54.19	-3.18	-2.77	-2.77	-1.44	-0.262	-2.96	-4.25	-3.81	-2.97	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.65	13.5	1.01	5.33	-60.32	0.071	-4.43	-3.59	-1.80	-26.08	-3.41	-2.77	-2.77	-1.44	-0.262	-3.06	-3.40	-3.59	-2.96	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.50	13.5	1.01	5.57	-63.38	0.014	-4.11	-3.46	-1.80	-20.19	-4.12	-2.77	-2.77	-1.44	-0.262	-3.63	-3.15	-3.46	-2.95	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.46	13.5	1.01	6.10	-68.28	-0.086	-3.72	-3.42	-1.80	-10.95	-5.73	-2.77	-2.77	-1.44	-0.262	-4.09	-3.09	-3.42	-2.94	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.20	13.5	1.01	6.32	-68.52	-0.103	-3.39	-3.19	-1.80	-10.67	-6.39	-2.77	-2.77	-1.44	-0.262	-4.11	-3.51	-3.19	-2.91	-1.88	-4.22	-0.320	-4.28	-1.80	-2.98
-5.03	13.5	1.01	6.51	-68.73	-0.116	-3.51	-3.37	-1.79	-10.44	-6.94	-2.77	-2.77	-1.44	-0.262	-4.12	-3.87	-3.37	-2.88	-1.87	-4.22	-0.320	-4.28	-1.79	-3.05
-5.00	13.5	1.01	6.59	-68.82	-0.122	-3.53	-3.41	-1.79	-10.34	-7.16	-2.77	-2.77	-1.43	-0.262	-4.12	-4.03	-3.41	-2.87	-1.87	-4.22	-0.320	-4.28	-1.79	-3.11
-5.00	13.5	1.01	6.60	-68.82	-0.123	-3.53	-3.41	-1.79	-10.34	-7.17	-2.77	-2.77	-1.43	-0.262	-4.12	-4.03	-3.41	-2.88	-1.87	-4.22	-0.320	-4.28	-1.79	-3.11
-4.79	13.5	1.01	7.18	-69.48	-0.165	-3.43	-3.40	-1.79	-9.62	-7.73	-2.77	-2.77	-1.43	-0.262	-4.12	-5.14	-3.40	-3.46	-1.86	-4.22	-0.320	-4.27	-1.79	-3.80
-4.61	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.79	-9.62	-7.73	-2.77	-2.77	-1.42	-0.262	-4.13	-5.14	-2.96	-3.46	-1.87	-4.26	-0.320	-4.27	-1.79	-4.24
-4.50	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.79	-9.62	-7.72	-2.77	-2.77	-1.42	-0.262	-4.13	-5.15	-2.96	-3.46	-1.88	-4.29	-0.320	-4.27	-1.79	-4.24
-4.00	13.5	1.01	7.21	-69.52	-0.167	-2.98	-2.95	-1.80	-9.58	-7.71	-2.77	-2.77	-1.39	-0.262	-4.16	-5.20	-2.95	-3.49	-1.99	-4.70	-0.320	-4.27	-1.80	-4.28
-3.69	13.5	1.01	7.88	-70.30	-0.217	-3.45	-3.45	-1.81	-8.69	-7.10	-2.77	-2.77	-1.33	-0.262	-4.21	-6.60	-3.45	-4.16	-2.41	-228.23	-0.320	-4.25	-1.81	-4.47
-3.50	13.5	1.01	7.90	-70.34	-0.218	-3.46	-3.47	-1.83	-8.64	-7.09	-2.77	-2.77	-1.34	-0.262	-4.21	-6.67	-3.47	-4.18	-2.42	-231.57	-0.320	-4.25	-1.83	-4.47
-3.24	13.5	1.01	7.91	-70.38	-0.219	-3.46	-3.47	-1.87	-8.61	-7.08	-2.77	-2.77	-1.35	-0.262	-4.20	-6.71	-3.47	-4.19	-2.43	-232.58	-0.319	-4.25	-1.87	-4.49
-3.16	13.5	1.01	8.15	-70.66	-0.237	-3.70	-3.72	-1.89	-8.32	-6.84	-2.77	-2.77	-1.33	-0.262	-4.23	-7.17	-3.72	-4.43	-2.94	-268.43	-0.320	-4.23	-1.89	-4.47
-3.00	13.5	1.01	8.16	-70.70	-0.238	-3.77	-3.79	-1.95	-8.30	-6.83	-2.77	-2.77	-1.28	-0.262	-4.25	-7.18	-3.79	-4.44	-2.98	-274.54	-0.334	-4.23	-1.95	-4.41
-2.51	13.5	1.01	8.27	-78.56	-0.356	-4.11	-4.16	-8.39	-7.22	-6.72	-2.78	-2.78	-1.03	-0.263	-4.37	-5.44	-4.16	-4.56	-3.23	-371.64	-0.447	-4.22	-7.19	-4.17
-2.50	13.5	1.01	8.28	-78.57	-0.357	-4.11	-4.17	-8.39	-7.21	-6.72	-2.78	-2.78	-1.02	-0.263	-4.37	-5.45	-4.17	-4.56	-3.23	-372.77	-0.451	-4.22	-7.18	-4.16
-2.21	13.5	1.01	8.44	-78.93	-0.371	-4.37	-4.49	-8.30	-6.96	-6.56	-2.78	-2.78	-0.82	-0.265	-4.45	-5.78	-4.49	-4.72	-3.53	-409.47	-0.614	-4.21	-6.94	-3.95
-2.07	13.5	1.01	8.44	-79.14	-0.374	-4.37	-4.49	-8.25	-6.90	-6.55	-2.78	-2.78	-0.82	-0.266	-4.45	-5.79	-4.49	-4.73	-3.52	-409.66	-0.617	-4.21	-6.88	-3.95
-2.01	13.5	1.01	8.52	-79.31	-0.381	-4.43	-4.60	-8.21	-6.78	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-5.93	-4.60	-4.80	-3.68	-420.08	-0.690	-4.20	-6.77	-3.90
-2.00	13.5	1.01	8.52	-79.33	-0.381	-4.43	-4.60	-8.20	-6.78	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-5.93	-4.60	-4.80	-3.68	-420.02	-0.690	-4.20	-6.76	-3.90
-1.57	13.5	1.01	8.51	-80.07	-0.392	-4.40	-4.50	-8.02	-6.60	-6.48	-2.78	-2.78	-0.77	-0.265	-4.47	-5.93	-4.50	-4.80	-3.66	-416.08	-0.689	-4.21	-6.58	-3.90
-1.50	13.5	1.01	8.52	-80.20	-0.393	-4.37	-4.44	-7.98	-6.56	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-5.93	-4.44	-4.80	-3.66	-415.20	-0.690	-4.20	-6.55	-3.90
-1.40	13.5	1.01	8.52	-80.39	-0.396	-4.30	-4.28	-7.94	-6.51	-6.48	-2.78	-2.78	-0.78	-0.272	-4.46	-5.94	-4.28	-4.80	-3.66	-413.84	-0.691	-4.20	-6.50	-3.90
-1.18	13.5	1.01	8.52	-80.43	-0.397	-4.27	-4.24	-7.93	-6.50	-6.48	-2.79	-2.79	-0.79	-0.279	-4.46	-5.95	-4.24	-4.81	-3.67	-413.53	-0.695	-4.20	-6.49	-3.91
-1.05	13.5	1.01	8.52	-80.46	-0.397	-4.25	-4.19	-7.92	-6.49	-6.48	-2.80	-2.80	-0.79	-0.282	-4.46	-5.95	-4.19	-4.81	-3.67	-413.27	-0.696	-4.20	-6.48	-3.92
-1.00	13.5	1.01	8.52	-80.48	-0.398	-4.24	-4.18	-7.92	-6.49	-6.48	-2.80	-2.80	-0.79	-0.282	-4.46	-5.95	-4.18	-4.81	-3.67	-413.17	-0.696	-4.20	-6.47	-3.92
-0.50	13.5	1.01	8.52	-80.73	-0.401	-3.98	-3.79	-7.85	-6.43	-6.48	-2.79	-2.79	-0.79	-0.279	-4.46	-5.95	-3.79	-4.81	-3.66	-411.16	-0.695	-4.20	-6.41	-3.91
-0.19	13.5	1.01	8.52	-81.01	-0.405	-3.56	-3.30	-7.78	-6.36	-6.48	-2.79	-2.79	-0.78	-0.275	-4.46	-5.94	-3.30	-4.80	-3.66	-408.96	-0.693	-4.20	-6.34	-3.91
-0.19	13.5	1.01	8.52	-81.01	-0.405	-3.56	-3.29	-7.78	-6.36	-6.48	-2.79	-2.79	-0.78	-0.275	-4.46	-5.94	-3.29	-4.80	-3.66	-408.96	-0.693	-4.20	-6.34	-3.91
-0.19	13.5	1.01	8.52	-81.01	-0.405	-3.56	-3.29	-7.78	-6.36	-6.48	-2.79	-2.79	-0.78	-0.275	-4.46	-5.94	-3.29	-4.80	-3.66	-408.96	-0.693	-4.20	-6.34	-3.91
-0.19	13.5	1.01	8.52	-81.01	-0.405	-3.56	-3.29	-7.78	-6.36	-6.48	-2.79	-2.79	-0.78	-0.275	-4.46	-5.94	-3.29	-4.80	-3.66	-408.96	-0.693	-4.20	-6.34	-3.91

Table 2b. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, CH_4 Suppression, Pyrite Present.
Log moles of product minerals.

Log xi	Calcite	Celestite	Daphnite -14A	Dolomite -ordered	Fluorite	Hematite	Kaolinite	Laumontite	Muscovite	Paragonite	Pyrite	Pyrolusite	Quartz	Smectite-Reykjanes	Stron-tianite	Ca-smec-tite	Na-smec-tite
-999		-3.45			-4.25	-3.46						-4.37					
-6		-3.45				-3.42						-4.86	1.46				
-5.9031		-3.43				-3.45							1.46				-5.629
-5.6478		-3.43			-3.99		0.464						1.46				-3.647
-5.5		-3.43			-3.37		0.464						1.46				-4.021
-5.4584		-3.43			-3.30		0.464				-0.0789		1.46				-4.287
-5.2032		-3.44			-3.30		0.464				-0.0788		1.46		-5.29		-3.452
-5.0332					-3.30		0.464				-0.0788		1.46		-3.28		-3.300
-5.002					-3.30		0.464		-5.0893		-0.0788		1.46		-3.19		-3.270
-5					-3.30		0.464		-4.7864		-0.0788		1.46		-3.19		-3.268
-4.7889					-3.30		0.464		-2.9200		-0.0788		1.46	-6.07	-2.90		-3.135
-4.6123				-5.31	-3.30		0.464		-2.8394		-0.0788		1.46	-3.26	-2.87		-3.155
-4.5				-3.44	-3.30		0.464		-2.7772		-0.0788		1.46	-3.05	-2.87		-3.138
-4				-2.42	-3.29		0.464		-2.4217		-0.0788		1.46	-2.40	-2.87		-3.001
-3.6861	0.999			-2.03	-3.29		0.464		-2.1323		-0.0786		1.46	-2.22	-2.86		-2.328
-3.5	0.999			-2.18	-3.29		0.464		-1.9625		-0.0785		1.46	-2.22	-2.86		-1.953
-3.2384	1.000				-3.29		0.465		-1.7152		-0.0781		1.46	-2.22	-2.86		-1.578
-3.162	1.000				-3.29		0.465		-1.6411	-4.2153	-0.0780		1.46	-2.22	-2.86		-1.467
-3	1.000				-3.29		0.462		-1.4839	-1.7777	-0.0775		1.46	-2.22	-2.86		-1.303
-2.5111	1.000		-7.465		-3.28		0.442		-1.0024	-0.8917	-0.0747		1.46	-2.22	-2.87		-0.812
-2.5	1.000		-3.196		-3.28		0.441		-0.9913	-0.8782	-0.0747		1.46	-2.22	-2.87		-0.806
-2.2136	1.000		-1.615		-3.28		0.413		-0.7066	-0.5488	-0.0747		1.46	-2.22	-2.89	-1.6664	-0.669
-2.0743	1.000		-1.369		-3.28		0.389		-0.5678	-0.3971	-0.0747		1.47	-2.22	-2.89	-0.5250	
-2.0119	1.000		-1.274		-3.28		0.375	-3.260	-0.5056	-0.3336	-0.0747		1.47	-2.22	-2.89	-0.4684	
-2	1.000		-1.257		-3.28		0.373	-2.325	-0.4937	-0.3285	-0.0747		1.47	-2.22	-2.89	-0.4590	
-1.5694	1.000		-0.719		-3.28		0.272	-0.574	-0.0639	-0.0921	-0.0747		1.47	-2.22	-2.89	-0.0899	
-1.5	1.000		-0.642		-3.28		0.240	-0.609	0.0055	-0.0449	-0.0747		1.47	-2.22	-2.89	-0.0262	
-1.3985	1.000		-0.530		-3.28		0.176	-0.681	0.1069	0.0282	-0.0747		1.48	-2.22	-2.89	0.0682	
-1.1772	1.000		-0.530		-3.28		-0.251	-0.696	0.3281	0.2031	-0.0747		1.51	-2.22	-2.89	0.0885	
-1.0458	1.000		-0.530		-3.28		-0.702	-0.715	0.4595	0.2028	-0.0747		1.53	-2.22	-2.89	0.1057	
-1	1.000		-0.530		-3.28		-0.612	-0.723	0.4772	0.2028	-0.0747		1.53	-2.22	-2.89	0.1128	
-0.5	1.000		-0.530		-3.28		0.089	-0.945	0.7478	0.2030	-0.0747		1.58	-2.22	-2.89	0.2439	
-0.1961	1.000		-0.531		-3.28		0.431	-3.494	0.9766	0.2034	-0.0747		1.64	-2.22	-2.89	0.3870	
-0.19382	1.000		-0.531		-3.28		0.432	-3.796	0.9768	0.2034	-0.0747		1.64	-2.22	-2.89	0.3871	
-0.19382	1.000		-0.531		-3.28		0.432	-3.804	0.9768	0.2034	-0.0747		1.64	-2.22	-2.89	0.3871	
-0.19382	1.000		-0.531		-3.28		0.432	-3.804	0.9768	0.2034	-0.0747		1.64	-2.22	-2.89	0.3871	

Table 2c. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, CH_4 Suppression, Pyrite Present.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	K-feldspar	Albite	Anorthite	Calcite	Kaolinite	Ripidolite -14A	$g^{b}Des^{c}$	$g^{b}Cre^{d}$	$g^{b}Net$	$cm^{3a}Des^{c}$	$cm^{3a}Cre^{d}$	$cm^{3a}Net$	Water:Rock Ratio
-999	-999.00	-999.000	-999.00	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	0.000	0.13	0.13	0.000	0.017	0.017	
-6	-6.00	-4.699	-4.70	-4.699	-4.699	-4.699	-4.00	-4.70	-4.699	0.054	1749.00	1749.00	0.015	660.200	660.200	18497.965
-5.903	-6.00	-4.602	-4.60	-4.602	-4.602	-4.602	-3.90	-4.60	-4.602	0.068	1749.00	1749.00	0.018	660.200	660.200	14801.658
-5.647	-6.00	-4.347	-4.35	-4.347	-4.347	-4.347	-3.65	-4.35	-4.347	0.122	2500.00	2500.00	0.033	949.800	949.800	8223.684
-5.5	-6.00	-4.199	-4.20	-4.199	-4.199	-4.199	-3.50	-4.35	-4.199	0.166	2500.00	2500.00	0.045	949.900	949.800	6020.470
-5.458	-6.00	-4.157	-4.16	-4.157	-4.157	-4.157	-3.46	-4.35	-4.157	0.182	2600.00	2600.00	0.049	949.900	949.800	5503.577
-5.203	-6.00	-3.902	-4.16	-3.902	-3.902	-3.902	-3.20	-4.35	-3.902	0.311	2600.00	2600.00	0.084	949.900	949.800	3216.468
-5.033	-6.00	-3.732	-4.16	-3.732	-3.732	-3.732	-3.03	-4.35	-3.732	0.450	2600.00	2600.00	0.122	949.900	949.800	2221.235
-5.002	-6.00	-3.701	-4.16	-3.701	-3.701	-3.701	-3.00	-4.35	-3.701	0.482	2600.00	2600.00	0.131	949.900	949.800	2073.398
-5	-6.00	-3.699	-4.16	-3.699	-3.699	-3.699	-3.00	-4.35	-3.699	0.484	2600.00	2600.00	0.131	949.900	949.800	2064.410
-4.788	-6.00	-3.488	-4.16	-3.488	-3.488	-3.488	-2.79	-4.35	-3.488	0.775	2601.00	2600.00	0.211	950.000	949.800	1290.156
-4.612	-6.00	-3.311	-4.16	-3.311	-3.311	-3.311	-2.61	-4.35	-3.311	1.154	2601.00	2600.00	0.314	950.000	949.700	866.551
-4.5	-6.00	-3.199	-4.16	-3.199	-3.199	-3.199	-2.50	-4.35	-3.199	1.489	2601.00	2600.00	0.405	950.100	949.700	671.592
-4	-6.00	-2.699	-4.16	-2.699	-2.699	-2.699	-2.00	-4.35	-2.699	4.664	2604.00	2600.00	1.272	950.700	949.400	214.408
-3.686	-6.00	-2.385	-4.16	-2.385	-2.385	-2.385	-1.69	-4.35	-2.385	9.587	3607.00	3598.00	2.615	1320.000	1318.000	104.308
-3.5	-6.00	-2.199	-4.16	-2.199	-2.199	-2.199	-1.69	-4.35	-2.199	13.600	3611.00	3598.00	3.604	1321.000	1318.000	73.529
-3.238	-6.00	-1.937	-4.16	-1.937	-1.937	-1.937	-1.69	-4.35	-1.937	23.120	3621.00	3598.00	5.950	1324.000	1318.000	43.253
-3.162	-6.00	-1.861	-4.16	-1.861	-1.861	-1.861	-1.69	-4.35	-1.861	27.170	3625.00	3598.00	6.968	1325.000	1318.000	36.805
-3	-6.00	-1.699	-4.16	-1.699	-1.699	-1.699	-1.69	-4.35	-1.699	38.510	3636.00	3598.00	9.742	1328.000	1318.000	25.967
-2.511	-6.00	-1.210	-4.16	-1.210	-1.210	-1.210	-1.69	-4.35	-1.210	116.400	3711.00	3596.00	28.430	1347.000	1318.000	8.741
-2.5	-6.00	-1.199	-4.16	-1.199	-1.199	-1.199	-1.69	-4.35	-1.199	117.300	3713.00	3596.00	29.150	1348.000	1318.000	8.525
-2.213	-6.00	-0.913	-4.16	-0.913	-0.913	-0.913	-1.69	-4.35	-0.913	224.800	3817.00	3592.00	55.660	1377.000	1321.000	4.448
-2.074	-6.00	-0.773	-4.16	-0.773	-0.773	-0.773	-1.69	-4.35	-0.773	309.100	3898.00	3589.00	76.420	1399.000	1323.000	3.235
-2.011	-6.00	-0.711	-4.16	-0.711	-0.711	-0.711	-1.69	-4.35	-0.711	356.500	3944.00	3588.00	88.110	1412.000	1324.000	2.805
-2	-6.00	-0.699	-4.16	-0.699	-0.699	-0.699	-1.69	-4.35	-0.699	366.400	3954.00	3588.00	90.560	1415.000	1324.000	2.729
-1.569	-6.00	-0.268	-4.16	-0.268	-0.268	-0.268	-1.69	-4.35	-0.268	983.900	4576.00	3592.00	242.700	1606.000	1364.000	1.016
-1.5	-6.00	-0.199	-4.16	-0.199	-0.199	-0.268	-1.69	-4.35	-0.199	1128.000	4715.00	3587.00	275.200	1644.000	1369.000	0.887
-1.398	-6.00	-0.098	-4.16	-0.098	-0.098	-0.268	-1.69	-4.35	-0.098	1385.000	4963.00	3577.00	333.200	1711.000	1378.000	0.722
-1.177	-6.00	0.124	-4.16	0.124	0.124	-0.268	-1.69	-4.35	-0.098	1876.000	5435.00	3559.00	518.000	1873.000	1355.000	0.533
-1.045	-6.00	0.255	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	2187.000	5739.00	3552.00	634.500	1979.000	1344.000	0.457
-1	-6.00	0.301	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	2264.000	5816.00	3552.00	662.300	2006.000	1344.000	0.442
-0.5	-6.00	0.801	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3924.000	7483.00	3559.00	1263.000	2606.000	1343.000	0.255
-0.194	-6.00	1.107	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6407.000	9976.00	3570.00	2162.000	3503.000	1341.000	0.156
-0.193	-6.00	1.107	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6407.000	9976.00	3570.00	2162.000	3503.000	1341.000	0.156
-0.193	-6.00	1.107	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6407.000	9976.00	3570.00	2162.000	3503.000	1341.000	0.156
-0.193	-6.00	1.107	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6407.000	9976.00	3570.00	2162.000	3503.000	1341.000	0.156

[a] cm^3 = cubic centimeters
[b] g = grams
[c] Des = Destroyed
[d] Cre = Created

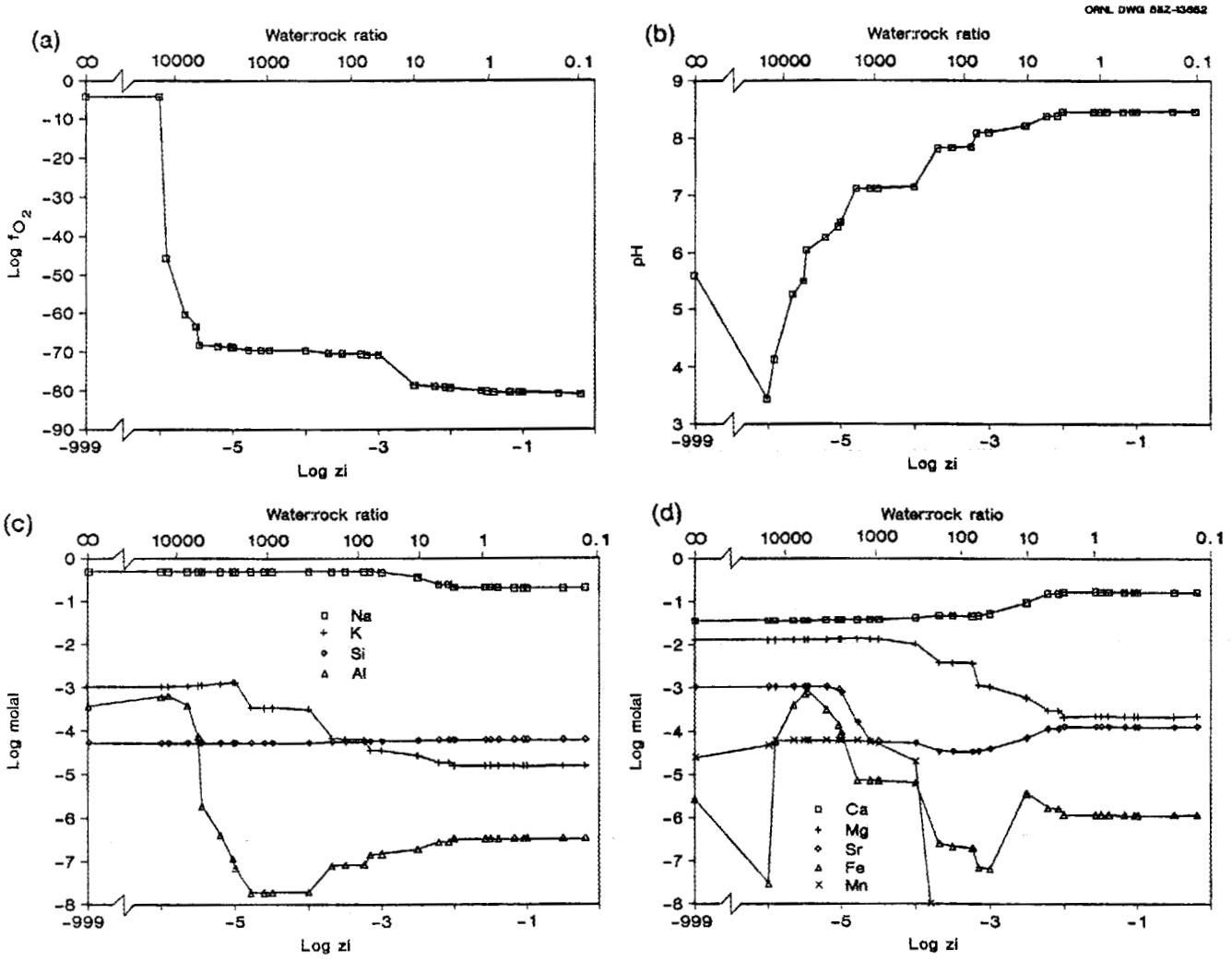

Fig. 1. Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, CH_4 suppression, pyrite present: (a) Log f_{O_2}, (b) pH, (c) Na, K, Si, and Al, (d) Ca, Mg, Sr, Fe, and Mn.

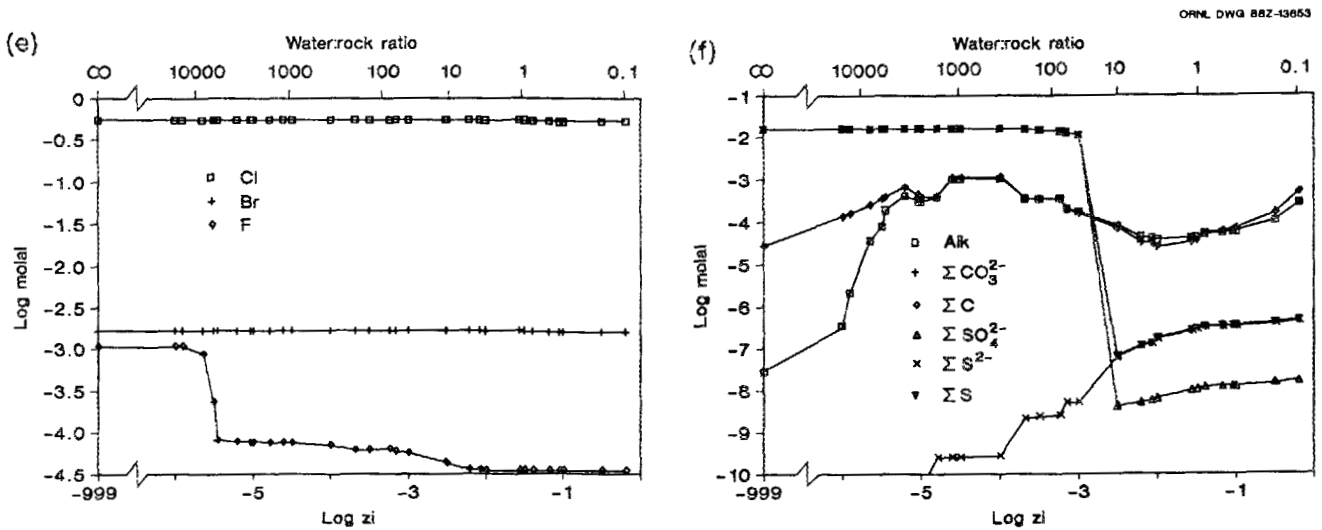

Fig. 1 (continued). Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, CH_4 suppression, pyrite present: (e) Cl, Br, and F, (f) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

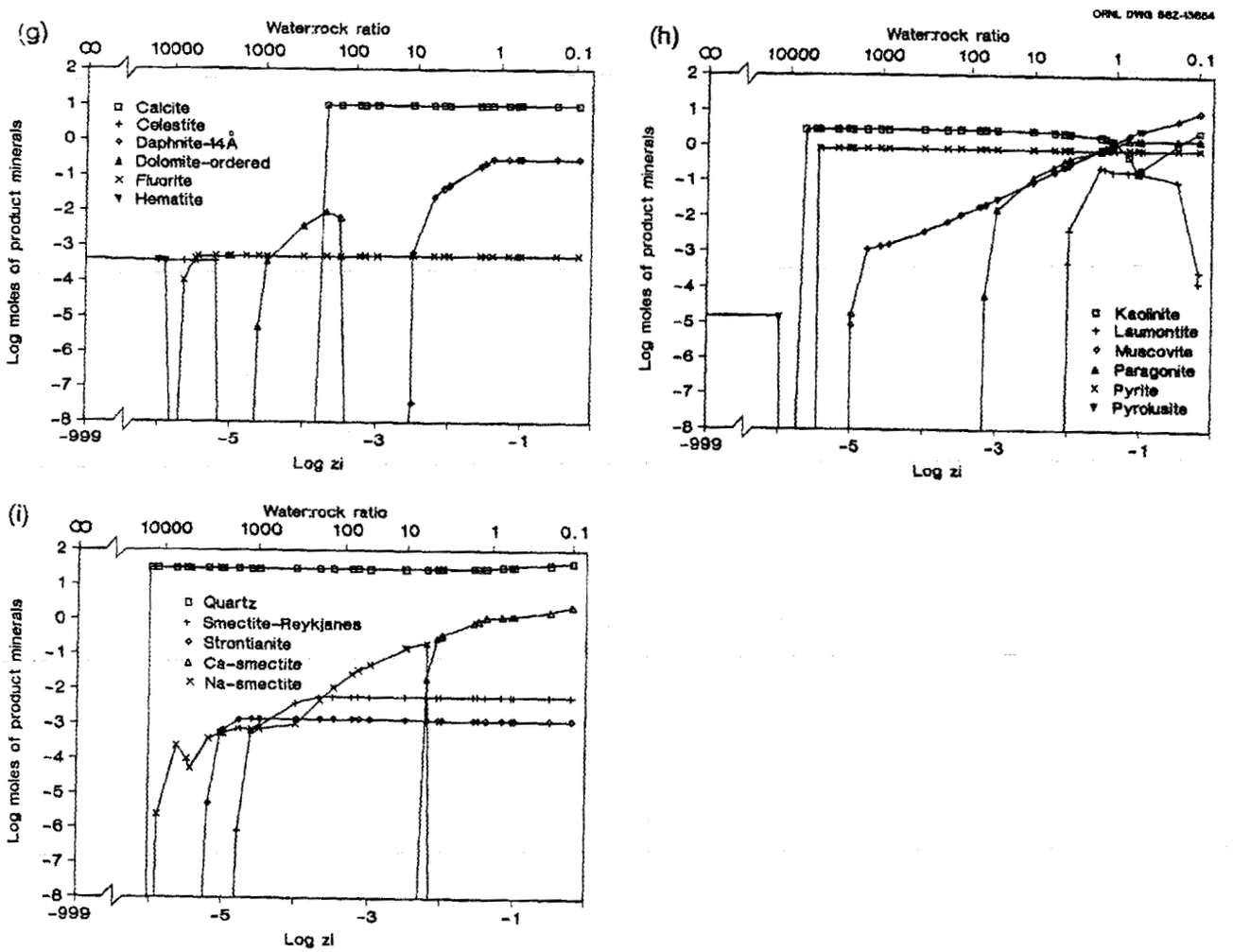

Fig. 1 (continued). Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, CH_4 suppression, pyrite present: (g) product minerals 1, (h) product minerals 2, (i) product minerals 3.

In Case 1b, where CH_4 is not suppressed, the groundwaters are also assumed to be initially oxic. At the termination of the reaction progress, the groundwaters in this case remained slightly more oxic than in Case 1a, while many of the elemental and species concentrations, including the pH, are the same. This case did have lower total alkalinity, total carbonate, total SO_4^{2-}, total H_2S, and Fe, and higher total C (Table 3) than Case 1a. Most of the additional C is accounted for by CH_4. In the CH_4 suppressed case (1a) substantial CH_3COO^- is present, presumably because no CH_4 was permitted, while in this case little CH_3COO^- is present. The final equilibrium mineral assemblage is lacking 14A-daphnite compared to Case 1a, where CH_4 was suppressed.

Case 2: Reaction of PVS groundwater and rock to T = 250°C. The starting conditions are identical to those of Case 1, including CH_4 suppression, but the temperature is gradually increased from 13.5° to 250°C. The temperature increase was included so that the temperature would reach its maximum value at the minimum water:rock ratio. The log f_{O_2} decreased from its starting value of -1.3 to a minimum of -78.2 and then increased to a final value of -38.6 at the maximum temperature of 250°C (Table 4, Fig. 2). This is quite reducing under the given temperature conditions. The pH increased from 5.6 to a maximum value of 8.4 at T = 17.1°C from which it decreased to 5.5. This pH is close to neutral at 250°C, as the dissociation constant of water changes as a function of temperature. EQ6 does not define alkalinity at temperatures greater than 50°C, but total carbonate continues to increase during the experiment, as does total H_2S while total SO_4^{2-} decreases. The total concentrations of F, Fe, C, K, Na, and Si increase in the solution while Al, Br, Ca, Cl, Mg, Mn, S, and Sr decrease. The predominant form of the C at the termination of the reaction is as CO_2(aq), followed by HCO_3^-, and the predominant form of the S is as H_2S(aq) followed by HS^-. A small amount of water is produced during the course of the reaction. The final equilibrium mineral assemblage at 250°C contains albite, calcite, 14A-daphnite,

Table 3a. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, no CH_4 Suppression, Pyrite Present.
Log molal concentrations of dissolved elements.

Log zi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Br	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	Si	S	Sr
-999	13.5	1.01	3.00	-1.28	1.043	-7.55	-4.51	-1.80	-141.85	-3.39	-2.77	-2.77	-1.44	-0.262	-3.01	-5.51	-4.51	-2.99	-1.89	-4.767	-0.320	-4.28	-1.80	-2.98
-6	13.5	1.01	3.49	-4.10	0.975	-6.47	-3.88	-1.80	-136.69	-3.21	-2.77	-2.77	-1.44	-0.262	-2.96	-7.53	-3.88	-2.97	-1.89	-4.335	-0.320	-4.28	-1.80	-2.98
-5.9031	13.5	1.01	4.19	-45.70	0.343	-5.68	-3.81	-1.80	-54.19	-3.18	-2.77	-2.77	-1.44	-0.262	-2.96	-4.25	-3.81	-2.97	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.6478	13.5	1.01	5.33	-60.32	0.071	-4.43	-3.59	-1.80	-26.08	-3.41	-2.77	-2.77	-1.44	-0.262	-3.06	-3.40	-3.59	-2.96	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.5	13.5	1.01	5.57	-63.38	0.014	-4.11	-3.46	-1.80	-20.19	-4.12	-2.77	-2.77	-1.44	-0.262	-3.63	-3.15	-3.46	-2.95	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.4584	13.5	1.01	6.10	-68.28	-0.086	-3.72	-3.42	-1.80	-10.95	-5.73	-2.77	-2.77	-1.44	-0.262	-4.09	-3.09	-3.42	-2.94	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.2032	13.5	1.01	6.32	-68.52	-0.103	-3.39	-3.19	-1.80	-10.67	-6.39	-2.77	-2.77	-1.44	-0.262	-4.11	-3.51	-3.19	-2.91	-1.88	-4.221	-0.320	-4.28	-1.80	-2.98
-5.0332	13.5	1.01	6.51	-68.73	-0.116	-3.51	-3.37	-1.79	-10.44	-6.94	-2.77	-2.77	-1.44	-0.262	-4.12	-3.87	-3.37	-2.88	-1.87	-4.221	-0.320	-4.28	-1.79	-3.05
-5.002	13.5	1.01	6.59	-68.82	-0.122	-3.53	-3.41	-1.79	-10.34	-7.16	-2.77	-2.77	-1.43	-0.262	-4.12	-4.03	-3.41	-2.87	-1.87	-4.221	-0.320	-4.28	-1.79	-3.11
-5	13.5	1.01	6.60	-68.82	-0.123	-3.53	-3.41	-1.79	-10.34	-7.17	-2.77	-2.77	-1.43	-0.262	-4.12	-4.03	-3.41	-2.88	-1.87	-4.221	-0.320	-4.28	-1.79	-3.11
-4.7889	13.5	1.01	7.18	-69.48	-0.165	-3.43	-3.40	-1.79	-9.62	-7.73	-2.77	-2.77	-1.43	-0.262	-4.12	-5.14	-3.40	-3.46	-1.86	-4.221	-0.320	-4.27	-1.79	-3.80
-4.6123	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.79	-9.62	-7.73	-2.77	-2.77	-1.42	-0.262	-4.13	-5.14	-2.96	-3.46	-1.87	-4.263	-0.320	-4.27	-1.79	-4.24
-4.5	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.79	-9.62	-7.72	-2.77	-2.77	-1.42	-0.262	-4.13	-5.15	-2.96	-3.46	-1.88	-4.290	-0.320	-4.27	-1.79	-4.24
-4	13.5	1.01	7.21	-69.52	-0.167	-2.98	-2.95	-1.80	-9.58	-7.71	-2.77	-2.77	-1.39	-0.262	-4.16	-5.20	-2.95	-3.49	-1.99	-4.702	-0.320	-4.27	-1.80	-4.22
-3.6861	13.5	1.01	7.88	-70.30	-0.217	-3.45	-3.45	-1.81	-8.69	-7.10	-2.77	-2.77	-1.33	-0.262	-4.21	-6.60	-3.45	-4.16	-2.41	-228.230	-0.320	-4.25	-1.81	-4.47
-3.5	13.5	1.01	7.90	-70.34	-0.218	-3.46	-3.47	-1.83	-8.64	-7.09	-2.77	-2.77	-1.34	-0.262	-4.21	-6.67	-3.47	-4.18	-2.42	-231.565	-0.320	-4.25	-1.83	-4.47
-3.2384	13.5	1.01	7.91	-70.38	-0.219	-3.46	-3.47	-1.87	-8.61	-7.08	-2.77	-2.77	-1.35	-0.262	-4.20	-6.71	-3.47	-4.19	-2.43	-232.580	-0.319	-4.25	-1.87	-4.45
-3.162	13.5	1.01	8.15	-70.66	-0.237	-3.70	-3.72	-1.89	-8.32	-6.84	-2.77	-2.77	-1.33	-0.262	-4.23	-7.17	-3.72	-4.43	-2.94	-268.432	-0.320	-4.23	-1.89	-4.47
-3	13.5	1.01	8.16	-70.70	-0.238	-3.77	-3.79	-1.95	-8.30	-6.83	-2.77	-2.77	-1.28	-0.262	-4.25	-7.18	-3.79	-4.44	-2.98	-274.536	-0.334	-4.23	-1.95	-4.41
-2.5	13.5	1.01	8.28	-77.04	-0.335	-4.12	-4.17	-8.59	-7.40	-6.72	-2.78	-2.78	-1.02	-0.263	-4.37	-5.84	-3.33	-4.56	-3.24	-0.452	-4.224	-7.37	-4.16	-4.15
-2.2628	13.5	1.01	8.44	-78.03	-0.358	-4.37	-4.49	-8.46	-7.12	-6.56	-2.78	-2.78	-0.82	-0.265	-4.45	-5.91	-1.93	-4.72	-3.57	-0.614	-4.212	-7.10	-3.95	-3.95
-2.0894	13.5	1.01	8.44	-78.20	-0.361	-4.37	-4.50	-8.44	-7.09	-6.55	-2.78	-2.78	-0.82	-0.266	-4.45	-5.87	-1.60	-4.73	-3.58	-0.617	-4.212	-7.08	-3.95	-3.95
-2.0274	13.5	1.01	8.52	-78.35	-0.367	-4.43	-4.60	-8.41	-6.99	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-6.00	-1.51	-4.80	-3.74	-0.689	-4.205	-6.98	-3.90	-3.86
-2	13.5	1.01	8.52	-78.37	-0.367	-4.43	-4.60	-8.41	-6.99	-6.48	-2.78	-2.78	-0.77	-0.267	-4.47	-5.99	-1.47	-4.80	-3.74	-0.689	-4.205	-6.98	-3.90	-3.86
-1.6348	13.5	1.01	8.51	-78.60	-0.371	-4.43	-4.60	-8.38	-6.96	-6.48	-2.78	-2.78	-0.77	-0.265	-4.47	-5.93	-1.00	-4.80	-3.74	-0.689	-4.205	-6.95	-3.90	-3.86
-1.5694	13.5	1.01	8.51	-78.62	-0.371	-4.44	-4.60	-8.38	-6.96	-6.48	-2.78	-2.78	-0.77	-0.265	-4.47	-5.93	-0.96	-4.80	-3.73	-0.688	-4.205	-6.94	-3.90	-3.86
-1.5	13.5	1.01	8.52	-78.65	-0.371	-4.43	-4.60	-8.37	-6.95	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-5.93	-0.91	-4.80	-3.73	-0.689	-4.205	-6.93	-3.90	-3.86
-1.3985	13.5	1.01	8.52	-78.68	-0.372	-4.43	-4.60	-8.36	-6.94	-6.48	-2.78	-2.78	-0.78	-0.271	-4.46	-5.94	-0.83	-4.80	-3.73	-0.691	-4.204	-6.92	-3.90	-3.86
-1.1772	13.5	1.01	8.52	-78.69	-0.372	-4.43	-4.60	-8.36	-6.94	-6.48	-2.79	-2.79	-0.79	-0.279	-4.46	-5.95	-0.82	-4.81	-3.74	-0.695	-4.204	-6.92	-3.91	-3.86
-1.0458	13.5	1.01	8.52	-78.69	-0.372	-4.43	-4.60	-8.36	-6.93	-6.48	-2.79	-2.79	-0.79	-0.282	-4.46	-5.95	-0.81	-4.81	-3.74	-0.696	-4.203	-6.92	-3.92	-3.86
-1	13.5	1.01	8.52	-78.70	-0.372	-4.43	-4.60	-8.36	-6.93	-6.48	-2.79	-2.79	-0.79	-0.282	-4.46	-5.95	-0.80	-4.81	-3.74	-0.696	-4.203	-6.92	-3.91	-3.86
-0.6989	13.5	1.01	8.52	-78.72	-0.373	-4.43	-4.60	-8.35	-6.93	-6.48	-2.79	-2.79	-0.79	-0.280	-4.46	-5.95	-0.75	-4.81	-3.74	-0.695	-4.203	-6.91	-3.91	-3.86
-0.5	13.5	1.01	8.52	-78.72	-0.373	-4.43	-4.60	-8.34	-6.92	-6.48	-2.79	-2.79	-0.79	-0.279	-4.46	-5.97	-0.75	-4.81	-3.73	-0.695	-4.204	-6.90	-3.91	-3.86
-0.1938	13.5	1.01	8.52	-78.73	-0.373	-4.43	-4.60	-8.32	-6.89	-6.48	-2.79	-2.79	-0.78	-0.274	-4.46	-6.01	-0.75	-4.80	-3.70	-0.693	-4.204	-6.88	-3.91	-3.86

Table 3b. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, No CH_4 Suppression, Pyrite Present.
Log moles of product minerals.

Log zi	Calcite	Celestite	Daphnite -14A	Dolomite -ordered	Fluorite	Hematite	Pyrolusite	Kaolinite	Laumontite	Muscovite	Paragonite	Pyrite	Quartz	Smectite-Reykjanes	Strontianite	Ca-smectite	Na-smectite
-999		-3.45			-4.25	-3.46	-4.37										
-6		-3.44				-3.42	-4.86						1.46				
-5.9031		-3.43				-3.45							1.46				-5.629
-5.6478		-3.43			-3.99			0.4639					1.46				-3.647
-5.5		-3.43			-3.37			0.4640					1.46				-4.021
-5.4584		-3.43			-3.30			0.4640				-0.0789	1.46				-4.287
-5.2032		-3.44			-3.30			0.4640				-0.0788	1.46		-5.29		-3.452
-5.0332					-3.30			0.4640				-0.0788	1.46		-3.28		-3.300
-5.002					-3.30			0.4640		-5.0893		-0.0788	1.46		-3.19		-3.270
-5					-3.30			0.4640		-4.7864		-0.0788	1.46		-3.19		-3.268
-4.7889					-3.30			0.4638		-2.9200		-0.0788	1.46	-6.07	-2.90		-3.135
-4.6123				-5.31	-3.30			0.4638		-2.8394		-0.0788	1.46	-3.26	-2.87		-3.155
-4.5				-3.44	-3.30			0.4638		-2.7772		-0.0788	1.46	-3.05	-2.87		-3.138
-4				-2.42	-3.29			0.4639		-2.4217		-0.0788	1.46	-2.40	-2.87		-3.001
-3.6861	0.999			-2.03	-3.29			0.4641		-2.1323		-0.0786	1.46	-2.22	-2.86		-2.328
-3.5	0.999			-2.18	-3.29			0.4644		-1.9625		-0.0785	1.46	-2.22	-2.86		-1.953
-3.2384	1.000				-3.29			0.4650		-1.7152		-0.0781	1.46	-2.22	-2.86		-1.578
-3.162	1.000				-3.29			0.4650		-1.6411	-4.2153	-0.0780	1.46	-2.22	-2.86		-1.467
-3	1.000				-3.29			0.4621		-1.4839	-1.7777	-0.0775	1.46	-2.22	-2.86		-1.303
-2.5	1.000				-3.28			0.4410		-0.9913	-0.8778	-0.0747	1.46	-2.22	-2.87		-0.800
-2.2628	0.999				-3.28			0.4177		-0.7555	-0.5962	-0.0747	1.46	-2.22	-2.89	-1.856	-0.579
-2.0894	0.998				-3.28			0.3887		-0.5829	-0.4033	-0.0747	1.46	-2.22	-2.89	-0.380	
-2.0274	0.998				-3.28			0.3736	-3.401	-0.5211	-0.3400	-0.0747	1.46	-2.22	-2.89	-0.309	
-2	0.998				-3.28			0.3701	-1.985	-0.4937	-0.3285	-0.0747	1.46	-2.22	-2.89	-0.282	
-1.6348	0.995		-3.07		-3.28			0.2864	-0.648	-0.1292	-0.1346	-0.0747	1.45	-2.22	-2.89	0.085	
-1.5694	0.995		-1.91		-3.28			0.2600	-0.545	-0.0639	-0.0921	-0.0747	1.44	-2.22	-2.89	0.140	
-1.5	0.994		-1.57		-3.28			0.2251	-0.575	0.0055	-0.0449	-0.0747	1.44	-2.22	-2.89	0.199	
-1.3985	0.993		-1.26		-3.28			0.1551	-0.633	0.1069	0.0283	-0.0747	1.45	-2.22	-2.89	0.286	
-1.1772	0.993		-1.35		-3.28			-0.3122	-0.646	0.3281	0.2031	-0.0747	1.48	-2.22	-2.89	0.305	
-1.0458	0.992		-1.45		-3.28			-0.9110	-0.659	0.4595	0.2028	-0.0747	1.50	-2.22	-2.89	0.322	
-1	0.992		-1.49		-3.28			-0.7766	-0.666	0.4772	0.2029	-0.0747	1.50	-2.22	-2.89	0.328	
-0.6989	0.991				-3.28			-0.2125	-0.735	0.6234	0.2030	-0.0747	1.52	-2.22	-2.89	0.388	
-0.5	0.991				-3.28			0.0575	-0.843	0.7478	0.2031	-0.0747	1.55	-2.22	-2.89	0.429	
-0.1938	0.991				-3.28			0.4174	-1.523	0.9768	0.2034	-0.0747	1.62	-2.22	-2.89	0.528	

Table 3c. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, No CH_4 Suppression, Pyrite Present.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	K-feldspar	Albite	Anorthite	Calcite	Kaolinite	Ripidolite -14a	g[b]Des[c]	g[b]Cre[d]	g[b]Net	cm[3a]Des[c]	cm[3a]Cre[d]	cm[3a]Net	Water:Rock Ratio
-999	-999.00	-999.000	-999.00	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	0.000	0.13	0.13	0.000	0.017	0.017	
-6	-6.00	-4.699	-4.70	-4.699	-4.699	-4.699	-4.00	-4.70	-4.699	0.054	1749.00	1749.00	0.015	660.200	660.200	18497.965
-5.9031	-6.00	-4.602	-4.60	-4.602	-4.602	-4.602	-3.90	-4.60	-4.602	0.068	1749.00	1749.00	0.018	660.200	660.200	14801.658
-5.6478	-6.00	-4.347	-4.35	-4.347	-4.347	-4.347	-3.65	-4.35	-4.347	0.122	2500.00	2500.00	0.033	949.800	949.800	8223.684
-5.5	-6.00	-4.199	-4.20	-4.199	-4.199	-4.199	-3.50	-4.35	-4.199	0.166	2500.00	2500.00	0.045	949.900	949.800	6020.470
-5.4584	-6.00	-4.157	-4.16	-4.157	-4.157	-4.157	-3.46	-4.35	-4.157	0.182	2600.00	2600.00	0.049	949.900	949.800	5503.577
-5.2032	-6.00	-3.902	-4.16	-3.902	-3.902	-3.902	-3.20	-4.35	-3.902	0.311	2600.00	2600.00	0.084	949.900	949.800	3216.468
-5.0332	-6.00	-3.732	-4.16	-3.732	-3.732	-3.732	-3.03	-4.35	-3.732	0.450	2600.00	2600.00	0.122	949.900	949.800	2221.235
-5.002	-6.00	-3.701	-4.16	-3.701	-3.701	-3.701	-3.00	-4.35	-3.701	0.482	2600.00	2600.00	0.131	949.900	949.800	2073.398
-5	-6.00	-3.699	-4.16	-3.699	-3.699	-3.699	-3.00	-4.35	-3.699	0.484	2600.00	2600.00	0.131	949.900	949.800	2064.410
-4.7889	-6.00	-3.488	-4.16	-3.488	-3.488	-3.488	-2.79	-4.35	-3.488	0.775	2601.00	2600.00	0.211	950.000	949.800	1290.156
-4.6123	-6.00	-3.311	-4.16	-3.311	-3.311	-3.311	-2.61	-4.35	-3.311	1.154	2601.00	2600.00	0.314	950.000	949.700	866.551
-4.5	-6.00	-3.199	-4.16	-3.199	-3.199	-3.199	-2.50	-4.35	-3.199	1.489	2601.00	2600.00	0.405	950.100	949.700	671.592
-4	-6.00	-2.699	-4.16	-2.699	-2.699	-2.699	-2.00	-4.35	-2.699	4.664	2604.00	2600.00	1.272	950.700	949.400	214.408
-3.6861	-6.00	-2.385	-4.16	-2.385	-2.385	-2.385	-1.69	-4.35	-2.385	9.587	3607.00	3598.00	2.615	1320.000	1318.000	104.308
-3.5	-6.00	-2.199	-4.16	-2.199	-2.199	-2.199	-1.69	-4.35	-2.199	13.600	3611.00	3598.00	3.604	1321.000	1318.000	73.529
-3.2384	-6.00	-1.937	-4.16	-1.937	-1.937	-1.937	-1.69	-4.35	-1.937	23.120	3621.00	3598.00	5.950	1324.000	1318.000	43.253
-3.162	-6.00	-1.861	-4.16	-1.861	-1.861	-1.861	-1.69	-4.35	-1.861	27.170	3625.00	3598.00	6.948	1325.000	1318.000	36.805
-3	-6.00	-1.699	-4.16	-1.699	-1.699	-1.699	-1.69	-4.35	-1.699	38.510	3636.00	3598.00	9.742	1328.000	1318.000	25.967
-2.5	-6.00	-1.199	-4.16	-1.199	-1.199	-1.199	-1.69	-4.35	-1.199	117.300	3713.00	3596.00	29.150	1347.000	1318.000	8.525
-2.2628	-6.00	-0.962	-4.16	-0.962	-0.962	-0.962	-1.69	-4.35	-0.962	201.000	3794.00	3593.00	49.790	1367.000	1318.000	4.975
-2.0894	-6.00	-0.788	-4.16	-0.788	-0.788	-0.788	-1.69	-4.35	-0.788	298.600	3888.00	3589.00	73.830	1390.000	1317.000	3.349
-2.0274	-6.00	-0.726	-4.16	-0.726	-0.726	-0.726	-1.69	-4.35	-0.726	344.100	3931.00	3587.00	85.040	1401.000	1316.000	2.906
-2	-6.00	-0.699	-4.16	-0.699	-0.699	-0.699	-1.69	-4.35	-0.699	366.400	3954.00	3587.00	90.540	1407.000	1317.000	2.729
-1.6348	-6.00	-0.334	-4.16	-0.334	-0.334	-0.334	-1.69	-4.35	-0.334	846.700	4437.00	3590.00	208.900	1542.000	1333.000	1.181
-1.5694	-6.00	-0.268	-4.16	-0.268	-0.268	-0.268	-1.69	-4.35	-0.268	983.900	4575.00	3591.00	242.700	1582.000	1339.000	1.016
-1.5	-6.00	-0.199	-4.16	-0.199	-0.199	-0.268	-1.69	-4.35	-0.199	1128.000	4714.00	3586.00	275.200	1617.000	1341.000	0.887
-1.3985	-6.00	-0.098	-4.16	-0.098	-0.098	-0.268	-1.69	-4.35	-0.098	1385.000	4961.00	3576.00	333.200	1679.000	1345.000	0.722
-1.1772	-6.00	0.124	-4.16	0.124	0.124	-0.268	-1.69	-4.35	-0.098	1876.000	5434.00	3558.00	518.000	1838.000	1320.000	0.533
-1.0458	-6.00	0.255	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	2187.000	5737.00	3550.00	634.500	1943.000	1309.000	0.457
-1	-6.00	0.301	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	2264.000	5815.00	3550.00	662.300	1971.000	1308.000	0.442
-0.6989	-6.00	0.602	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3032.000	6586.00	3554.00	940.300	2244.000	1303.000	0.330
-0.5	-6.00	0.801	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3924.000	7482.00	3557.00	1263.000	2566.000	1303.000	0.255
-0.1938	-6.00	1.107	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6410.000	9978.00	3568.00	2163.000	3464.000	1301.000	0.156

[1]cm3 = cubic centimeters
[2]g = grams
[3]Des = Destroyed
[4]Cre = Created

Table 4a. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 250°C.
Log molal concentrations of dissolved elements.

Log xi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Br	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	Si	S	Sr
-999	13.5	1.01	3.00	-1.28	1.043	-7.55	-4.51	-1.80	-141.85	-3.39	-2.77	-2.77	-1.44	-0.262	-3.01	-5.51	-4.51	-2.99	-1.89	-4.767	-0.320	-4.28	-1.80	-2.98
-6	13.5	1.01	3.49	-4.10	0.975	-6.47	-3.88	-1.80	-136.69	-3.21	-2.77	-2.77	-1.44	-0.262	-2.96	-7.53	-3.88	-2.97	-1.89	-4.335	-0.320	-4.28	-1.80	-2.98
-5.9031	13.5	1.01	4.19	-45.70	0.343	-5.68	-3.81	-1.80	-54.19	-3.18	-2.77	-2.77	-1.44	-0.262	-2.96	-4.25	-3.81	-2.97	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.6478	13.5	1.01	5.33	-60.32	0.071	-4.43	-3.59	-1.80	-26.08	-3.41	-2.77	-2.77	-1.44	-0.262	-3.06	-3.40	-3.59	-2.96	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.5	13.5	1.01	5.57	-63.38	0.014	-4.11	-3.46	-1.80	-20.19	-4.12	-2.77	-2.77	-1.44	-0.262	-3.63	-3.15	-3.46	-2.95	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.4584	13.5	1.01	6.10	-68.28	-0.086	-3.72	-3.42	-1.80	-10.95	-5.73	-2.77	-2.77	-1.44	-0.262	-4.09	-3.09	-3.42	-2.94	-1.89	-4.221	-0.320	-4.28	-1.80	-2.98
-5.2032	13.5	1.01	6.32	-68.52	-0.103	-3.39	-3.19	-1.80	-10.67	-6.39	-2.77	-2.77	-1.44	-0.262	-4.11	-3.51	-3.19	-2.91	-1.88	-4.221	-0.320	-4.28	-1.80	-2.98
-5.0332	13.5	1.01	6.51	-68.73	-0.116	-3.51	-3.37	-1.79	-10.44	-6.94	-2.77	-2.77	-1.44	-0.262	-4.12	-3.87	-3.37	-2.88	-1.87	-4.221	-0.320	-4.28	-1.79	-3.05
-5.002	13.5	1.01	6.59	-68.82	-0.122	-3.53	-3.41	-1.79	-10.34	-7.16	-2.77	-2.77	-1.43	-0.262	-4.12	-4.03	-3.41	-2.87	-1.87	-4.221	-0.320	-4.28	-1.79	-3.11
-5	13.5	1.01	6.60	-68.82	-0.123	-3.53	-3.41	-1.79	-10.34	-7.17	-2.77	-2.77	-1.43	-0.262	-4.12	-4.03	-3.41	-2.88	-1.87	-4.221	-0.320	-4.28	-1.79	-3.11
-4.7889	13.5	1.01	7.18	-69.48	-0.165	-3.43	-3.40	-1.79	-9.62	-7.73	-2.77	-2.77	-1.43	-0.262	-4.12	-5.14	-3.40	-3.46	-1.86	-4.221	-0.320	-4.27	-1.79	-3.80
-4.6123	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.79	-9.62	-7.73	-2.77	-2.77	-1.42	-0.262	-4.13	-5.14	-2.96	-3.46	-1.87	-4.263	-0.320	-4.27	-1.79	-4.24
-4.5	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.79	-9.62	-7.72	-2.77	-2.77	-1.42	-0.262	-4.13	-5.15	-2.96	-3.46	-1.88	-4.290	-0.320	-4.27	-1.79	-4.24
-4	13.5	1.01	7.21	-69.52	-0.167	-2.98	-2.95	-1.80	-9.58	-7.71	-2.77	-2.77	-1.39	-0.262	-4.16	-5.20	-2.95	-3.49	-1.99	-4.702	-0.320	-4.27	-1.80	-4.28
-3.6861	13.5	1.01	7.88	-70.30	-0.217	-3.45	-3.45	-1.81	-8.69	-7.10	-2.77	-2.77	-1.33	-0.262	-4.21	-6.60	-3.45	-4.16	-2.41	-228.230	-0.320	-4.25	-1.81	-4.47
-3.5	13.5	1.01	7.90	-70.34	-0.218	-3.46	-3.47	-1.83	-8.64	-7.09	-2.77	-2.77	-1.34	-0.262	-4.21	-6.67	-3.47	-4.18	-2.42	-231.565	-0.320	-4.25	-1.83	-4.47
-3.2384	13.5	1.01	7.91	-70.38	-0.219	-3.46	-3.47	-1.87	-8.61	-7.08	-2.77	-2.77	-1.35	-0.262	-4.20	-6.71	-3.47	-4.19	-2.43	-232.580	-0.319	-4.25	-1.87	-4.49
-3.162	13.5	1.01	8.15	-70.66	-0.237	-3.70	-3.72	-1.89	-8.32	-6.84	-2.77	-2.77	-1.33	-0.262	-4.23	-7.17	-3.72	-4.43	-2.94	-268.432	-0.320	-4.23	-1.89	-4.47
-3	13.5	1.01	8.16	-70.70	-0.238	-3.77	-3.79	-1.95	-8.30	-6.83	-2.77	-2.77	-1.28	-0.262	-4.25	-7.18	-3.79	-4.44	-2.98	-274.536	-0.334	-4.25	-1.95	-4.41
-2.5	13.5	1.01	8.28	-77.04	-0.335	-4.12	-4.17	-8.59	-7.40	-6.72	-2.78	-2.78	-1.02	-0.263	-4.37	-5.84	-3.33	-4.56	-3.24	-0.452	-4.224	-7.37	-4.16	-4.15
-2.2628	13.5	1.01	8.44	-78.03	-0.358	-4.37	-4.49	-8.46	-7.12	-6.56	-2.78	-2.78	-0.82	-0.265	-4.45	-5.91	-1.93	-4.72	-3.57	-0.614	-4.212	-7.10	-3.95	-3.95
-2.0894	13.5	1.01	8.44	-78.20	-0.361	-4.37	-4.50	-8.44	-7.09	-6.55	-2.78	-2.78	-0.82	-0.266	-4.45	-5.87	-1.60	-4.73	-3.58	-0.617	-4.212	-7.08	-3.95	-3.95
-2.0274	13.5	1.01	8.52	-78.35	-0.367	-4.43	-4.60	-8.41	-6.99	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-6.00	-1.51	-4.80	-3.74	-0.689	-4.205	-6.98	-3.90	-3.89
-2	13.5	1.01	8.52	-78.37	-0.367	-4.43	-4.60	-8.41	-6.99	-6.48	-2.78	-2.78	-0.77	-0.267	-4.47	-5.99	-1.47	-4.80	-3.74	-0.689	-4.205	-6.98	-3.90	-3.89
-1.6348	13.5	1.01	8.51	-78.60	-0.371	-4.43	-4.60	-8.38	-6.96	-6.48	-2.78	-2.78	-0.77	-0.265	-4.47	-5.93	-1.00	-4.80	-3.74	-0.689	-4.205	-6.95	-3.90	-3.89
-1.5694	13.5	1.01	8.51	-78.62	-0.371	-4.44	-4.60	-8.38	-6.96	-6.48	-2.78	-2.78	-0.77	-0.265	-4.47	-5.93	-0.96	-4.80	-3.73	-0.688	-4.205	-6.94	-3.90	-3.89
-1.5	13.5	1.01	8.52	-78.65	-0.371	-4.43	-4.60	-8.37	-6.95	-6.48	-2.78	-2.78	-0.77	-0.267	-4.46	-5.93	-0.91	-4.80	-3.73	-0.689	-4.205	-6.93	-3.90	-3.89
-1.3985	13.5	1.01	8.52	-78.68	-0.372	-4.43	-4.60	-8.36	-6.94	-6.48	-2.78	-2.78	-0.78	-0.271	-4.46	-5.94	-0.83	-4.80	-3.73	-0.691	-4.204	-6.92	-3.90	-3.89
-1.1772	13.5	1.01	8.52	-78.69	-0.372	-4.43	-4.60	-8.36	-6.94	-6.48	-2.79	-2.79	-0.79	-0.279	-4.46	-5.95	-0.82	-4.81	-3.74	-0.695	-4.204	-6.92	-3.91	-3.89
-1.0458	13.5	1.01	8.52	-78.69	-0.372	-4.43	-4.60	-8.36	-6.93	-6.48	-2.79	-2.79	-0.79	-0.282	-4.46	-5.95	-0.81	-4.81	-3.74	-0.696	-4.203	-6.92	-3.92	-3.89
-1	13.5	1.01	8.52	-78.70	-0.372	-4.43	-4.60	-8.36	-6.93	-6.48	-2.79	-2.79	-0.79	-0.282	-4.46	-5.95	-0.80	-4.81	-3.74	-0.696	-4.203	-6.92	-3.91	-3.89
-0.6989	13.5	1.01	8.52	-78.72	-0.373	-4.43	-4.60	-8.35	-6.93	-6.48	-2.79	-2.79	-0.79	-0.280	-4.46	-5.95	-0.75	-4.81	-3.74	-0.695	-4.203	-6.91	-3.91	-3.89
-0.5	13.5	1.01	8.52	-78.72	-0.373	-4.43	-4.60	-8.34	-6.92	-6.48	-2.79	-2.79	-0.79	-0.279	-4.46	-5.97	-0.75	-4.81	-3.73	-0.695	-4.204	-6.90	-3.91	-3.89
-0.1938	13.5	1.01	8.52	-78.73	-0.373	-4.43	-4.60	-8.32	-6.89	-6.48	-2.79	-2.79	-0.78	-0.274	-4.46	-6.01	-0.75	-4.80	-3.70	-0.693	-4.204	-6.88	-3.91	-3.89

Table 4b. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 250°C.
Log moles of product minerals.

Log zi	Albite	Calcite	Celestite	Daphnite -14A	Dolomite -ordered	Fluorite	Hematite	Pyrolusite	Kaolinite	Laumontite	Graphite	Heulandite	Muscovite	Paragonite	Pyrite	Quartz	Smectite-Reykjanes	Strontianite	Ca-smectite	Na-smectite
-999			-3.45			-4.25	-3.46	-4.37								1.46				
-6			-3.44				-3.42	-4.86								1.46				
-5.9031			-3.43				-3.45									1.46				-5.629
-5.6478			-3.43			-3.99			0.464							1.46				-3.647
-5.5			-3.43			-3.37			0.464							1.46				-4.021
-5.4584			-3.43			-3.30			0.464						-0.0789	1.46				-4.287
-5.2031			-3.44			-3.30			0.464						-0.0788	1.46		-5.29		-3.452
-5.0332						-3.30			0.464						-0.0788	1.46		-3.28		-3.300
-5.002						-3.30			0.464				-5.0891		-0.0788	1.46		-3.19		-3.270
-5						-3.30			0.464				-4.7863		-0.0788	1.46		-3.19		-3.268
-4.7889						-3.30			0.464				-2.9201		-0.0788	1.46	-6.07	-2.90		-3.135
-4.6123					-5.299	-3.30			0.464				-2.8394		-0.0788	1.46	-3.26	-2.87		-3.155
-4.5					-3.439	-3.30			0.464				-2.7773		-0.0788	1.46	-3.05	-2.87		-3.138
-4					-2.424	-3.29			0.464				-2.4217		-0.0788	1.46	-2.40	-2.87		-3.001
-3.6862		0.999			-2.028	-3.29			0.464				-2.1324		-0.0786	1.46	-2.22	-2.86		-2.328
-3.5		0.999			-2.181	-3.29			0.464				-1.9625		-0.0785	1.46	-2.22	-2.86		-1.953
-3.2382		1.000				-3.29			0.465				-1.7150		-0.0781	1.46	-2.22	-2.86		-1.467
-3.1619		1.000				-3.29			0.465				-1.6411	-4.2205	-0.0780	1.46	-2.22	-2.86		-1.303
-3		1.000				-3.29			0.462				-1.4860	-1.7780	-0.0775	1.46	-2.22	-2.86		
-2.5111		1.000		-7.283		-3.28			0.442				-1.0024	-0.8922	-0.0747	1.46	-2.22	-2.87		-0.810
-2.5		1.000		-3.194		-3.28			0.441				-0.9913	-0.8787	-0.0747	1.46	-2.22	-2.87		-0.804
-2.2343		1.000		-1.658		-3.28			0.415				-0.7272	-0.5723	-0.0747	1.46	-2.22	-2.89	-1.6337	-0.685
-2.1001		1.000		-1.410		-3.28			0.394				-0.5935	-0.4256	-0.0747	1.47	-2.22	-2.89	-0.5411	
-2.0138		1.000		-1.277		-3.28			0.374	-3.328			-0.5075	-0.3375	-0.0747	1.47	-2.22	-2.90	-0.4616	
-2		1.000		-1.257		-3.28			0.372	-2.276			-0.4937	-0.3317	-0.0747	1.47	-2.22	-2.90	-0.4505	
-1.5694		1.000		-0.719		-3.28			0.263	-0.580			-0.0639	-0.0968	-0.0747	1.47	-2.22	-2.91	-0.0651	
-1.5		1.000		-0.642		-3.28			0.226	-0.620			0.0055	-0.0498	-0.0747	1.47	-2.22	-2.91	0.0035	
-1.3985		1.000		-0.530		-3.28			0.147	-0.706			0.1069	0.0232	-0.0747	1.47	-2.22	-2.92	0.1072	
-1.1772		1.000		-0.530		-3.29			-0.452	-0.763			0.3281	0.1980	-0.0747	1.51	-2.22	-2.95	0.1619	
-1.0801		1.000		-0.530		-3.29				-0.818			0.4252	0.1970	-0.0747	1.52	-2.22	-2.98	0.2005	
-1.0458		1.000		-0.530		-3.29				-0.756			0.4595	0.1899	-0.0747	1.53	-2.22	-2.98	0.1821	
-1		1.000		-0.530		-3.29				-0.781			0.4772	0.1890	-0.0747	1.53	-2.22	-2.99	0.2017	
-0.5969		1.000		-0.530		-3.33				-1.541			0.6845	0.1620	-0.0747	1.55	-2.22	-3.34	0.4322	
-0.5565	-1.4831	1.000		-0.530		-3.33				-2.945			0.7103	0.1476	-0.0747	1.56	-2.22	-3.42	0.4649	
-0.5557	-1.4353	1.000		-0.530		-3.34							0.7108	0.1464	-0.0747	1.56	-2.22	-3.43	0.4660	
-0.5381		1.000		-0.530		-3.34							0.7223	0.1517	-0.0747	1.56	-2.22	-3.38	0.4747	
-0.5235		1.000		-0.530		-3.34					-4.477		0.7319	0.1420	-0.0747	1.56	-2.22	-3.25	0.4887	
-0.5		0.999		-0.540		-3.35					-2.091		0.7477	0.1306	-0.0747	1.56	-2.22	-3.13	0.5109	
-0.4166		0.996		-0.603	-3.527	-3.40					-1.247		0.8060	0.1071	-0.0747	1.57	-2.22	-2.93	0.5838	
-0.2737	-1.1480	0.988		-0.671	-1.485	-3.52					-0.993		0.9130	0.0780	-0.0748	1.58	-2.22	-2.91	0.6874	
-0.2674	-0.2215	0.883		-0.637	0.035	-3.49					-1.097	0.0689	0.9179	-0.1744	-0.0748	1.52	-2.22	-2.92	0.6029	
-0.2654	0.1049	0.628		-0.574	0.449	-3.44					-1.458	0.6939	0.9195		-0.0748	1.41	-2.22	-2.93	0.3657	
-0.21	0.1040	0.975		-0.801	-1.322	-3.95					-0.768		0.9633		-0.0751	1.54	-2.22	-2.92	0.8157	
-0.1981	0.1044	0.976		-0.823	-4.810						-0.744		0.9729		-0.0752	1.55	-2.22	-2.92	0.8247	
-0.1955	0.1046	0.976		-0.823							-0.745		0.9750		-0.0752	1.55	-2.22	-2.92	0.8261	
-0.1938	0.1047	0.975		-0.823							-0.745		0.9764		-0.0752	1.55	-2.22	-2.92	0.8270	

Table 4c. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 250°C.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	K-feldspar	Albite	Anorthite	Calcite	Kaolinite	Ripidolite -14a	g[b]Des[c]	g[b]Cre[d]	g[b]Net	cm[3a]Des[c]	cm[3a]Cre[d]	cm[3a]Net	Water:Rock Ratio
-999	-999.00	-999.000	-999.00	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	0.000	0.13	0.13	0.000	0.017	0.017	
-6	-6.00	-4.699	-4.70	-4.699	-4.699	-4.699	-4.00	-4.70	-4.699	0.054	1749.00	1749.00	0.015	660.200	660.200	18497.965
-5.9031	-6.00	-4.602	-4.60	-4.602	-4.602	-4.602	-3.90	-4.60	-4.602	0.068	1749.00	1749.00	0.018	660.200	660.200	14801.658
-5.6478	-6.00	-4.347	-4.35	-4.347	-4.347	-4.347	-3.65	-4.35	-4.347	0.122	2500.00	2500.00	0.033	949.800	949.800	8223.684
-5.5	-6.00	-4.199	-4.20	-4.199	-4.199	-4.199	-3.50	-4.35	-4.199	0.166	2500.00	2500.00	0.045	949.900	949.800	6020.470
-5.4584	-6.00	-4.157	-4.16	-4.157	-4.157	-4.157	-3.46	-4.35	-4.157	0.182	2600.00	2600.00	0.049	949.900	949.800	5503.577
-5.2031	-6.00	-3.902	-4.16	-3.902	-3.902	-3.902	-3.20	-4.35	-3.902	0.311	2600.00	2600.00	0.084	949.900	949.800	3216.468
-5.0332	-6.00	-3.732	-4.16	-3.732	-3.732	-3.732	-3.03	-4.35	-3.732	0.450	2600.00	2600.00	0.122	949.900	949.800	2221.235
-5.002	-6.00	-3.701	-4.16	-3.701	-3.701	-3.701	-3.00	-4.35	-3.701	0.482	2600.00	2600.00	0.131	949.900	949.800	2073.398
-5	-6.00	-3.699	-4.16	-3.699	-3.699	-3.699	-3.00	-4.35	-3.699	0.484	2600.00	2600.00	0.131	949.900	949.800	2064.410
-4.7889	-6.00	-3.488	-4.16	-3.488	-3.488	-3.488	-2.79	-4.35	-3.488	0.775	2601.00	2600.00	0.211	950.000	949.800	1290.323
-4.6123	-6.00	-3.311	-4.16	-3.311	-3.311	-3.311	-2.61	-4.35	-3.311	1.154	2601.00	2600.00	0.314	950.000	949.700	866.551
-4.5	-6.00	-3.199	-4.16	-3.199	-3.199	-3.199	-2.50	-4.35	-3.199	1.489	2601.00	2600.00	0.405	950.100	949.700	671.592
-4	-6.00	-2.699	-4.16	-2.699	-2.699	-2.699	-2.00	-4.35	-2.699	4.664	2604.00	2600.00	1.272	950.700	949.400	214.608
-3.6862	-6.00	-2.385	-4.16	-2.385	-2.385	-2.385	-1.69	-4.35	-2.385	9.586	3607.00	3598.00	2.614	1320.000	1318.000	104.319
-3.5	-6.00	-2.199	-4.16	-2.199	-2.199	-2.199	-1.69	-4.35	-2.199	13.600	3611.00	3598.00	3.604	1321.000	1318.000	73.529
-3.2382	-6.00	-1.937	-4.16	-1.937	-1.937	-1.937	-1.69	-4.35	-1.937	23.130	3621.00	3598.00	5.952	1324.000	1318.000	43.234
-3.1619	-6.00	-1.861	-4.16	-1.861	-1.861	-1.861	-1.69	-4.35	-1.861	27.170	3625.00	3598.00	6.948	1325.000	1318.000	36.805
-3	-6.00	-1.699	-4.16	-1.699	-1.699	-1.699	-1.69	-4.35	-1.699	38.510	3636.00	3598.00	9.742	1328.000	1318.000	25.967
-2.5111	-6.00	-1.210	-4.16	-1.210	-1.210	-1.210	-1.69	-4.35	-1.210	114.400	3711.00	3596.00	28.430	1347.000	1318.000	8.761
-2.5	-6.00	-1.199	-4.16	-1.199	-1.199	-1.199	-1.69	-4.35	-1.199	117.300	3713.00	3596.00	29.150	1348.000	1318.000	8.525
-2.2343	-6.00	-0.933	-4.16	-0.933	-0.933	-0.933	-1.69	-4.35	-0.933	214.500	3807.00	3593.00	53.100	1374.000	1321.000	4.662
-2.1001	-6.00	-0.799	-4.16	-0.799	-0.799	-0.799	-1.69	-4.35	-0.799	291.400	3881.00	3590.00	72.060	1394.000	1322.000	3.432
-2.0138	-6.00	-0.713	-4.16	-0.713	-0.713	-0.713	-1.69	-4.35	-0.713	355.000	3942.00	3587.00	87.730	1411.000	1324.000	2.817
-2	-6.00	-0.699	-4.16	-0.699	-0.699	-0.699	-1.69	-4.35	-0.699	366.400	3954.00	3588.00	90.540	1415.000	1324.000	2.729
-1.5694	-6.00	-0.268	-4.16	-0.268	-0.268	-0.268	-1.69	-4.35	-0.268	983.900	4575.00	3591.00	242.700	1606.000	1363.000	1.016
-1.5	-6.00	-0.199	-4.16	-0.199	-0.199	-0.268	-1.69	-4.35	-0.199	1126.000	4716.00	3586.00	275.200	1643.000	1368.000	0.887
-1.3985	-6.00	-0.098	-4.16	-0.098	-0.098	-0.268	-1.69	-4.35	-0.098	1385.000	4960.00	3575.00	333.200	1709.000	1376.000	0.722
-1.1772	-6.00	0.124	-4.16	0.124	0.124	-0.268	-1.69	-4.35	-0.098	1876.000	5430.00	3553.00	518.000	1867.000	1349.000	0.533
-1.0801	-6.00	0.221	-4.16	0.221	0.124	-0.268	-1.69	-4.35	-0.098	2097.000	5642.00	3545.00	600.600	1940.000	1339.000	0.477
-1.0458	-6.00	0.255	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	2187.000	5734.00	3547.00	634.500	1974.000	1340.000	0.457
-1	-6.00	0.301	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	2264.000	5810.00	3546.00	662.300	2001.000	1338.000	0.442
-0.5969	-6.00	0.704	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3439.000	6971.00	3532.00	1087.000	2408.000	1321.000	0.291
-0.5565	-6.00	0.743	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3628.000	7157.00	3529.00	1156.000	2474.000	1318.000	0.276
-0.5557	-6.00	0.745	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3632.000	7161.00	3529.00	1157.000	2475.000	1318.000	0.275
-0.5381	-6.00	0.763	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3720.000	7249.00	3529.00	1189.000	2506.000	1317.000	0.269
-0.5235	-6.00	0.778	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3796.000	7325.00	3528.00	1217.000	2533.000	1316.000	0.263
-0.5	-6.00	0.801	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	3924.000	7452.00	3528.00	1263.000	2577.000	1314.000	0.255
-0.4166	-6.00	0.885	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	4439.000	7962.00	3524.00	1449.000	2753.000	1304.000	0.225
-0.2737	-6.00	1.027	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	5584.000	9097.00	3513.00	1864.000	3152.000	1288.000	0.179
-0.2674	-6.00	1.034	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	5645.000	9259.00	3614.00	1886.000	2921.000	1036.000	0.177
-0.2654	-6.00	1.036	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	5663.000	9449.00	3785.00	1893.000	2510.000	617.700	0.177
-0.21	-6.00	1.091	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6230.000	9727.00	3496.00	2098.000	3374.000	1277.000	0.161
-0.1981	-6.00	1.103	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6362.000	9855.00	3493.00	2145.000	3419.000	1274.000	0.157
-0.1955	-6.00	1.106	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6391.000	9884.00	3493.00	2156.000	3429.000	1273.000	0.156
-0.1938	-6.00	1.107	-4.16	0.255	0.124	-0.268	-1.69	-4.35	-0.098	6410.000	9903.00	3492.00	2163.000	3436.000	1273.000	0.156

[1] cm3 = cubic centimeters
[2] g = grams
[3] Des = Destroyed
[4] Cre = Created

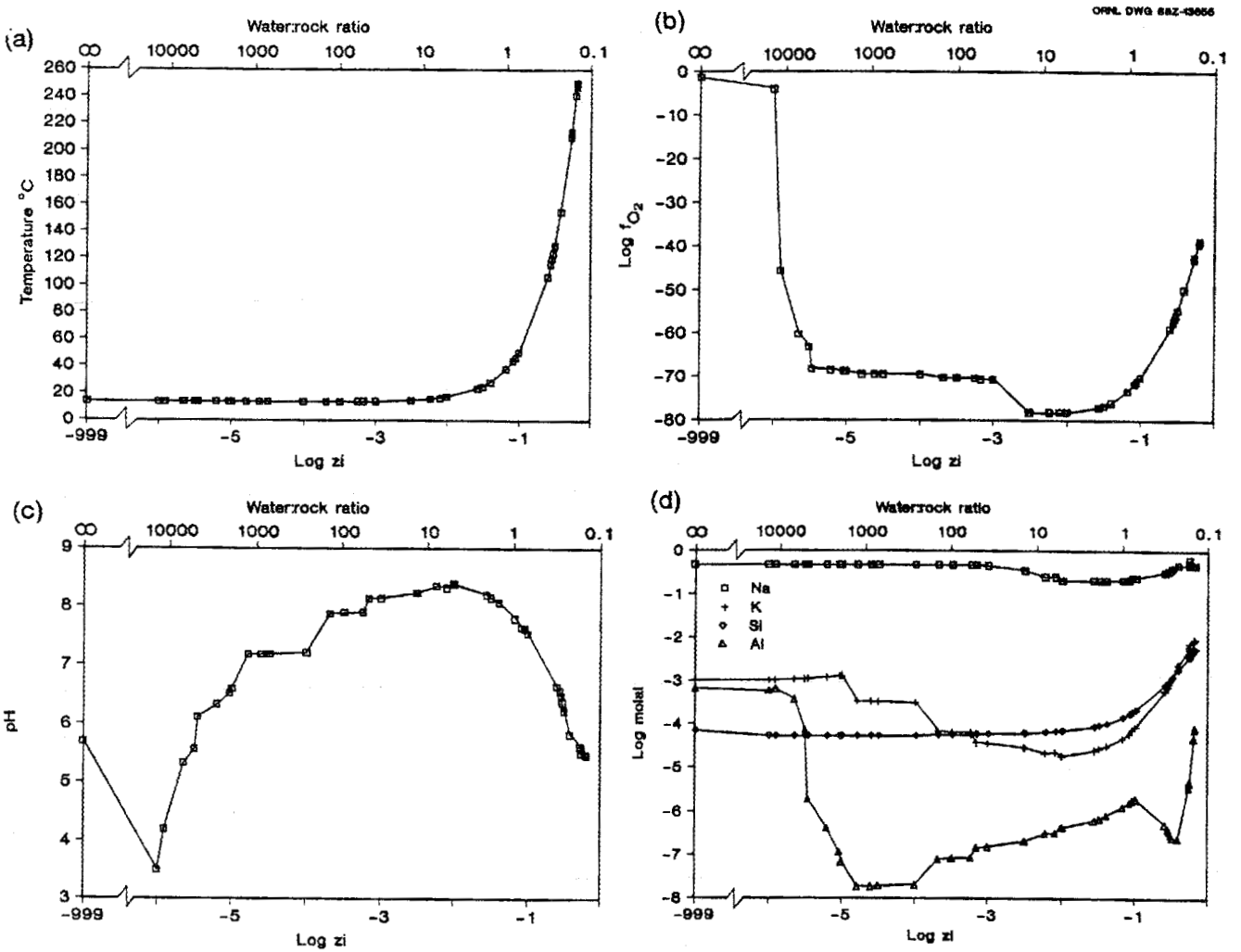

Fig. 2. Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, CH_4 suppression, pyrite present: (a) Temperature, (b) Log f_{O_2}, (c) pH, (d) Na, K, Si, and Al.

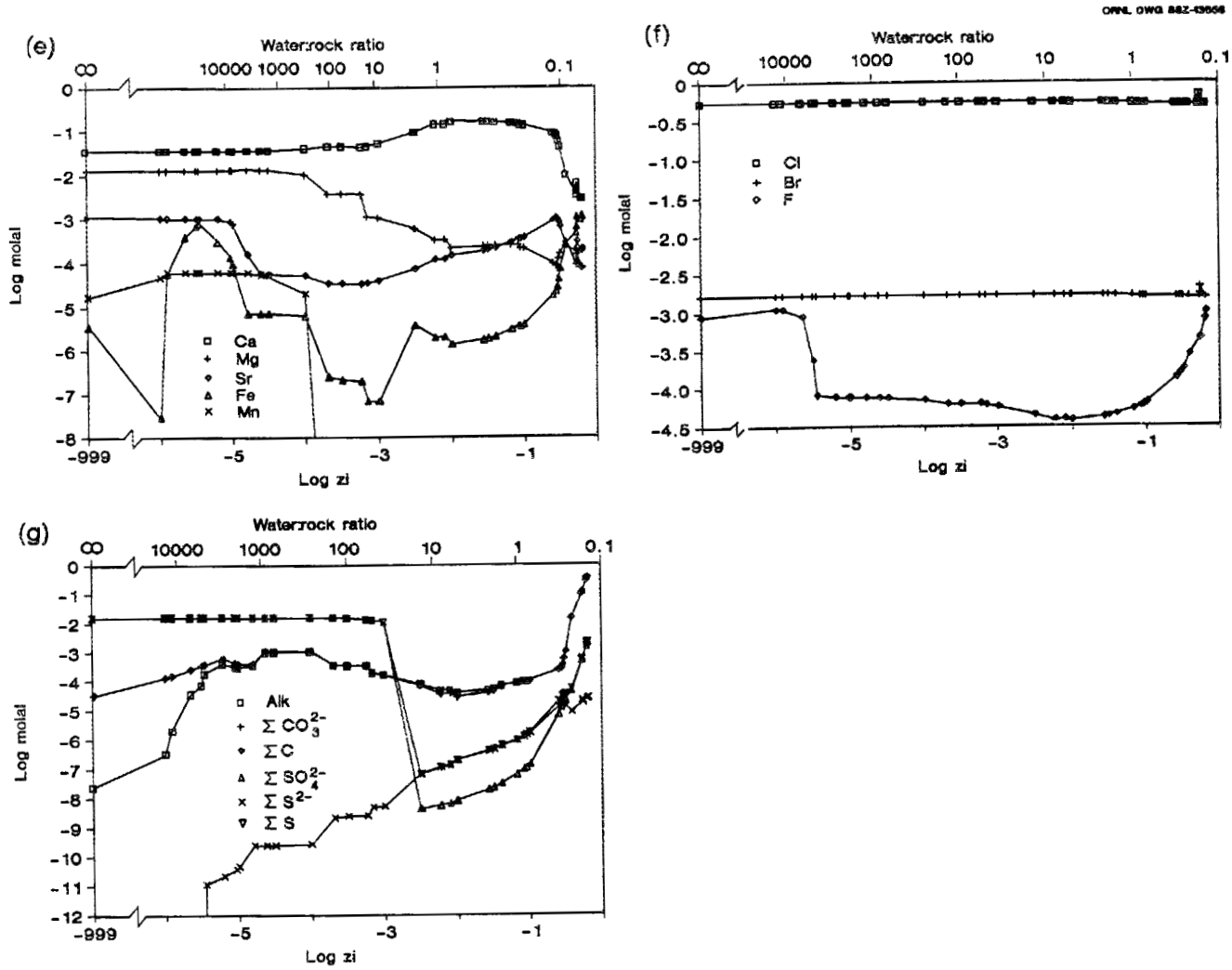

Fig. 2 (continued). Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, CH_4 suppression, pyrite present: (e) Ca, Mg, Sr, Fe, and Mn, (f) Cl, Br, and F, (g) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

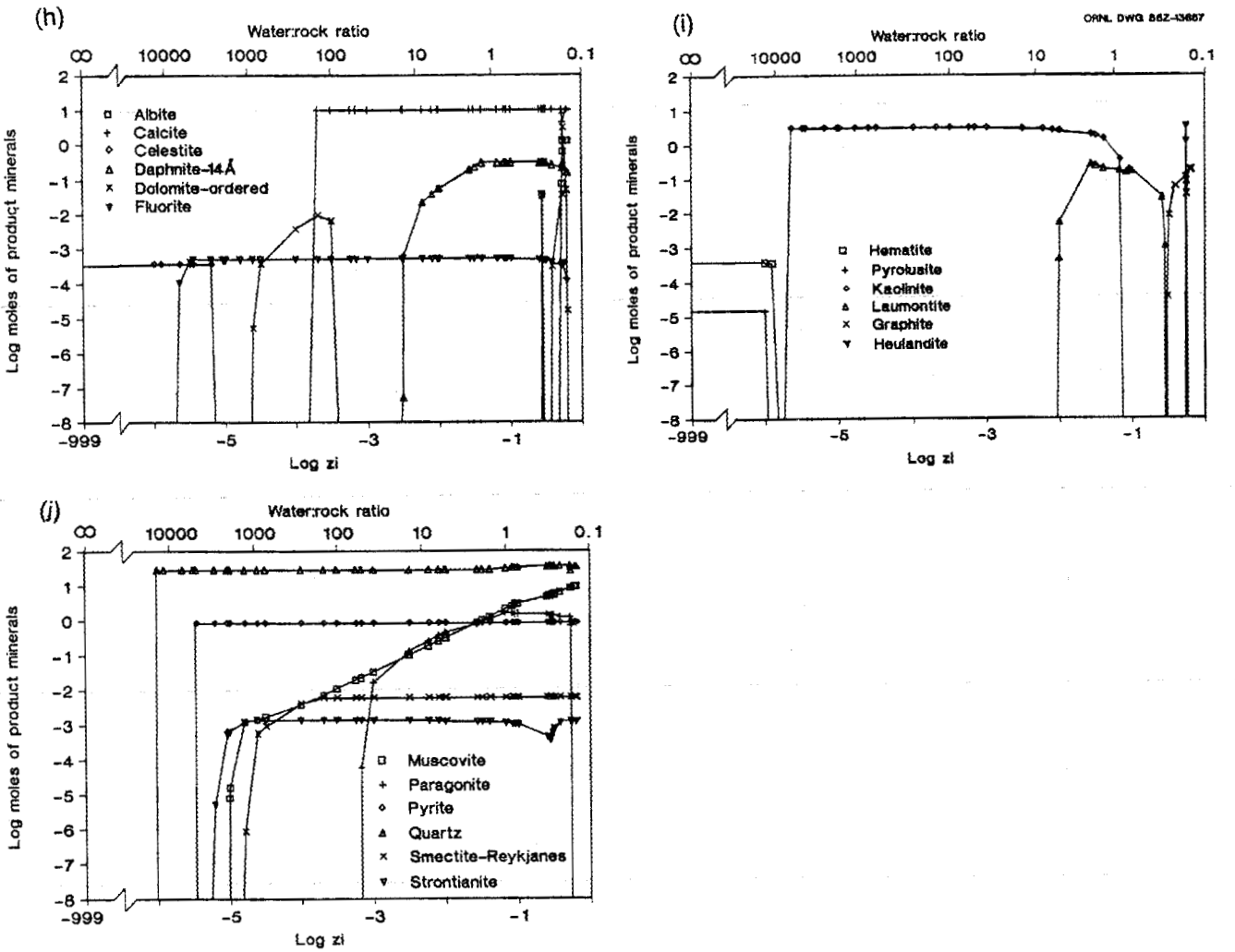

Fig. 2 (continued). Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, CH_4 suppression, pyrite present: (h) product minerals 1, (i) product minerals 2, (j) product minerals 3.

graphite, muscovite, pyrite, quartz, strontianite, and Reykjanes-, and Ca-smectite. Celestite, ordered dolomite, hematite, pyrolusite, kaolinite, laumontite, heulandite, paragonite, and Na-smectite are part of the equilibrium mineral assemblage at various points during the reaction progress. The final water:rock ratio is 0.16.

Case 3: Reaction of PVS groundwater and rock with graphite replacing pyrite at T = 13.5°C. In this case graphite replaced pyrite on an equimolar basis in the initial rock composition and the formation of CH_4 was not suppressed. CH_4 cannot be suppressed when graphite is present, as CH_4(aq) is incorporated in the equation for the formation/dissolution of graphite in the data base. The water was initially assumed to be in equilibrium with air but quickly became reducing, the log f_{O_2} decreasing from -1.3 to -78.9. The pH steadily increased from 5.6 to 8.4 (Table 5, Fig. 3). The alkalinity increased while the total carbonate decreased slightly. The total SO_4^{2-} decreased markedly while the total H_2S increased. Total dissolved Br, Ca, Cl, C, and Si increased while Al, F, Fe, K, Mg, Mn, Na, S, and Sr decreased. The predominant form of C present at the end of the reaction was CH_4(aq) and the predominant form of S changed from SO_4^{2-} early in the reaction progress to HS^- at the end. A small amount of H_2O was consumed during the reaction progress. An assemblage containing calcite, fluorite, kaolinite, muscovite, paragonite, pyrite, quartz, strontianite, and Reykjanes-, Ca-, and Na-smectite was present at the end of the experiment. Ordered dolomite, 14A-daphnite, hematite, and pyrolusite were present at various points during the reaction progress, the last two being present only in the very earliest stages of the reaction progress when the system was relatively oxidizing. The final water:rock ratio achieved was 0.16.

Case 4: Reaction of PVS groundwater and rock with graphite replacing pyrite to T = 250°C. The initial conditions of this case are identical to those of Case 3, but during the course of the experiment the temperature is raised from 13.5° to 250°C. As a

Table 5a. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, No CH_4 Suppression, Graphite Replacing Pyrite.
Log molal concentrations of dissolved elements.

Log xi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Br	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	Si	S	Sr
-999	13.5	1.01	3.00	-1.28	1.043	-7.55	-4.51	-1.80	-141.85	-3.39	-2.77	-2.77	-1.444	-0.262	-3.01	-5.51	-4.509	-2.99	-1.89	-4.77	-0.320	-4.28	-1.80	-2.98
-6	13.5	1.01	3.49	-1.98	1.005	-6.36	-3.77	-1.80	-140.93	-3.21	-2.77	-2.77	-1.441	-0.262	-2.96	-7.51	-3.767	-2.97	-1.89	-5.39	-0.320	-4.28	-1.80	-2.98
-5.8685	13.5	1.01	4.17	-5.59	0.915	-5.56	-3.66	-1.80	-134.39	-3.17	-2.77	-2.77	-1.441	-0.262	-2.96	-9.26	-3.657	-2.97	-1.89	-4.94	-0.320	-4.28	-1.80	-2.98
-5.677	13.5	1.01	5.04	-54.31	0.173	-4.58	-3.49	-1.80	-37.83	-3.23	-2.77	-2.77	-1.440	-0.262	-2.96	-4.28	-3.487	-2.96	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.6013	13.5	1.01	5.29	-58.13	0.104	-4.29	-3.42	-1.80	-30.44	-3.32	-2.77	-2.77	-1.439	-0.262	-2.97	-3.88	-3.418	-2.95	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.5	13.5	1.01	5.36	-59.91	0.075	-4.14	-3.32	-1.80	-26.94	-3.52	-2.77	-2.77	-1.441	-0.262	-3.15	-3.58	-3.325	-2.95	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.337	13.5	1.01	6.19	-68.38	-0.093	-3.43	-3.17	-1.80	-10.84	-6.00	-2.77	-2.77	-1.442	-0.262	-4.10	-3.26	-3.171	-2.93	-1.88	-4.22	-0.320	-4.28	-1.80	-2.98
-5.2664	13.5	1.01	6.26	-68.46	-0.098	-3.33	-3.11	-1.80	-10.75	-6.21	-2.77	-2.77	-1.441	-0.262	-4.11	-3.40	-3.105	-2.92	-1.88	-4.22	-0.320	-4.28	-1.80	-2.98
-5.1299	13.5	1.01	6.33	-68.53	-0.103	-3.38	-3.18	-1.80	-10.67	-6.41	-2.77	-2.77	-1.438	-0.262	-4.11	-3.52	-3.177	-2.90	-1.88	-4.22	-0.320	-4.28	-1.80	-3.00
-5	13.5	1.01	6.54	-68.76	-0.118	-3.36	-3.22	-1.80	-10.41	-7.01	-2.77	-2.77	-1.435	-0.262	-4.12	-3.92	-3.219	-2.87	-1.87	-4.22	-0.320	-4.28	-1.80	-3.23
-4.982	13.5	1.01	6.59	-68.82	-0.122	-3.35	-3.23	-1.80	-10.35	-7.15	-2.77	-2.77	-1.434	-0.262	-4.12	-4.02	-3.227	-2.87	-1.87	-4.22	-0.320	-4.28	-1.80	-3.29
-4.7912	13.5	1.01	7.18	-69.48	-0.165	-3.06	-3.02	-1.80	-9.62	-7.73	-2.77	-2.77	-1.426	-0.262	-4.12	-5.14	-3.023	-3.46	-1.86	-4.22	-0.320	-4.27	-1.80	-4.17
-4.7581	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.80	-9.62	-7.73	-2.77	-2.77	-1.425	-0.262	-4.12	-5.14	-2.955	-3.46	-1.86	-4.23	-0.320	-4.27	-1.80	-4.24
-4.5	13.5	1.01	7.19	-69.49	-0.166	-2.99	-2.95	-1.81	-9.61	-7.72	-2.77	-2.77	-1.421	-0.262	-4.13	-5.15	-2.953	-3.47	-1.89	-4.27	-0.320	-4.27	-1.81	-4.25
-4	13.5	1.01	7.23	-69.56	-0.169	-2.97	-2.94	-1.86	-9.56	-7.70	-2.77	-2.77	-1.401	-0.262	-4.15	-5.22	-2.937	-3.51	-2.03	-4.55	-0.320	-4.27	-1.86	-4.31
-3.6959	13.5	1.01	7.88	-70.36	-0.217	-3.41	-3.41	-1.96	-8.71	-7.11	-2.77	-2.77	-1.372	-0.262	-4.20	-6.53	-3.414	-4.16	-2.46	-221.87	-0.319	-4.25	-1.96	-4.51
-3.5	13.5	1.01	7.93	-70.51	-0.222	-3.44	-3.44	-2.10	-8.58	-7.06	-2.77	-2.77	-1.405	-0.262	-4.18	-6.72	-3.441	-4.21	-2.49	-233.20	-0.318	-4.25	-2.10	-4.55
-3	13.5	1.01	7.98	-77.17	-0.320	-3.39	-3.40	-8.58	-7.69	-7.01	-2.77	-2.77	-1.509	-0.261	-4.15	-5.18	-2.000	-4.26	-2.60	-287.92	-0.316	-4.24	-7.64	-4.66
-2.6391	13.5	1.01	7.99	-77.49	-0.325	-3.38	-3.38	-8.54	-7.65	-7.01	-2.77	-2.77	-1.530	-0.261	-4.14	-5.11	-1.372	-4.27	-2.62	-290.10	-0.312	-4.24	-7.60	-4.68
-2.5856	13.5	1.01	8.14	-77.69	-0.336	-3.54	-3.55	-8.50	-7.46	-6.86	-2.77	-2.77	-1.510	-0.261	-4.15	-5.39	-1.302	-4.42	-2.95	-313.76	-0.313	-4.23	-7.42	-4.66
-2.5	13.5	1.01	8.14	-77.77	-0.338	-3.58	-3.60	-8.49	-7.45	-6.85	-2.77	-2.77	-1.472	-0.260	-4.17	-5.38	-1.193	-4.43	-2.96	-317.58	-0.317	-4.23	-7.41	-4.62
-2	13.5	1.01	8.21	-78.27	-0.348	-3.92	-3.96	-8.44	-7.32	-6.79	-2.77	-2.77	-1.167	-0.258	-4.31	-5.37	-0.626	-4.49	-3.10	-350.69	-0.381	-4.23	-7.29	-4.31
-1.8033	13.5	1.01	8.27	-78.52	-0.355	-4.11	-4.16	-8.41	-7.23	-6.73	-2.77	-2.77	-1.013	-0.256	-4.37	-5.43	-0.418	-4.55	-3.22	-371.34	-0.443	-4.23	-7.20	-4.15
-1.6809	13.5	1.01	8.29	-78.61	-0.358	-4.15	-4.20	-8.38	-7.19	-6.71	-2.77	-2.77	-0.979	-0.255	-4.39	-5.47	-0.305	-4.57	-3.24	-376.62	-0.460	-4.22	-7.16	-4.12
-1.6102	13.5	1.01	8.44	-78.84	-0.369	-4.37	-4.49	-8.33	-6.98	-6.56	-2.77	-2.77	-0.811	-0.257	-4.45	-5.77	-0.325	-4.72	-3.52	-409.34	-0.610	-4.21	-6.96	-3.94
-1.5694	13.5	1.01	8.44	-78.84	-0.370	-4.37	-4.49	-8.32	-6.98	-6.56	-2.77	-2.77	-0.813	-0.258	-4.45	-5.77	-0.321	-4.72	-3.53	-409.36	-0.610	-4.21	-6.96	-3.94
-1.5	13.5	1.01	8.44	-78.84	-0.370	-4.37	-4.49	-8.32	-6.98	-6.56	-2.77	-2.77	-0.815	-0.260	-4.45	-5.77	-0.312	-4.72	-3.53	-409.37	-0.611	-4.21	-6.96	-3.95
-1.3985	13.5	1.01	8.44	-78.85	-0.370	-4.37	-4.49	-8.32	-6.98	-6.56	-2.78	-2.78	-0.819	-0.262	-4.45	-5.78	-0.296	-4.72	-3.53	-409.40	-0.612	-4.21	-6.96	-3.95
-1.1772	13.5	1.01	8.44	-78.85	-0.370	-4.37	-4.49	-8.32	-6.97	-6.55	-2.78	-2.78	-0.829	-0.270	-4.45	-5.79	-0.299	-4.73	-3.54	-409.44	-0.616	-4.21	-6.96	-3.96
-1.0458	13.5	1.01	8.44	-78.85	-0.370	-4.37	-4.49	-8.32	-6.97	-6.55	-2.79	-2.79	-0.833	-0.272	-4.45	-5.79	-0.298	-4.73	-3.54	-409.45	-0.618	-4.21	-6.95	-3.96
-1	13.5	1.01	8.44	-78.85	-0.370	-4.37	-4.49	-8.32	-6.97	-6.55	-2.79	-2.79	-0.833	-0.272	-4.45	-5.79	-0.296	-4.73	-3.54	-409.45	-0.618	-4.21	-6.95	-3.96
-0.5	13.5	1.01	8.44	-78.87	-0.370	-4.37	-4.49	-8.32	-6.97	-6.56	-2.78	-2.78	-0.824	-0.266	-4.45	-5.78	-0.259	-4.73	-3.53	-409.44	-0.614	-4.21	-6.95	-3.95
-0.23	13.5	1.01	8.44	-78.89	-0.370	-4.37	-4.49	-8.31	-6.97	-6.56	-2.77	-2.77	-0.812	-0.258	-4.45	-5.77	-0.217	-4.72	-3.52	-409.41	-0.610	-4.21	-6.95	-3.94
-0.1938	13.5	1.01	8.44	-78.89	-0.370	-4.37	-4.49	-8.31	-6.97	-6.56	-2.77	-2.77	-0.810	-0.256	-4.45	-5.78	-0.215	-4.72	-3.52	-409.19	-0.609	-4.21	-6.95	-3.94

Table 5b. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, No CH_4 Suppression, Graphite Replacing Pyrite.
Log moles of product minerals.

Log zi	Calcite	Celestite	Daphnite -14A	Dolomite -ordered	Fluorite	Hematite	Pyrolusite	Kaolinite	Muscovite	Paragonite	Pyrite	Quartz	Smectite-Reykjanes	Strontianite	Ca-smectite	Na-smectite
-999		-3.45			-4.25	-3.46	-4.37									
-6		-3.44				-3.43	-4.25					1.46				
-5.8685		-3.44				-3.43	-4.31					1.46				-5.437
-5.677		-3.44						0.464				1.46				-3.427
-5.6013		-3.44			-5.77			0.464				1.46				-3.465
-5.5		-3.44			-3.73			0.464				1.46				-3.539
-5.337		-3.44			-3.30			0.464			-6.69	1.46				-3.753
-5.2664		-3.45			-3.30			0.464			-4.68	1.46		-5.42		-3.584
-5.1299					-3.30			0.464			-4.27	1.46		-3.39		-3.471
-5					-3.30			0.464			-4.00	1.46		-3.08		-3.330
-4.982					-3.30			0.464	-5.2711		-3.97	1.46		-3.05		-3.313
-4.7912					-3.30			0.464	-2.9210		-3.72	1.46	-6.33	-2.87		-3.197
-4.7581				-5.34	-3.30			0.464	-2.9073		-3.69	1.46	-6.05	-2.87		-3.206
-4.5				-3.00	-3.30			0.464	-2.7765		-3.42	1.46	-3.21	-2.87		-3.195
-4				-2.24	-3.29			0.464	-2.4177		-2.91	1.46	-2.50	-2.86		-3.147
-3.6959	0.999			-1.88	-3.29			0.464	-2.1411		-2.60	1.46	-2.22	-2.86		-2.736
-3.5	0.999			-1.91	-3.29			0.465	-1.9623		-2.39	1.46	-2.22	-2.86		-2.150
-3	1.000			-2.10	-3.29			0.466	-1.4842		-2.09	1.46	-2.22	-2.86		-1.385
-2.6391	1.002				-3.29			0.470	-1.1292		-2.09	1.46	-2.22	-2.86		-0.959
-2.5856	1.002				-3.29			0.470	-1.0763	-4.1066	-2.09	1.46	-2.22	-2.86		-0.890
-2.5	1.002				-3.29			0.470	-0.9914	-2.1369	-2.09	1.46	-2.22	-2.86		-0.801
-2	1.007				-3.28			0.467	-0.4937	-1.0232	-2.09	1.46	-2.22	-2.86		-0.290
-1.8033	1.010		-3.288		-3.28			0.464	-0.2974	-0.7742	-2.09	1.46	-2.22	-2.87		-0.095
-1.6809	1.014		-1.528		-3.28			0.464	-0.1752	-0.6427	-2.09	1.46	-2.22	-2.87		-0.008
-1.6102	1.015		-1.046		-3.28			0.432	-0.1046	-0.3889	-2.09	1.46	-2.22	-2.89	-1.536	-0.019
-1.5694	1.015		-1.002		-3.28			0.408	-0.0639	-0.2723	-2.09	1.46	-2.22	-2.89	-0.443	-0.142
-1.5	1.014		-0.927		-3.28			0.391	0.0055	-0.2289	-2.09	1.46	-2.22	-2.89	-0.364	-0.080
-1.3985	1.014		-0.818		-3.28			0.359	0.1069	-0.1610	-2.09	1.47	-2.22	-2.89	-0.253	0.014
-1.1772	1.013		-0.844		-3.28			0.133	0.3281	0.0810	-2.09	1.50	-2.22	-2.89	-0.223	0.032
-1.0458	1.013		-0.867		-3.28			0.004	0.4595	0.0758	-2.09	1.52	-2.22	-2.89	-0.202	0.048
-1	1.013		-0.876		-3.28			0.025	0.4772	0.0735	-2.09	1.52	-2.22	-2.89	-0.194	0.055
-0.5	1.011		-1.141		-3.28			0.337	0.7478	0.0213	-2.09	1.56	-2.22	-2.89	-0.066	0.190
-0.23	1.010				-3.28			0.554	0.9478	-0.0554	-2.09	1.61	-2.22	-2.89	0.053	0.316
-0.1938	1.010				-3.28			0.585	0.9768	-0.0730	-2.09	1.62	-2.22	-2.89	0.053	0.338

Table 5c. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 13.5°C, No CH_4 Suppression, Graphite Replacing Pyrite.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Graphite	K-feldspar	Albite	Anorthite	Calcite	Kaolinite	Ripidolite -14A	g[b]Des[d]	g[b]Cre[c]	g[b]Net	cm[3][a]Des[c]	cm[3][a]Cre[d]	cm[3][a]Net	Water:Rock Ratio
-999	-999.00	-999.000	-999.000	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	0.00	0.13	0.13	0.000	0.017	0.017	
-6	-6.00	-4.699	-4.398	-4.699	-4.699	-4.699	-4.00	-4.70	-4.699	0.05	1749.00	1749.00	0.015	660.200	660.200	19179.133
-5.8685	-6.00	-4.567	-4.266	-4.567	-4.567	-4.567	-3.87	-4.57	-4.567	0.07	1749.00	1749.00	0.020	660.200	660.200	14170.327
-5.677	-6.00	-4.376	-4.075	-4.376	-4.376	-4.376	-3.68	-4.38	-4.376	0.11	2500.00	2500.00	0.031	949.800	949.800	9124.088
-5.6013	-6.00	-4.300	-3.999	-4.300	-4.300	-4.300	-3.60	-4.38	-4.300	0.13	2500.00	2500.00	0.036	949.800	949.800	7786.162
-5.5	-6.00	-4.199	-3.898	-4.199	-4.199	-4.199	-3.50	-4.38	-4.199	0.16	2500.00	2500.00	0.044	949.900	949.800	6277.464
-5.337	-6.00	-4.036	-3.735	-4.036	-4.036	-4.036	-3.34	-4.38	-4.036	0.23	2500.00	2500.00	0.063	949.900	949.800	4407.228
-5.2664	-6.00	-3.965	-3.664	-3.965	-3.965	-3.965	-3.27	-4.38	-3.965	0.27	2500.00	2500.00	0.073	949.900	949.800	3773.585
-5.1299	-6.00	-3.829	-3.528	-3.829	-3.829	-3.829	-3.13	-4.38	-3.829	0.36	2500.00	2500.00	0.098	949.900	949.800	2787.068
-5	-6.00	-3.699	-3.398	-3.699	-3.699	-3.699	-3.00	-4.38	-3.699	0.48	2500.00	2500.00	0.131	949.900	949.800	2082.899
-4.982	-6.00	-3.681	-3.380	-3.681	-3.681	-3.681	-2.98	-4.38	-3.681	0.50	2500.00	2500.00	0.136	949.900	949.800	2000.000
-4.7912	-6.00	-3.490	-3.189	-3.490	-3.490	-3.490	-2.79	-4.38	-3.490	0.77	2501.00	2500.00	0.209	950.000	949.800	1299.039
-4.7581	-6.00	-3.457	-3.156	-3.457	-3.457	-3.457	-2.76	-4.38	-3.457	0.83	2501.00	2500.00	0.225	950.000	949.800	1204.964
-4.5	-6.00	-3.199	-2.898	-3.199	-3.199	-3.199	-2.50	-4.38	-3.199	1.50	2501.00	2500.00	0.405	950.200	949.800	668.896
-4	-6.00	-2.699	-2.398	-2.699	-2.699	-2.699	-2.00	-4.38	-2.699	4.70	2505.00	2500.00	1.271	950.900	949.700	212.630
-3.6959	-6.00	-2.395	-2.094	-2.395	-2.395	-2.395	-1.70	-4.38	-2.395	9.46	3508.00	3498.00	2.556	1320.000	1318.000	105.686
-3.5	-6.00	-2.199	-1.898	-2.199	-2.199	-2.199	-1.70	-4.38	-2.199	13.70	3512.00	3499.00	3.587	1322.000	1318.000	72.993
-3	-6.00	-1.699	-1.398	-1.699	-1.699	-1.699	-1.70	-4.38	-1.699	38.94	3539.00	3500.00	9.725	1329.000	1320.000	25.681
-2.6391	-6.00	-1.338	-1.037	-1.338	-1.338	-1.338	-1.70	-4.38	-1.338	86.77	3588.00	3501.00	21.360	1343.000	1322.000	11.525
-2.5856	-6.00	-1.285	-0.984	-1.285	-1.285	-1.285	-1.70	-4.38	-1.285	97.86	3599.00	3501.00	24.060	1346.000	1322.000	10.219
-2.5	-6.00	-1.199	-0.898	-1.199	-1.199	-1.199	-1.70	-4.38	-1.199	118.80	3620.00	3502.00	29.140	1352.000	1323.000	8.418
-2	-6.00	-0.699	-0.398	-0.699	-0.699	-0.699	-1.70	-4.38	-0.699	371.10	3875.00	3504.00	90.520	1421.000	1330.000	2.695
-1.8033	-6.00	-0.502	-0.201	-0.502	-0.502	-0.502	-1.70	-4.38	-0.502	582.70	4089.00	3506.00	142.000	1479.000	1337.000	1.716
-1.6809	-6.00	-0.380	-0.079	-0.380	-0.380	-0.380	-1.70	-4.38	-0.380	771.60	4280.00	3508.00	187.900	1535.000	1347.000	1.296
-1.6102	-6.00	-0.309	-0.079	-0.309	-0.309	-0.309	-1.70	-4.38	-0.309	905.80	4410.00	3504.00	221.000	1575.000	1355.000	1.104
-1.5694	-6.00	-0.268	-0.079	-0.268	-0.268	-0.268	-1.70	-4.38	-0.268	993.90	4494.00	3501.00	242.700	1598.000	1355.000	1.006
-1.5	-6.00	-0.199	-0.079	-0.199	-0.199	-0.268	-1.70	-4.38	-0.199	1138.00	4635.00	3497.00	275.200	1635.000	1359.000	0.879
-1.3985	-6.00	-0.098	-0.079	-0.098	-0.098	-0.268	-1.70	-4.38	-0.098	1395.00	4886.00	3491.00	333.200	1701.000	1368.000	0.717
-1.1772	-6.00	0.124	-0.079	0.124	0.124	-0.268	-1.70	-4.38	-0.098	1886.00	5360.00	3474.00	518.000	1862.000	1344.000	0.530
-1.0458	-6.00	0.255	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	2197.00	5664.00	3467.00	634.500	1967.000	1333.000	0.455
-1	-6.00	0.301	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	2274.00	5742.00	3467.00	662.300	1995.000	1333.000	0.440
-0.5	-6.00	0.801	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	3934.00	7416.00	3482.00	1263.000	2594.000	1331.000	0.254
-0.23	-6.00	1.071	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	6027.00	9528.00	3500.00	2021.000	3349.000	1328.000	0.166
-0.1938	-6.00	1.107	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	6420.00	9924.00	3504.00	2163.000	3493.000	1330.000	0.156

[a] cm^3 = cubic centimeters
[b] g = grams
[c] Des = Destroyed
[d] Cre = Created

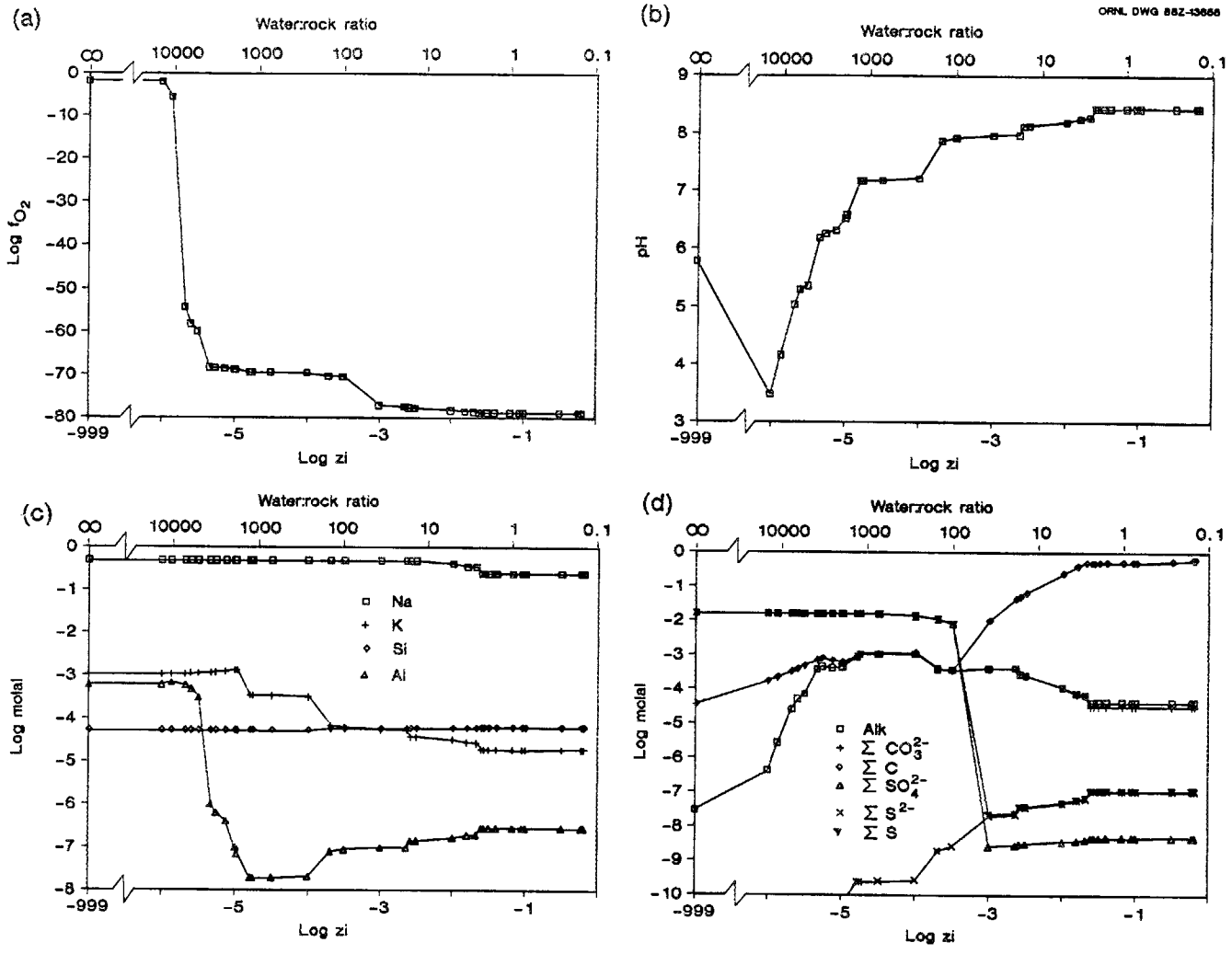

Fig. 3. Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, no CH_4 suppession, graphite replacing pyrite: (a) Log f_{O_2}, (b) pH, (c) Na, K, Si, and Al, (d) Ca, Mg, Sr, Fe, and Mn.

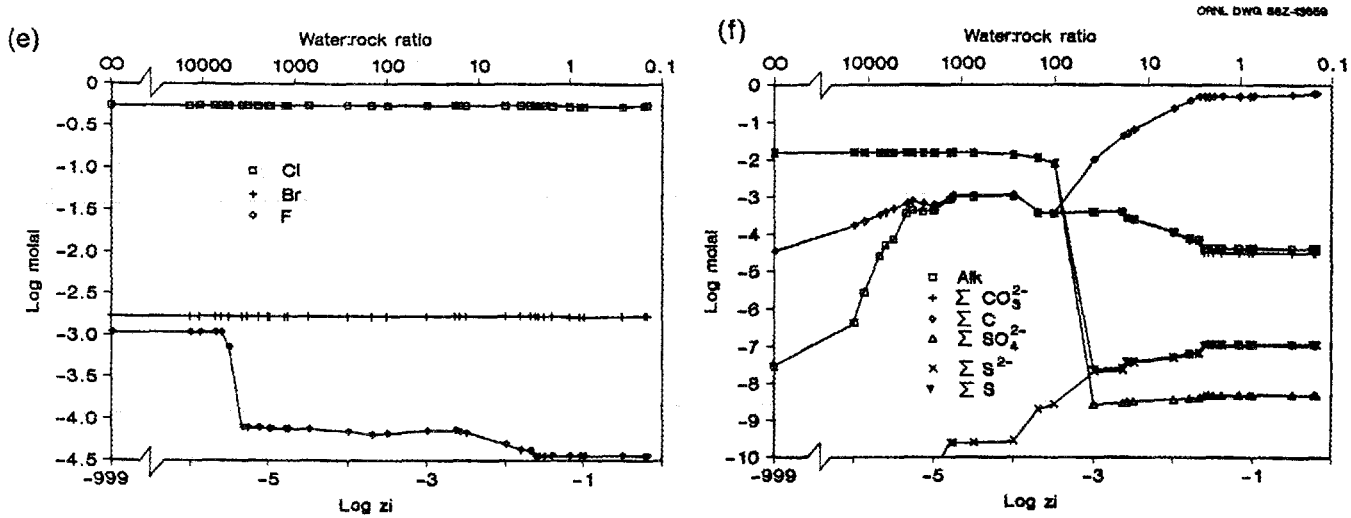

Fig. 3 (continued). Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, no CH_4 suppession, graphite replacing pyrite: (e) Cl, Br, and F, (f) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

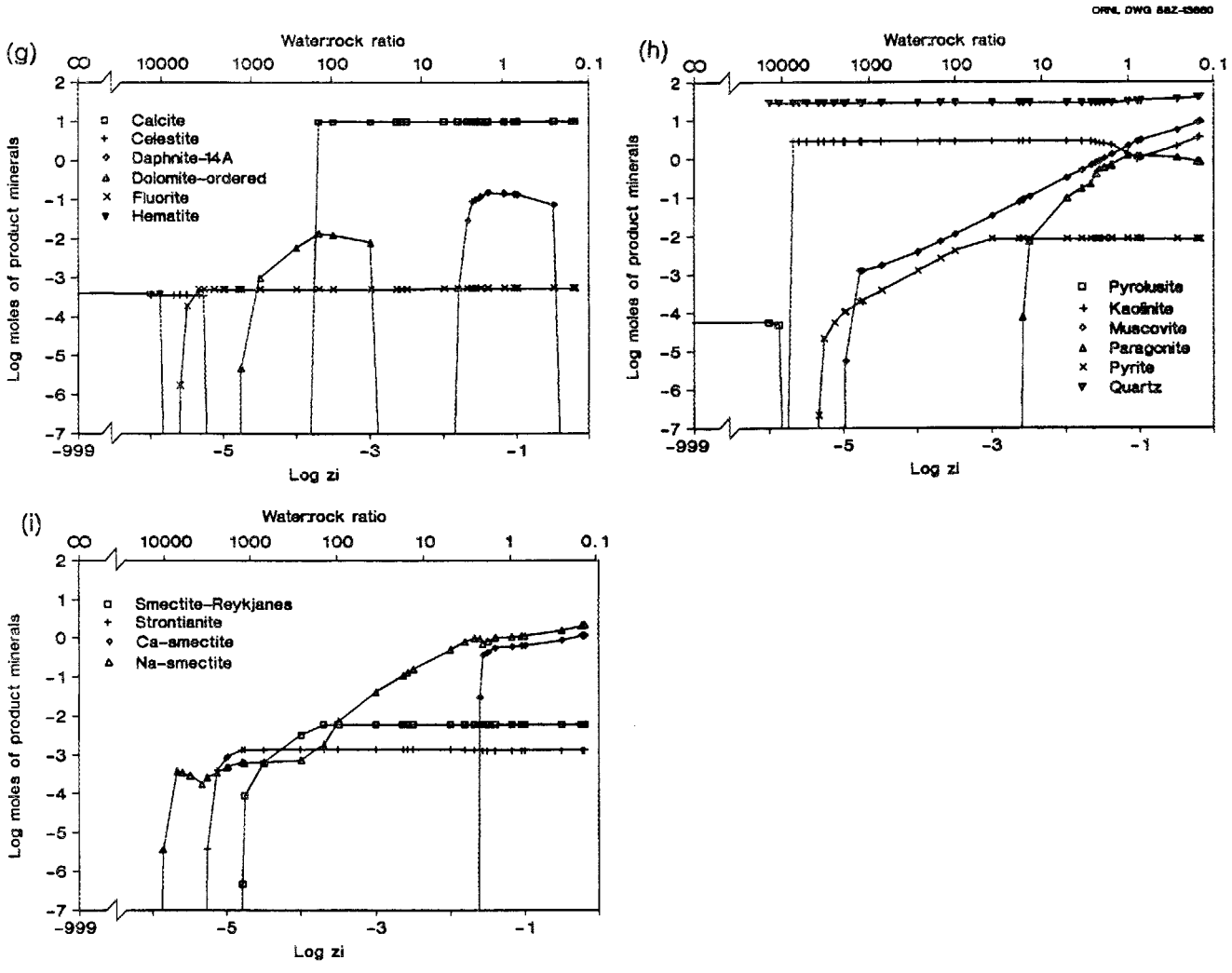

Fig. 3 (continued). Reaction of Pumpkin Valley Shale groundwater and rock at T = 13.5°C, no CH_4 suppression, graphite replacing pyrite: (g) product minerals 1, (h) product minerals 2, (i) product minerals 3.

consequence of the temperature increase the log f_{O_2} decreased from an initial value of -1.3 to -77.4 and then increased to -38.5 which is quite reducing under the elevated temperature conditions (Table 6, Fig. 4). The pH is initially acid at 5.6, increases to a maximum of 8.1 and then decreases to 5.5. Under the elevated temperature conditions this final pH is actually quite close to neutral. In the EQ6 code, alkalinity is undefined at temperatures greater than 50°C, hence no values are given for this property for the later part of the reaction progress. Earlier, however, alkalinity is increasing, and the total carbonate increases throughout the reaction. Total SO_4^{2-} reaches a minimum during the reaction progress at a temperature of 13.9°C and then begins to increase but is never as high as the initial value, while total H_2S gradually increases throughout the reaction progress. F, Fe, C, K, Na, and Si increase in the solution while Al, Br, Ca, Cl, Mg, Mn, S, and Sr decrease. The predominant form of C is CO_2(aq), followed closely by CH_4(aq) and smaller amounts of HCO_3^-. The predominant form of S is as H_2S(aq) followed by HS^-. A small amount of water is produced during the course of the reaction. The minerals albite, calcite, 14A-daphnite, ordered dolomite, graphite, muscovite, pyrite, quartz, strontianite, and Reykjanes-, and Ca-smectite comprise the final equilibrium assemblage while celestite, fluorite, hematite, pyrolusite, kaolinite, heulandite, paragonite, and Na-smectite are present at various points during the reaction progress. The final water:rock ratio achieved is 0.16.

Modeling of Smectitic Shales

The smectitic shale used in all cases is the Pierre Shale. A wide range in compositions has been reported for this shale formation which is quite extensive in area. Two different compositions were used, the first was based on literature data from Schultz et al. (1980) and the second was based on the data of Lee et al. (1987). The major difference in the two mineralogies is the relative amount of calcite, graphite, and illite which are present. Evaluation of two compositions (Table 7) is helpful in understanding the range of

Table 6a. Reaction of Pumpkin Valley Shale Groundwater and Rock at Y = 250°C, No CH_4 Suppression, Graphite Replacing Pyrite.
Log molal concentrations of dissolved elements.

Log zi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Br	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Mo	Si	S	Sr
-999	13.5	1.01	3.00	-1.28	1.043	-7.55	-4.51	-1.80	-141.65	-3.39	-2.77	-2.77	-1.44	-0.262	-3.01	-5.51	-4.509	-2.99	-1.89	-4.77	-0.320	-4.28	-1.80	-2.98
-6	13.5	1.01	3.49	-1.98	1.005	-6.36	-3.77	-1.80	-140.93	-3.21	-2.77	-2.77	-1.44	-0.262	-2.96	-7.51	-3.767	-2.97	-1.89	-5.39	-0.320	-4.28	-1.80	-2.98
-5.8685	13.5	1.01	4.17	-5.59	0.915	-5.56	-3.66	-1.80	-134.39	-3.17	-2.77	-2.77	-1.44	-0.262	-2.96	-9.26	-3.657	-2.97	-1.89	-4.94	-0.320	-4.28	-1.80	-2.98
-5.677	13.5	1.01	5.04	-54.31	0.173	-4.58	-3.49	-1.80	-37.83	-3.23	-2.77	-2.77	-1.44	-0.262	-2.96	-4.28	-3.487	-2.96	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.6013	13.5	1.01	5.29	-58.13	0.104	-4.29	-3.42	-1.80	-30.44	-3.32	-2.77	-2.77	-1.44	-0.262	-2.97	-3.88	-3.418	-2.95	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.5	13.5	1.01	5.36	-59.91	0.075	-4.14	-3.32	-1.80	-26.94	-3.52	-2.77	-2.77	-1.44	-0.262	-3.15	-3.58	-3.325	-2.95	-1.89	-4.22	-0.320	-4.28	-1.80	-2.98
-5.337	13.5	1.01	6.19	-68.38	-0.093	-3.43	-3.17	-1.80	-10.84	-6.00	-2.77	-2.77	-1.44	-0.262	-4.10	-3.26	-3.171	-2.93	-1.88	-4.22	-0.320	-4.28	-1.80	-2.98
-5.2664	13.5	1.01	6.26	-68.46	-0.098	-3.33	-3.11	-1.80	-10.75	-6.21	-2.77	-2.77	-1.44	-0.262	-4.11	-3.40	-3.105	-2.92	-1.88	-4.22	-0.320	-4.28	-1.80	-2.98
-5.1299	13.5	1.01	6.33	-68.53	-0.103	-3.38	-3.18	-1.80	-10.67	-6.41	-2.77	-2.77	-1.44	-0.262	-4.11	-3.52	-3.177	-2.90	-1.88	-4.22	-0.320	-4.28	-1.80	-3.00
-5	13.5	1.01	6.54	-68.76	-0.118	-3.36	-3.22	-1.80	-10.41	-7.01	-2.77	-2.77	-1.43	-0.262	-4.12	-3.92	-3.219	-2.87	-1.87	-4.22	-0.320	-4.28	-1.80	-3.23
-4.982	13.5	1.01	6.59	-68.82	-0.122	-3.35	-3.23	-1.80	-10.35	-7.15	-2.77	-2.77	-1.43	-0.262	-4.12	-4.02	-3.227	-2.87	-1.87	-4.22	-0.320	-4.28	-1.80	-3.29
-4.7912	13.5	1.01	7.18	-69.48	-0.165	-3.06	-3.02	-1.80	-9.62	-7.73	-2.77	-2.77	-1.43	-0.262	-4.12	-5.14	-3.023	-3.46	-1.86	-4.22	-0.320	-4.27	-1.80	-4.17
-4.7581	13.5	1.01	7.18	-69.48	-0.165	-2.99	-2.96	-1.80	-9.62	-7.73	-2.77	-2.77	-1.42	-0.262	-4.12	-5.14	-2.955	-3.46	-1.86	-4.23	-0.320	-4.27	-1.80	-4.24
-4.5	13.5	1.01	7.19	-69.49	-0.166	-2.99	-2.95	-1.81	-9.61	-7.72	-2.77	-2.77	-1.42	-0.262	-4.13	-5.15	-2.953	-3.47	-1.89	-4.27	-0.320	-4.27	-1.81	-4.25
-4	13.5	1.01	7.23	-69.55	-0.169	-2.97	-2.94	-1.86	-9.56	-7.70	-2.77	-2.77	-1.40	-0.262	-4.15	-5.22	-2.937	-3.50	-2.03	-4.55	-0.320	-4.27	-1.86	-4.31
-3.6955	13.6	1.01	7.88	-70.34	-0.217	-3.41	-3.41	-1.96	-8.71	-7.11	-2.77	-2.77	-1.37	-0.262	-4.20	-6.53	-3.414	-4.16	-2.46	-221.95	-0.319	-4.25	-1.96	-4.51
-3.5	13.6	1.01	7.93	-70.48	-0.222	-3.44	-3.44	-2.10	-8.58	-7.05	-2.77	-2.77	-1.40	-0.262	-4.18	-6.72	-3.440	-4.21	-2.49	-233.14	-0.318	-4.25	-2.10	-4.55
-3	13.9	1.01	7.97	-77.06	-0.320	-3.39	-3.40	-8.56	-7.68	-7.00	-2.77	-2.77	-1.51	-0.261	-4.14	-5.18	-2.000	-4.26	-2.60	-287.68	-0.316	-4.24	-7.63	-4.65
-2.6377	14.4	1.01	7.96	-77.24	-0.324	-3.37	-3.38	-8.51	-7.63	-6.98	-2.77	-2.77	-1.53	-0.261	-4.13	-5.09	-1.370	-4.26	-2.63	-289.54	-0.312	-4.23	-7.58	-4.67
-2.5842	14.5	1.01	8.11	-77.40	-0.336	-3.53	-3.55	-8.47	-7.44	-6.82	-2.77	-2.77	-1.51	-0.261	-4.15	-5.37	-1.300	-4.40	-2.95	-312.87	-0.313	-4.21	-7.40	-4.64
-2.5	14.7	1.01	8.11	-77.42	-0.337	-3.57	-3.59	-8.46	-7.42	-6.81	-2.77	-2.77	-1.47	-0.260	-4.16	-5.36	-1.193	-4.40	-2.96	-316.43	-0.317	-4.21	-7.38	-4.60
-2	17.2	1.01	8.10	-77.16	-0.347	-3.89	-3.92	-8.32	-7.24	-6.67	-2.77	-2.77	-1.17	-0.258	-4.29	-5.30	-0.626	-4.42	-3.09	-346.99	-0.361	-4.16	-7.21	-4.25
-1.8822	18.3	1.01	8.09	-76.96	-0.351	-3.98	-4.02	-8.27	-7.17	-6.61	-2.77	-2.77	-1.08	-0.257	-4.32	-5.31	-0.501	-4.43	-3.16	-357.24	-0.413	-4.14	-7.13	-4.13
-1.6809	21.2	1.01	8.02	-76.25	-0.352	-3.99	-4.03	-8.15	-7.06	-6.51	-2.77	-2.77	-1.04	-0.255	-4.31	-5.29	-0.318	-4.38	-3.15	-359.07	-0.425	-4.09	-7.02	-4.05
-1.6243	22.3	1.01	8.10	-76.12	-0.360	-4.19	-4.26	-8.07	-6.88	-6.38	-2.77	-2.77	-0.89	-0.256	-4.36	-5.49	-0.333	-4.47	-3.35	-383.00	-0.530	-4.07	-6.85	-3.87
-1.5694	23.5	1.01	8.06	-75.77	-0.359	-4.16	-4.23	-8.03	-6.87	-6.35	-2.77	-2.77	-0.90	-0.258	-4.35	-5.46	-0.329	-4.43	-3.33	-379.55	-0.522	-4.05	-6.84	-3.86
-1.5	25.2	1.01	8.00	-75.26	-0.358	-4.12	-4.18	-7.98	-6.85	-6.32	-2.77	-2.77	-0.92	-0.260	-4.33	-5.41	-0.322	-4.39	-3.30	-374.52	-0.509	-4.02	-6.81	-3.85
-1.3985	28.3	1.01	7.89	-74.37	-0.355	-4.05	-4.10	-7.89	-6.81	-6.27	-2.78	-2.78	-0.96	-0.262	-4.30	-5.32	-0.311	-4.31	-3.25	-365.65	-0.487	-3.97	-6.77	-3.84
-1.1772	38.1	1.01	7.57	-71.61	-0.346	-3.82	-3.84	-7.62	-6.70	-6.12	-2.78	-2.78	-1.08	-0.270	-4.20	-5.06	-0.321	-4.08	-3.11	-338.16	-0.429	-3.83	-6.65	-3.82
-1.0458	46.8	1.01	7.32	-69.32	-0.339	-3.61	-3.61	-7.39	-6.61	-6.03	-2.79	-2.79	-1.21	-0.273	-4.12	-4.84	-0.326	-3.89	-3.01	-314.77	-0.389	-3.71	-6.54	-3.83
-1	50.5	1.01	7.21	-68.38	-0.336	-999.00	-3.51	-7.29	-6.57	-6.01	-2.79	-2.79	-1.26	-0.273	-4.08	-4.75	-0.327	-3.82	-2.97	-305.07	-0.374	-3.66	-6.50	-3.84
-0.8293	68.2	1.01	6.77	-64.14	-0.322	-999.00	-3.02	-6.81	-6.41	-6.01	-2.79	-2.79	-1.54	-0.277	-3.91	-4.35	-0.334	-3.52	-2.84	-260.62	-0.328	-3.45	-6.26	-3.91
-0.6684	92.8	1.01	6.31	-59.23	-0.313	-999.00	-2.77	-6.05	-6.10	-6.34	-2.80	-2.80	-1.48	-0.284	-3.84	-3.92	-0.333	-3.23	-2.86	-230.21	-0.345	-3.20	-5.77	-3.60
-0.6108	104.0	1.17	6.19	-57.19	-0.314	-999.00	-2.62	-5.70	-5.91	-6.56	-2.80	-2.80	-1.56	-0.285	-3.78	-3.84	-0.335	-3.09	-2.98	-222.26	-0.334	-3.10	-5.49	-3.59
-0.5	130.3	2.73	5.97	-52.90	-0.320	-999.00	-2.24	-5.03	-5.53	-6.71	-2.80	-2.80	-1.78	-0.286	-3.66	-3.67	-0.339	-2.82	-3.27	-205.83	-0.315	-2.89	-4.91	-3.60
-0.2669	213.3	20.39	5.56	-42.34	-0.346	-999.00	-0.98	-3.28	-4.72	-5.33	-2.76	-2.76	-2.38	-0.247	-3.35	-3.17	-0.240	-2.18	-3.98	-170.34	-0.256	-2.41	-3.27	-3.68
-0.2642	214.6	20.89	5.46	-42.26	-0.338	-999.00	-0.97	-3.25	-4.79	-5.29	-2.64	-2.64	-2.13	-0.130	-3.35	-2.85	-0.171	-2.06	-3.75	-169.18	-0.143	-2.42	-3.24	-3.46
-0.264	214.7	20.94	5.45	-42.24	-0.337	-999.00	-0.96	-3.25	-4.80	-5.28	-2.63	-2.63	-2.11	-0.122	-3.35	-2.83	-0.173	-2.06	-3.73	-169.10	-0.135	-2.42	-3.24	-3.44
-0.2099	241.4	34.31	5.48	-39.39	-0.352	-999.00	-0.56	-2.82	-4.63	-4.30	-2.81	-2.81	-2.54	-0.295	-3.10	-3.02	-0.263	-2.08	-4.11	-156.70	-0.305	-2.29	-2.81	-3.73
-0.1966	248.5	38.76	5.46	-38.69	-0.353	-999.00	-0.48	-2.71	-4.62	-4.07	-2.81	-2.81	-2.55	-0.296	-3.00	-2.95	-0.249	-2.03	-4.12	-155.19	-0.307	-2.26	-2.70	-3.72
-0.1938	250.0	39.76	5.46	-38.54	-0.353	-999.00	-0.46	-2.69	-4.62	-4.07	-2.81	-2.81	-2.55	-0.296	-3.00	-2.94	-0.244	-2.02	-4.12	-154.89	-0.307	-2.26	-2.68	-3.72

Table 6b. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 250°C, No CH_4 Suppression, Graphite Replacing Pyrite.
Log moles of product minerals.

Log zi	Albite	Calcite	Celestite	Daphnite -14A	Dolomite -ordered	Fluorite	Hematite	Pyrolusite	Kaolinite	Graphite	Heulandite	Muscovite	Paragonite	Pyrite	Quartz	Smectite-Reykjanes	Strontianite	Ca-smectite	Na-smectite
-999			-3.45			-4.25	-3.46	-4.37											
-6			-3.44				-3.43	-4.25							1.46				
-5.8685			-3.44				-3.43	-4.31							1.46				-5.437
-5.677			-3.44						0.4639						1.46				-3.427
-5.6013			-3.44			-5.77			0.4639						1.46				-3.465
-5.5			-3.44			-3.73			0.4639						1.46				-3.539
-5.337			-3.44			-3.30			0.4640					-6.69	1.46				-3.753
-5.2664			-3.45			-3.30			0.4640					-4.68	1.46		-5.43		-3.584
-5.1299						-3.30			0.4640					-4.27	1.46		-3.39		-3.471
-5						-3.30			0.4640					-4.00	1.46		-3.08		-3.330
-4.982						-3.30			0.4640			-5.2711		-3.97	1.46		-3.05		-3.313
-4.7912						-3.30			0.4638			-2.9210		-3.72	1.46	-6.33	-2.87		-3.197
-4.7581					-5.347	-3.30			0.4638			-2.9073		-3.69	1.46	-4.05	-2.87		-3.206
-4.5					-3.003	-3.30			0.4639			-2.7745		-3.42	1.46	-3.21	-2.87		-3.196
-4					-2.240	-3.29			0.4640			-2.4178		-2.91	1.46	-2.50	-2.86		-3.147
-3.6955		0.999			-1.880	-3.29			0.4642			-2.1408		-2.60	1.46	-2.22	-2.86		-2.734
-3.5		0.999			-1.906	-3.29			0.4645			-1.9623		-2.39	1.46	-2.22	-2.86		-2.150
-3		1.000			-2.097	-3.29			0.4664			-1.4842		-2.09	1.46	-2.22	-2.86		-1.385
-2.6377		1.002				-3.30			0.4696			-1.1279		-2.09	1.46	-2.22	-2.86		-0.957
-2.5842		1.002				-3.29			0.4698			-1.0749	-4.030	-2.09	1.46	-2.22	-2.86		-0.887
-2.5		1.002				-3.29			0.4695			-0.9914	-2.146	-2.09	1.46	-2.22	-2.86		-0.799
-2		1.007				-3.29			0.4662			-0.4937	-1.031	-2.09	1.46	-2.22	-2.87		-0.286
-1.8822		1.009		-3.212		-3.28			0.4645			-0.3762	-0.880	-2.09	1.46	-2.22	-2.87		-0.167
-1.6809		1.015		-1.282		-3.28			0.4635			-0.1752	-0.664	-2.09	1.46	-2.22	-2.88		-0.031
-1.6243		1.016		-1.010		-3.28			0.4384			-0.1187	-0.446	-2.09	1.47	-2.22	-2.89	-1.5321	-0.039
-1.5694		1.015		-0.946		-3.28			0.4057			-0.0639	-0.282	-2.09	1.47	-2.22	-2.89	-0.3209	-0.229
-1.5		1.015		-0.866		-3.28			0.3875			0.0055	-0.241	-2.09	1.47	-2.22	-2.89	-0.2500	-0.164
-1.3985		1.014		-0.747		-3.29			0.3525			0.1069	-0.178	-2.09	1.47	-2.22	-2.90	-0.1507	-0.063
-1.1772		1.014		-0.735		-3.29			0.1125			0.3281	0.064	-2.09	1.50	-2.22	-2.90	-0.0707	-0.090
-1.0458		1.014		-0.728		-3.30			-0.0398			0.4595	0.051	-2.09	1.52	-2.22	-2.90	-0.0175	-0.098
-1		1.015		-0.725		-3.30			-0.0237			0.4772	0.044	-2.09	1.52	-2.22	-2.90	0.0009	-0.096
-0.8293		1.003		-0.710	-0.862	-3.32			-0.1672			0.5537	0.120	-2.09	1.53	-2.22	-2.89	0.2959	
-0.6684		0.989		-0.742	-0.538	-3.33						0.6410	0.124	-2.09	1.54	-2.22	-2.94	0.4660	
-0.6108		0.987		-0.729	-0.503	-3.34						0.6758	0.120	-2.09	1.54	-2.22	-2.94	0.4903	
-0.5		0.982		-0.706	-0.432	-3.37						0.7477	0.112	-2.09	1.55	-2.22	-2.94	0.5421	
-0.2669	-0.491	0.865		-0.634	0.167	-3.49					0.0627	0.9183	-0.026	-2.11	1.54	-2.22	-2.92	0.5648	
-0.2642	0.085	0.442		-0.542	0.577	-3.42				-2.209	0.5781	0.9204	-1.231	-2.11	1.39	-2.22	-2.94	0.1362	
-0.264	0.106	0.398		-0.537	0.592	-3.42				-1.622	0.5959	0.9206		-2.11	1.38	-2.22	-2.94	0.0930	
-0.2099	0.104	0.962		-0.796	-0.483	-3.96				-0.385		0.9635		-2.14	1.55	-2.22	-2.92	0.8101	
-0.1966	0.105	0.965		-0.821	-0.638					-0.287		0.9741		-2.16	1.55	-2.22	-2.92	0.8211	
-0.1938	0.105	0.966		-0.827	-0.681					-0.270		0.9764		-2.16	1.55	-2.22	-2.92	0.8234	

Table 6c. Reaction of Pumpkin Valley Shale Groundwater and Rock at T = 250°C, No CH_4 Suppression, Graphite Replacing Pyrite.
Log molal of destroyed reactants.

Log xi	Quartz	Illite	Graphite	K-feld-spar	Albite	Anorthite	Calcite	Kaolinite	Ripidolite -14A	g^bDes[d]	g^bCre[c]	g^bNet	cm^{3a}Des[c]	cm^{3a}Cre[d]	cm^{3a}Net	Water:Rock Ratio
-999	-999.00	-999.000	-999.000	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	0.000	0.13	0.13	0.000	0.02	0.02	
-6	-6.00	-4.699	-4.398	-4.699	-4.699	-4.699	-4.00	-4.70	-4.699	0.052	1749.00	1749.00	0.015	660.20	660.20	19179.133
-5.8685	-6.00	-4.567	-4.266	-4.567	-4.567	-4.567	-3.87	-4.57	-4.567	0.071	1749.00	1749.00	0.020	660.20	660.20	14170.327
-5.677	-6.00	-4.376	-4.075	-4.376	-4.376	-4.376	-3.68	-4.38	-4.376	0.110	2500.00	2500.00	0.031	949.80	949.80	9124.088
-5.6013	-6.00	-4.300	-3.999	-4.300	-4.300	-4.300	-3.60	-4.38	-4.300	0.128	2500.00	2500.00	0.036	949.80	949.80	7788.162
-5.5	-6.00	-4.199	-3.898	-4.199	-4.199	-4.199	-3.50	-4.38	-4.199	0.159	2500.00	2500.00	0.044	949.90	949.80	6277.464
-5.337	-6.00	-4.036	-3.735	-4.036	-4.036	-4.036	-3.34	-4.38	-4.036	0.227	2500.00	2500.00	0.063	949.90	949.80	4407.228
-5.2664	-6.00	-3.965	-3.664	-3.965	-3.965	-3.965	-3.27	-4.38	-3.965	0.265	2500.00	2500.00	0.073	949.90	949.80	3773.585
-5.1299	-6.00	-3.829	-3.528	-3.829	-3.829	-3.829	-3.13	-4.38	-3.829	0.359	2500.00	2500.00	0.098	949.90	949.80	2787.068
-5	-6.00	-3.699	-3.398	-3.699	-3.699	-3.699	-3.00	-4.38	-3.699	0.480	2500.00	2500.00	0.131	949.90	949.80	2082.899
-4.982	-6.00	-3.681	-3.380	-3.681	-3.681	-3.681	-2.98	-4.38	-3.681	0.500	2500.00	2500.00	0.136	949.90	949.80	2000.000
-4.7912	-6.00	-3.490	-3.189	-3.490	-3.490	-3.490	-2.79	-4.38	-3.490	0.770	2501.00	2500.00	0.209	950.00	949.80	1299.039
-4.7581	-6.00	-3.457	-3.156	-3.457	-3.457	-3.457	-2.76	-4.38	-3.457	0.830	2501.00	2500.00	0.225	950.00	949.80	1204.964
-4.5	-6.00	-3.199	-2.898	-3.199	-3.199	-3.199	-2.50	-4.38	-3.199	1.495	2501.00	2500.00	0.405	950.20	949.80	668.896
-4	-6.00	-2.699	-2.398	-2.699	-2.699	-2.699	-2.00	-4.38	-2.699	4.703	2505.00	2500.00	1.271	950.90	949.70	212.630
-3.6955	-6.00	-2.394	-2.093	-2.394	-2.394	-2.394	-1.70	-4.38	-2.394	9.471	3508.00	3498.00	2.559	1320.00	1318.00	105.585
-3.5	-6.00	-2.199	-1.898	-2.199	-2.199	-2.199	-1.70	-4.38	-2.199	13.700	3512.00	3499.00	3.588	1322.00	1318.00	72.993
-3	-6.00	-1.699	-1.398	-1.699	-1.699	-1.699	-1.70	-4.38	-1.699	38.940	3539.00	3500.00	9.726	1329.00	1320.00	25.681
-2.6377	-6.00	-1.337	-1.036	-1.337	-1.337	-1.337	-1.70	-4.38	-1.337	87.040	3588.00	3501.00	21.420	1343.00	1322.00	11.689
-2.5842	-6.00	-1.283	-0.982	-1.283	-1.283	-1.283	-1.70	-4.38	-1.283	98.180	3600.00	3501.00	24.130	1346.00	1322.00	10.185
-2.5	-6.00	-1.199	-0.898	-1.199	-1.199	-1.199	-1.70	-4.38	-1.199	118.800	3620.00	3502.00	29.140	1352.00	1323.00	8.618
-2	-6.00	-0.699	-0.398	-0.699	-0.699	-0.699	-1.70	-4.38	-0.699	371.100	3875.00	3504.00	90.520	1421.00	1330.00	2.695
-1.8822	-6.00	-0.581	-0.280	-0.581	-0.581	-0.581	-1.70	-4.38	-0.581	486.200	3991.00	3505.00	118.500	1452.00	1334.00	2.057
-1.6809	-6.00	-0.380	-0.079	-0.380	-0.380	-0.380	-1.70	-4.38	-0.380	771.600	4280.00	3508.00	187.900	1538.00	1350.00	1.296
-1.6243	-6.00	-0.323	-0.079	-0.323	-0.323	-0.323	-1.70	-4.38	-0.323	877.400	4382.00	3505.00	214.000	1570.00	1356.00	1.140
-1.5694	-6.00	-0.268	-0.079	-0.268	-0.268	-0.268	-1.70	-4.38	-0.268	993.900	4494.00	3500.00	242.700	1599.00	1357.00	1.006
-1.5	-6.00	-0.199	-0.079	-0.199	-0.199	-0.268	-1.70	-4.38	-0.199	1138.000	4635.00	3497.00	275.200	1637.00	1362.00	0.879
-1.3985	-6.00	-0.098	-0.079	-0.098	-0.098	-0.268	-1.70	-4.38	-0.098	1395.000	4886.00	3491.00	333.200	1704.00	1371.00	0.717
-1.1772	-6.00	0.124	-0.079	0.124	0.124	-0.268	-1.70	-4.38	-0.098	1886.000	5359.00	3473.00	518.000	1866.00	1348.00	0.530
-1.0458	-6.00	0.255	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	2197.000	5662.00	3465.00	634.500	1973.00	1338.00	0.455
-1	-6.00	0.301	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	2274.000	5739.00	3465.00	662.300	2001.00	1338.00	0.440
-0.8293	-6.00	0.472	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	2644.000	6100.00	3456.00	796.100	2126.00	1330.00	0.378
-0.6684	-6.00	0.633	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	3154.000	6592.00	3438.00	980.700	2292.00	1312.00	0.317
-0.6108	-6.00	0.690	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	3387.000	6824.00	3437.00	1065.000	2376.00	1311.00	0.295
-0.5	-6.00	0.801	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	3934.000	7368.00	3433.00	1263.000	2570.00	1307.00	0.254
-0.2669	-6.00	1.034	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	5659.000	9180.00	3521.00	1887.000	2932.00	1044.00	0.177
-0.2642	-6.00	1.037	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	5685.000	9436.00	3751.00	1897.000	2377.00	479.90	0.176
-0.264	-6.00	1.037	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	5687.000	9452.00	3765.00	1898.000	2343.00	445.80	0.176
-0.2099	-6.00	1.091	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	6242.000	9643.00	3401.00	2098.000	3379.00	1281.00	0.160
-0.1966	-6.00	1.104	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	6389.000	9785.00	3396.00	2151.000	3428.00	1277.00	0.157
-0.1938	-6.00	1.107	-0.079	0.255	0.124	-0.268	-1.70	-4.38	-0.098	6420.000	9815.00	3395.00	2163.000	3439.00	1276.00	0.156

[a] cm^3 = cubic centimeters
[b] g = grams
[c] Des = Destroyed
[d] Cre = Created

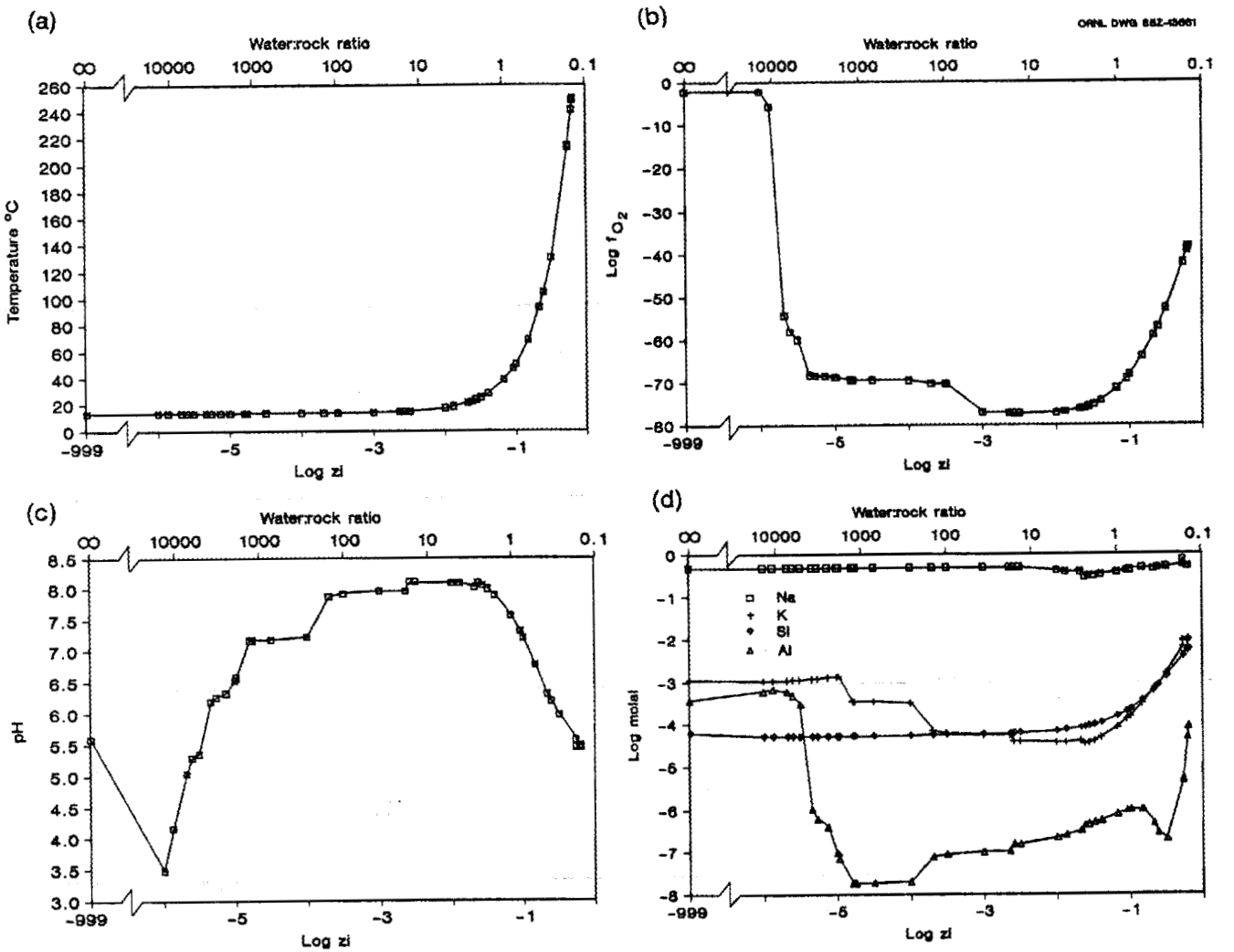

Fig. 4. Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, no CH_4 suppression, graphite replacing pyrite: (a) Temperature, (b) Log f_{O_2}, (c) pH, (d) Na, K, Si, and Al.

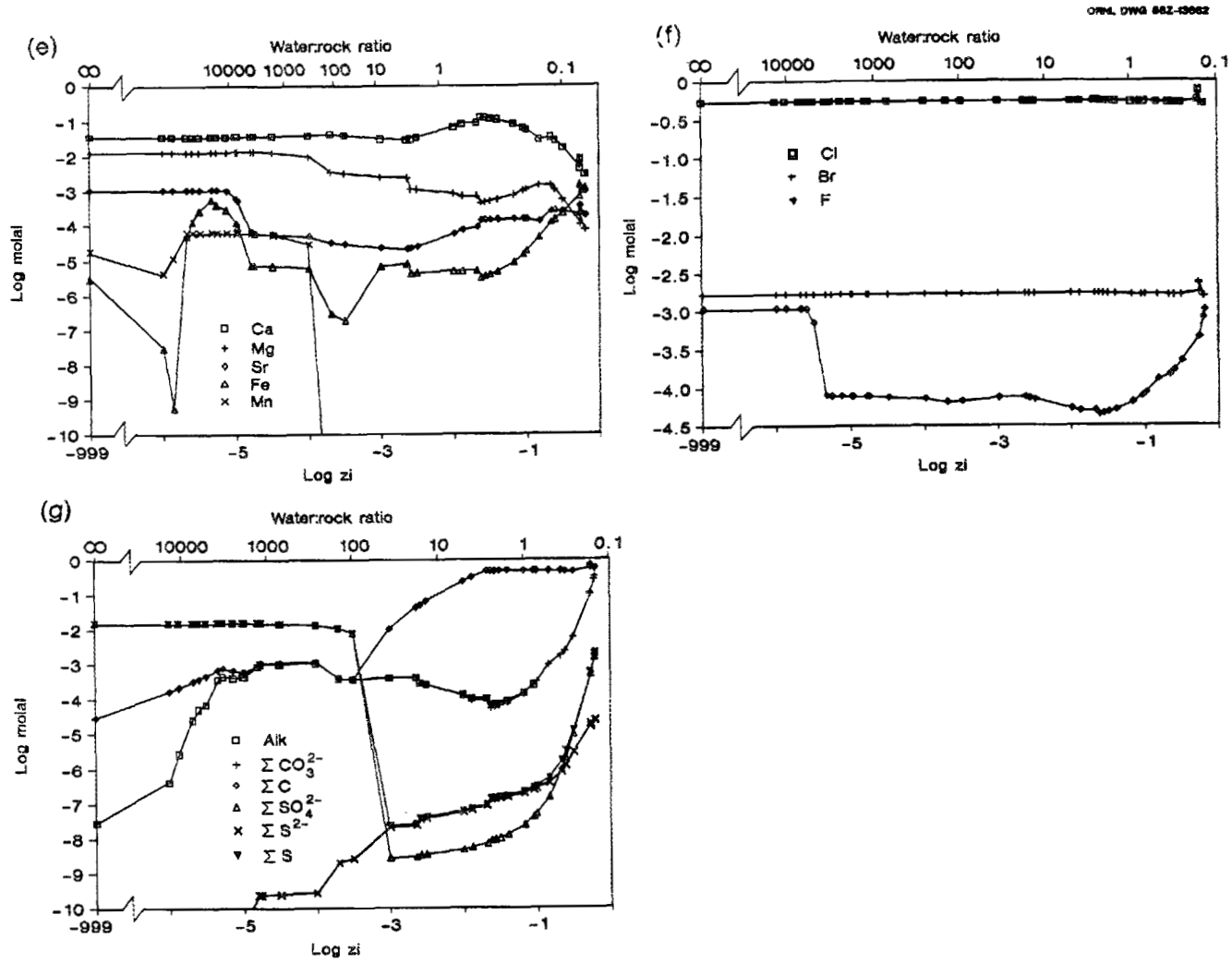

Fig. 4 (continued). Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, no CH_4 suppression, graphite replacing pyrite: (e) Ca, Mg, Sr, Fe, and Mn, (f) Cl, Br, and F, (g) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

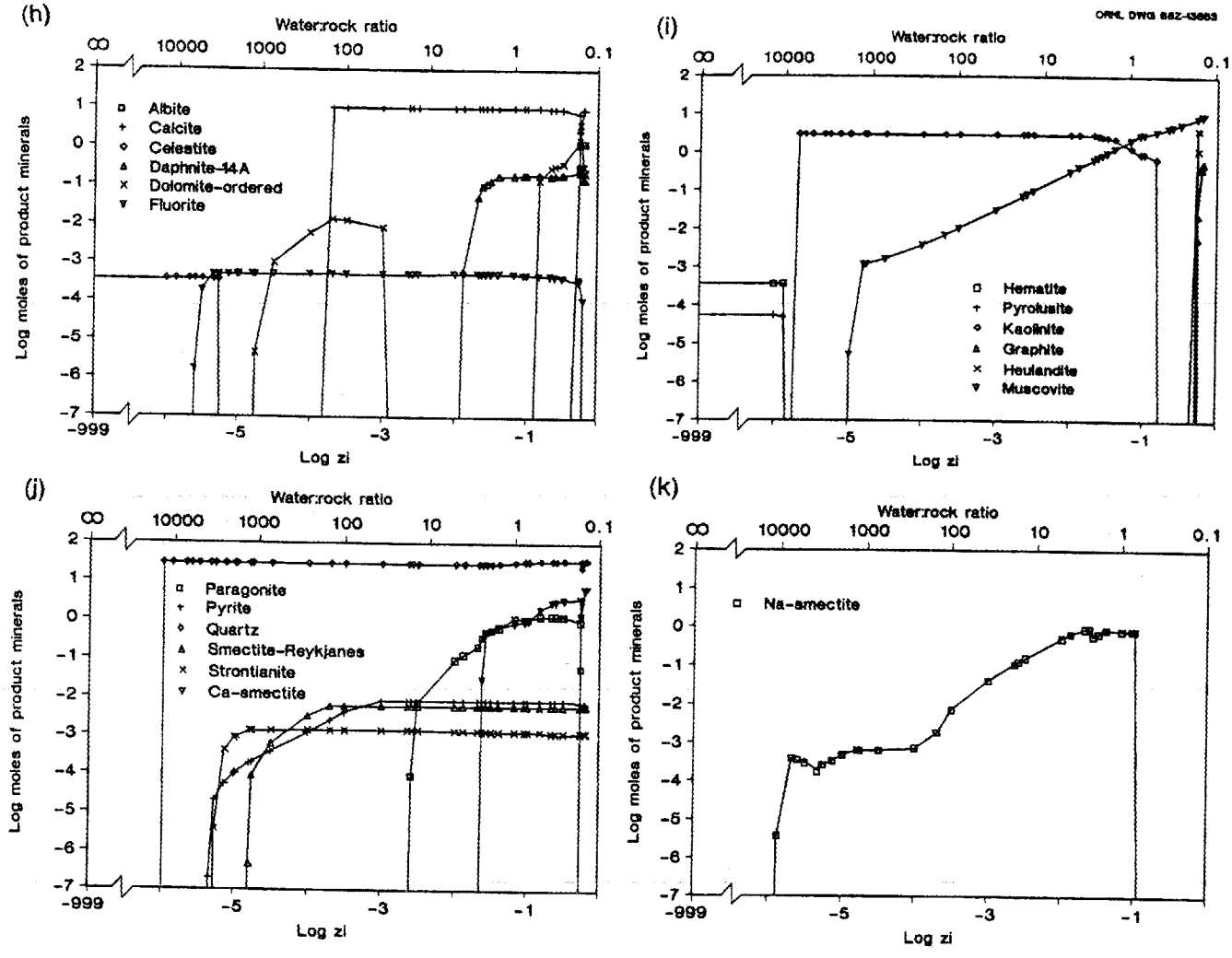

Fig. 4 (continued). Reaction of Pumpkin Valley Shale groundwater and rock to T = 250°C, no CH_4 suppression, graphite replacing pyrite: (h) product minerals 1, (i) product minerals 2, (j) product minerals 3, (k) product minerals 4.

Table 7. Pierre Shale Rock and Bearpaw Shale Groundwater Compositions

Pierre Shale

Mineral	Moles in ~10000 g (Schultz et al.)	Moles in ~10000 g (Lee et al.)	RRR[a]
Biotite		0.834	20
Annite		(30%)	
Pd-oxyannite		(30%)	
Phlogopite		(40%)	
Calcite	0.506	15.0	100
Na-clinoptilolite (zeolite)	0.189		20
Cristobalite	11.8		1
Graphite	5.73	41.6	20
Illite	8.52	0.521	20
Kaolinite	0.745	0.387	20
Quartz	26.3	16.6	1
Pyrite	0.506	1.67	20
Plagioclase	0.749	0.37	20
Albite	(90%)	(50%)	
Anorthite	(10%)	(50%)	
14A-Ripidolite (chlorite)	0.291	0.160	20
Siderite	0.437		100
Ca-smectite	8.29	14.1	20
Ca-beidellite	(46%)	(46%)	
Ca-nontronite	(54%)	(54%)	

Bearpaw Shale Groundwater (Stn no. 480758106431901)

Element or Species	Concentration	
pH	8.1	
T	10.5	°C
Na	43.50	mmoles/l
K	0.07673	mmoles/l
Mg	0.1234	mmoles/l
Ca	0.1871	mmoles/l
Li	24.49	μmoles/l
Fe	1.253	μmoles/l
Mn	0.3640	μmoles/l
Al	2.295×10^{-8}	molal
Si	0.1631	mmoles/l
F	0.1053	mmoles/l
Cl	28.21	mmoles/l
NO_3^-	7.139	μmoles/l
SO_4^{2-}	0.2915	mmoles/l
H_2S	15.60	μmoles/l
Alkalinity	17.38	meq/l

[a]Relative reaction (dissolution) rate

[b]Collected from 600 ft depth in Montana (from Von Damm (1987)) based on U.S.G.S. WATSTORE data base. Al based on equilibrium with kaolinite.

natural variability observed. The groundwater composition used (Table 7) was the same in all cases and is from Von Damm (1987). The groundwater was from the Bearpaw Formation, which is equivalent to the Pierre Formation. This particular groundwater had a very complete chemical analysis, was from a depth of 600 feet, and was close to the median composition (based on ionic strength) for waters from the Pierre Formation as summarized by Von Damm (1987). The water composition may be slightly low in potassium compared to other Pierre waters. The lower temperature chosen is the reported temperature for the groundwater when sampled.

Case 5: Reaction of Bearpaw water and Pierre Shale (Schultz et al.) at T = 10.5°C. Based on the measured ratio of SO_4^{2-}/H_2S the groundwater had an initial log f_{O_2} = -73.7 which decreased slightly during the course of the experiment to reach a final value of -78.6 (Table 8, Fig. 5). The pH increased slightly from 7.9 to a final value of 8.6, but reached a maximum of 9.3 during the course of the experiment. The concentration of alkalinity and total carbonate in solution decreased slightly, while both total SO_4^{2-} and H_2S decreased by several orders of magnitude. At the end of the experiment total dissolved Al, Cl, F, Fe, C, Li, Mg, Na, N (primarily as NH_4^+) and Si had increased while Ca, K, Mn, and S had decreased. Some of the small increases can be attributed to the consumption of water during the reaction progress. Total dissolved Mn, Fe, C and Ca show the largest changes in the solution (in that order). The increase in total C is primarily a result of the production of large amounts of CH_4. Sr is not modeled in this, or the subsequent smectitic cases as data were not available for it in the groundwater analysis. The final mineral assemblage consisted of 14A-daphnite, dawsonite, ordered dolomite, kaolinite, muscovite, pyrite, quartz, siderite, and Reykjanes- and Na-smectite, in addition calcite and paragonite were stable for parts of the reaction progress. The final value for the water:rock ratio was 0.127.

Table 8a. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Schultz et al.) at T = 10.5°C.
Log molal concentrations of dissolved elements.

Log xi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	N	Si	S
-999	10.5	1.01	7.95	-73.67	-0.252	-1.77	-1.76	-3.53	-4.95	-7.64	-3.99	-1.55	-3.98	-13.44	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-8	10.5	1.01	7.95	-73.63	-0.252	-1.77	-1.76	-3.53	-5.05	-7.37	-3.99	-1.55	-3.98	-13.28	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-7.2547	10.5	1.01	7.96	-71.68	-0.225	-1.77	-1.76	-3.54	-8.96	-7.36	-3.99	-1.55	-3.98	-6.42	-1.760	-4.13	-4.61	-4.43	-6.44	-1.34	-5.15	-4.27	-3.54
-6.2773	10.5	1.01	7.97	-71.70	-0.226	-1.77	-1.76	-3.57	-8.95	-7.30	-3.93	-1.55	-3.98	-6.44	-1.759	-4.28	-4.61	-4.50	-6.44	-1.34	-5.15	-4.27	-3.57
-5.7736	10.5	1.01	8.02	-71.81	-0.230	-1.77	-1.76	-3.65	-8.88	-7.25	-3.83	-1.55	-3.98	-6.52	-1.761	-4.34	-4.61	-4.71	-6.44	-1.34	-5.15	-4.27	-3.65
-5.5	10.5	1.01	8.06	-71.92	-0.234	-1.77	-1.76	-3.79	-8.82	-7.21	-3.87	-1.55	-3.98	-6.58	-1.763	-4.39	-4.61	-4.75	-6.44	-1.34	-5.15	-4.27	-3.79
-5.0345	10.5	1.01	8.19	-76.12	-0.300	-1.78	-1.77	-9.08	-8.16	-7.07	-3.98	-1.55	-3.98	-5.78	-1.771	-4.55	-4.61	-4.87	-6.44	-1.35	-5.15	-4.27	-8.11
-5	10.5	1.01	8.18	-76.19	-0.301	-1.78	-1.77	-9.07	-8.15	-7.08	-3.98	-1.55	-3.98	-5.76	-1.770	-4.54	-4.61	-4.87	-6.44	-1.35	-5.15	-4.27	-8.10
-4.9294	10.5	1.01	8.19	-76.30	-0.303	-1.78	-1.77	-9.06	-8.13	-7.07	-3.98	-1.55	-3.98	-5.73	-1.769	-4.55	-4.61	-4.87	-6.44	-1.35	-5.15	-4.27	-8.09
-4.5	10.5	1.01	8.27	-76.70	-0.313	-1.77	-1.77	-9.00	-7.99	-6.99	-4.06	-1.55	-3.98	-5.79	-1.751	-4.63	-4.61	-4.95	-6.44	-1.35	-5.15	-4.26	-7.95
-4	10.5	1.01	8.34	-77.03	-0.322	-1.77	-1.77	-8.95	-7.88	-6.92	-4.13	-1.55	-3.98	-5.84	-1.694	-4.70	-4.61	-5.02	-6.44	-1.35	-5.15	-4.26	-7.84
-3.5	10.5	1.01	8.40	-77.32	-0.329	-1.77	-1.77	-8.91	-7.77	-6.86	-4.18	-1.55	-3.98	-5.88	-1.550	-4.76	-4.61	-5.08	-6.44	-1.35	-5.15	-4.26	-7.74
-3	10.5	1.01	8.46	-77.61	-0.336	-1.77	-1.77	-8.87	-7.67	-6.81	-4.24	-1.55	-3.98	-5.92	-1.272	-4.82	-4.61	-5.14	-6.44	-1.35	-5.15	-4.26	-7.64
-2.8114	10.5	1.01	8.48	-77.71	-0.339	-1.77	-1.77	-8.85	-7.63	-6.78	-4.26	-1.55	-3.98	-5.93	-1.133	-4.84	-4.61	-5.16	-6.97	-1.35	-5.15	-4.26	-7.61
-2.5	10.5	1.01	8.52	-77.89	-0.344	-1.77	-1.77	-8.83	-7.57	-6.75	-4.29	-1.55	-3.98	-5.96	-0.875	-4.88	-4.61	-5.19	-16.39	-1.35	-5.15	-4.25	-7.55
-2.3412	10.5	1.01	8.54	-77.98	-0.346	-1.77	-1.77	-8.82	-7.54	-6.73	-4.31	-1.55	-3.98	-5.97	-0.733	-4.90	-4.61	-5.21	-21.19	-1.35	-5.15	-4.25	-7.52
-2.3239	10.5	1.01	9.18	-78.31	-0.387	-1.73	-1.76	-8.71	-6.80	-6.09	-4.84	-1.55	-3.98	-6.92	-0.722	-5.53	-4.61	-5.78	-165.27	-1.33	-5.15	-4.18	-6.79
-2.1543	10.5	1.01	9.18	-78.37	-0.388	-1.72	-1.76	-8.70	-6.79	-6.09	-4.84	-1.56	-3.98	-6.91	-0.613	-5.54	-4.62	-5.78	-165.76	-1.33	-5.15	-4.18	-6.78
-2.0246	10.5	1.01	9.27	-78.63	-0.397	-2.05	-2.10	-8.66	-6.66	-6.00	-4.69	-1.56	-3.99	-7.24	-0.533	-5.64	-4.62	-5.61	-250.58	-1.44	-5.16	-4.16	-6.65
-2	10.5	1.01	9.28	-78.65	-0.397	-2.07	-2.11	-8.66	-6.65	-6.00	-4.68	-1.56	-3.99	-7.25	-0.514	-5.64	-4.62	-5.59	-255.05	-1.44	-5.15	-4.16	-6.64
-1.8371	10.5	1.01	9.29	-78.77	-0.399	-2.15	-2.19	-8.63	-6.61	-5.99	-4.63	-1.56	-3.98	-7.31	-0.378	-5.66	-4.62	-5.54	-272.00	-1.46	-5.15	-4.16	-6.61
-1.7044	10.5	1.01	9.29	-78.80	-0.400	-2.13	-2.17	-8.63	-6.62	-5.99	-4.65	-1.55	-3.98	-7.28	-0.281	-5.65	-4.62	-5.55	-267.74	-1.45	-5.15	-4.16	-6.61
-1.6795	10.5	1.01	9.18	-78.56	-0.390	-1.72	-1.76	-8.66	-6.75	-6.09	-5.35	-1.55	-3.98	-6.89	-0.254	-5.53	-4.62	-5.27	-197.37	-1.33	-5.15	-4.18	-6.74
-1.5	10.5	1.01	9.17	-78.63	-0.391	-1.73	-1.76	-8.66	-6.74	-6.09	-5.33	-1.55	-3.98	-6.87	-0.108	-5.53	-4.61	-5.28	-197.05	-1.33	-5.15	-4.18	-6.74
-1.4265	10.5	1.01	9.17	-78.66	-0.391	-1.73	-1.76	-8.65	-6.74	-6.09	-5.32	-1.55	-3.97	-6.85	-0.045	-5.53	-4.61	-5.29	-196.84	-1.33	-5.14	-4.18	-6.73
-1.1947	10.5	1.01	9.17	-78.78	-0.393	-1.74	-1.77	-8.64	-6.74	-6.10	-5.29	-1.53	-3.95	-6.81	0.175	-5.52	-4.59	-5.30	-196.74	-1.32	-5.12	-4.18	-6.73
-1.1791	10.5	1.01	8.62	-78.50	-0.358	-1.77	-1.78	-8.73	-7.38	-6.65	-5.46	-1.52	-3.95	-5.99	0.192	-4.97	-4.59	-4.17	-112.92	-1.33	-5.12	-4.25	-7.36
-1.1304	10.5	1.01	8.62	-78.53	-0.358	-1.78	-1.78	-8.73	-7.37	-6.65	-5.47	-1.52	-3.95	-5.99	0.231	-4.98	-4.58	-4.17	-113.98	-1.33	-5.12	-4.25	-7.35
-1	10.5	1.01	8.61	-78.57	-0.359	-1.78	-1.79	-8.71	-7.36	-6.65	-5.52	-1.51	-3.94	-5.98	0.329	-4.97	-4.57	-4.11	-117.08	-1.33	-5.11	-4.25	-7.34
-0.8439	10.5	1.01	8.61	-78.65	-0.359	-1.79	-1.79	-8.70	-7.35	-6.66	-5.55	-1.50	-3.92	-5.96	0.476	-4.96	-4.56	-4.04	-119.82	-1.32	-5.09	-4.25	-7.33
-0.5	10.5	1.01	8.60	-78.63	-0.358	-1.79	-1.80	-8.70	-7.36	-6.67	-5.52	-1.48	-3.90	-5.94	0.434	-4.95	-4.54	-4.03	-119.16	-1.31	-5.07	-4.25	-7.34
-0.3825	10.5	1.01	8.59	-78.61	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.47	-3.89	-5.93	0.408	-4.95	-4.53	-4.03	-118.73	-1.30	-5.06	-4.25	-7.35
-0.3706	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35
0	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35
0.5	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35
1	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35
1.0544	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35
1.0707	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35
1.0719	10.5	1.01	8.59	-78.62	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67	-5.50	-1.46	-3.89	-5.93	0.412	-4.95	-4.53	-4.02	-118.79	-1.30	-5.06	-4.25	-7.35

Table 6b. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Schultz et al.) at T = 10.5°C.
Log moles of product minerals.

Log zi	Calcite	Daphnite -14A	Dawsonite	Dolomite -ordered	Kaolinite	Muscovite	Paragonite	Pyrite	Quartz	Siderite	Smectite-Reykjanes	Na-smectite
-999				-4.075				-0.296	1.42			
-8				-4.070		-6.153		-0.296	1.42			
-7.2547				-4.047		-5.407		-0.296	1.42			-6.709
-6.2773			-5.295	-3.900		-4.520		-0.296	1.42			-4.443
-5.7736	-0.296		-3.830	-3.671		-4.295		-0.296	1.42			-3.905
-5.5	-0.296		-3.470	-3.507		-4.134		-0.296	1.42			-3.624
-5.0345	-0.296		-2.985	-3.149	-0.128	-3.798		-0.296	1.42			-3.135
-5	-0.296		-2.975	-3.119	-0.128	-3.774		-0.296	1.42			-3.097
-4.9294	-0.297		-2.954	-3.058	-0.128	-3.723		-0.296	1.42	-0.361		-3.021
-4.5	-0.298		-2.790	-2.664	-0.128	-3.364		-0.296	1.42	-0.363		-2.579
-4	-0.301		-2.450	-2.180	-0.126	-2.901		-0.296	1.42	-0.369		-2.066
-3.5	-0.312		-2.011	-1.685	-0.122	-2.414		-0.296	1.42	-0.391		-1.559
-3	-0.350		-1.532	-1.186	-0.111	-1.919		-0.296	1.42	-0.467		-1.055
-2.8114	-0.383		-1.347	-0.998	-0.102	-1.731		-0.296	1.42	-0.539	-4.59	-0.865
-2.5	-0.499		-1.040	-0.687	-0.077	-1.420		-0.296	1.42	-0.874	-4.44	-0.552
-2.3412	-0.631		-0.883	-0.528	-0.056	-1.262		-0.296	1.42		-4.44	-0.393
-2.3239	-0.643		-0.904	-0.517	-0.071	-1.244	-3.559	-0.296	1.42		-4.44	-0.347
-2.1543	-1.032			-0.347	-0.158	-1.075	-0.643	-0.296	1.43		-4.44	-0.271
-2.0246	-1.138			-0.316	-0.184	-0.945	-0.479	-0.296	1.43		-4.44	-0.167
-2	-1.155			-0.311	-0.173	-0.921	-0.480	-0.296	1.43		-4.44	-0.147
-1.8371	-1.313			-0.272	-0.094	-0.758	-0.490	-0.296	1.43		-4.44	-0.005
-1.7044				-0.214	-0.086	-0.625	-0.397	-0.296	1.43		-4.44	0.016
-1.6795			-3.879	-0.210	-0.074	-0.600	-0.392	-0.296	1.44		-4.44	0.022
-1.5			-0.995	-0.172	-0.009	-0.421	-0.346	-0.296	1.45		-4.44	0.077
-1.4265			-0.8068	-0.152	0.0227	-0.3473	-0.3226	-0.2957	1.46		-4.44	0.1038
-1.1947			-0.2916	-0.1014	0.2838	-0.1155		-0.2957	1.47		-4.44	0.2146
-1.1791			-0.2654	-0.0971	0.318	-0.0998		-0.2957	1.48	-3.5293	-4.44	0.1898
-1.1304		-1.7131	-0.259	-0.0833	0.3425	-0.0512		-0.2957	1.49	-0.902	-4.44	0.183
-1		-0.7088	-0.1692	-0.0405	0.4022	0.0792		-0.2957	1.53	-0.2973	-4.44	0.0578
-0.8439		-0.4715	-0.1226	0.0228	0.5006	0.2353		-0.2957	1.57	0.0723	-4.44	-0.0401
-0.5		0.0073	-0.2634	0.2107	0.7353	0.5792		-0.2957	1.68	-0.2209	-4.44	0.1896
-0.3825		0.1396	-0.392	0.2898	0.8288	0.6967		-0.2957	1.72	-0.5543	-4.44	0.2951
-0.3706		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.72	-0.5311	-4.44	0.3155
0		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.73	-0.5311	-4.44	0.3155
0.5		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.74	-0.5311	-4.44	0.3155
1		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.79	-0.5311	-4.44	0.3155
1.0544		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.80	-0.5311	-4.44	0.3155
1.0707		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.81	-0.5311	-4.44	0.3155
1.0719		0.1304	-0.4271	0.2898	0.8336	0.7086		-0.2957	1.81	-0.5311	-4.44	0.3155

Table 8c. Reaction of Bearpaw Shale Groundwater and Pierre Shale at T = 10.5°C.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	Plagioclase	Siderite	Ca-Smectite	Calcite	Kaolinite	Ripidolite -14a	Cristobalite	Clinoptil -na	Graphite	g[b]Des[c]	g[b]Cre[d]	g[b]Net	cm[3a]Des[c]	cm[3a]Cre[d]	cm[3a]Net	Water:Rock Ratio
-999	-999	-999.000	-999	-999.000	-999.00	-999.000	-999.00	-999.00	-999.000	-999.00	-999.000	-999.000	0.000	1641	1641	0.000	596.70	596.70	
-8	-999	-6.699	-999	-6.699	-6.00	-6.699	-6.00	-6.70	-6.699	-8.00	-6.699	-6.398	0.001	1641	1641	0.000	596.70	596.70	1269680.041
-7.2547	-999	-5.954	-999	-5.954	-5.25	-5.954	-5.25	-5.95	-5.954	-7.25	-5.954	-5.653	0.004	1641	1641	0.001	596.70	596.70	228258.368
-6.2773	-999	-4.976	-999	-4.976	-4.28	-4.976	-4.28	-4.98	-4.976	-6.28	-4.976	-4.675	0.042	1641	1641	0.006	596.70	596.70	24038.462
-5.7736	-999	-4.473	-999	-4.473	-3.77	-4.473	-3.77	-4.47	-4.473	-5.77	-4.473	-4.172	0.133	1692	1692	0.020	615.40	615.40	7535.795
-5.5	-999	-4.199	-999	-4.199	-3.50	-4.199	-3.77	-4.20	-4.199	-5.50	-4.199	-3.898	0.234	1692	1692	0.032	615.40	615.40	4268.032
-5.0345	-999	-3.734	-999	-3.734	-3.03	-3.734	-3.77	-3.73	-3.734	-5.03	-3.734	-3.433	0.652	1885	1884	0.080	689.70	689.60	1534.213
-5	-999	-3.699	-999	-3.699	-3.00	-3.699	-3.77	-3.73	-3.699	-5.00	-3.699	-3.398	0.701	1885	1884	0.085	689.70	689.60	1427.552
-4.9294	-999	-3.628	-999	-3.628	-2.93	-3.628	-3.77	-3.73	-3.628	-4.93	-3.628	-3.327	0.813	1935	1934	0.095	689.70	689.60	1230.466
-4.5	-999	-3.199	-999	-3.199	-2.93	-3.199	-3.77	-3.73	-3.199	-4.50	-3.199	-2.898	1.845	1936	1934	0.215	689.90	689.70	542.005
-4	-999	-2.699	-999	-2.699	-2.93	-2.699	-3.77	-3.73	-2.699	-4.00	-2.699	-2.398	5.401	1940	1934	0.625	690.60	690.00	185.151
-3.5	-999	-2.199	-999	-2.199	-2.93	-2.199	-3.77	-3.73	-2.199	-3.50	-2.199	-1.898	16.650	1951	1934	1.926	692.90	691.00	60.060
-3	-999	-1.699	-999	-1.699	-2.93	-1.699	-3.77	-3.73	-1.699	-3.00	-1.699	-1.398	52.210	1986	1934	6.030	700.10	694.10	19.153
-2.8114	-999	-1.510	-999	-1.510	-2.93	-1.510	-3.77	-3.73	-1.510	-2.81	-1.510	-1.209	80.680	2013	1933	9.295	705.90	696.60	12.425
-2.5	-999	-1.199	-999	-1.199	-2.93	-1.199	-3.77	-3.73	-1.199	-2.50	-1.199	-0.898	164.700	2096	1932	19.020	722.90	703.90	6.072
-2.3412	-999	-1.040	-999	-1.040	-2.93	-1.040	-3.77	-3.73	-1.040	-2.34	-1.040	-0.739	237.300	2168	1930	27.400	737.70	710.30	4.214
-2.3239	-999	-1.023	-999	-1.023	-2.93	-1.023	-3.77	-3.73	-1.023	-2.32	-1.023	-0.722	246.900	2176	1929	28.510	739.40	710.90	4.050
-2.1543	-999	-0.853	-999	-0.853	-2.93	-0.853	-3.77	-3.73	-0.853	-2.15	-0.853	-0.552	364.700	2282	1917	42.120	763.50	721.40	2.742
-2.0246	-999	-0.724	-999	-0.724	-2.93	-0.724	-3.77	-3.73	-0.724	-2.02	-0.724	-0.423	491.700	2402	1910	56.780	794.50	737.70	2.034
-2	-999	-0.699	-999	-0.699	-2.93	-0.699	-3.77	-3.73	-0.699	-2.00	-0.724	-0.398	510.300	2421	1911	60.080	798.70	738.60	1.960
-1.8371	-999	-0.536	-999	-0.536	-2.93	-0.536	-3.77	-3.73	-0.536	-1.84	-0.724	-0.235	664.200	2578	1914	87.410	834.00	746.50	1.506
-1.7044	-999	-0.403	-999	-0.403	-2.93	-0.403	-3.77	-3.73	-0.536	-1.70	-0.724	-0.102	775.800	2692	1916	118.700	866.20	747.50	1.289
-1.6795	-999	-0.379	-999	-0.379	-2.93	-0.379	-3.77	-3.73	-0.536	-1.68	-0.724	-0.078	800.700	2717	1916	125.600	873.40	747.80	1.249
-1.5	-999	-0.199	-999	-0.199	-2.93	-0.199	-3.77	-3.73	-0.536	-1.50	-0.724	0.102	1030.000	2956	1925	189.900	943.50	753.50	0.971
-1.4265	-999	-0.126	-999	-0.126	-2.93	-0.126	-3.77	-3.73	-0.536	-1.43	-0.724	0.176	1155.000	3086	1930	224.900	981.60	756.60	0.866
-1.1947	-999	0.106	-999	-0.126	-2.93	0.106	-3.77	-3.73	-0.536	-1.19	-0.724	0.407	1583.000	3546	1963	330.500	1114.00	784.00	0.632
-1.1791	-999	0.122	-999	-0.126	-2.93	0.122	-3.77	-3.73	-0.536	-1.18	-0.724	0.423	1621.000	3588	1968	339.900	1128.00	787.70	0.617
-1.1304	-999	0.171	-999	-0.126	-2.93	0.171	-3.77	-3.73	-0.536	-1.13	-0.724	0.472	1748.000	3719	1972	371.300	1170.00	798.50	0.572
-1	-999	0.301	-999	-0.126	-2.93	0.301	-3.77	-3.73	-0.536	-1.00	-0.724	0.602	2167.000	4153	1986	474.900	1324.00	848.70	0.461
-0.8439	-999	0.457	-999	-0.126	-2.93	0.457	-3.77	-3.73	-0.536	-0.84	-0.724	0.758	2867.000	4875	2008	647.700	1561.00	913.00	0.349
-0.5	-999	0.801	-999	-0.126	-2.93	0.801	-3.77	-3.73	-0.536	-0.50	-0.724	0.758	5581.000	7634	2053	1339.000	2350.00	1011.00	0.179
-0.3825	-999	0.919	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	-0.38	-0.724	0.758	7123.000	9201	2078	1732.000	2795.00	1063.00	0.160
-0.3706	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	-0.37	-0.724	0.758	7212.000	9290	2078	1764.000	2824.00	1060.00	0.139
0	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.00	-0.724	0.758	7247.000	9325	2078	1779.000	2837.00	1058.00	0.138
0.5	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.50	-0.724	0.758	7377.000	9455	2078	1834.000	2886.00	1052.00	0.136
1	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	1.00	-0.724	0.758	7787.000	9865	2078	2010.000	3041.00	1031.00	0.128
1.0544	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	1.05	-0.724	0.758	7868.000	9946	2078	2045.000	3071.00	1027.00	0.127
1.0707	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	1.07	-0.724	0.758	7894.000	9972	2078	2056.000	3081.00	1025.00	0.127
1.0719	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	1.07	-0.724	0.758	7896.000	9974	2078	2057.000	3082.00	1025.00	0.127

[1]cm3 = cubic centimeters
[2]g = grams
[3]Des = Destroyed
[4]Cre = Created

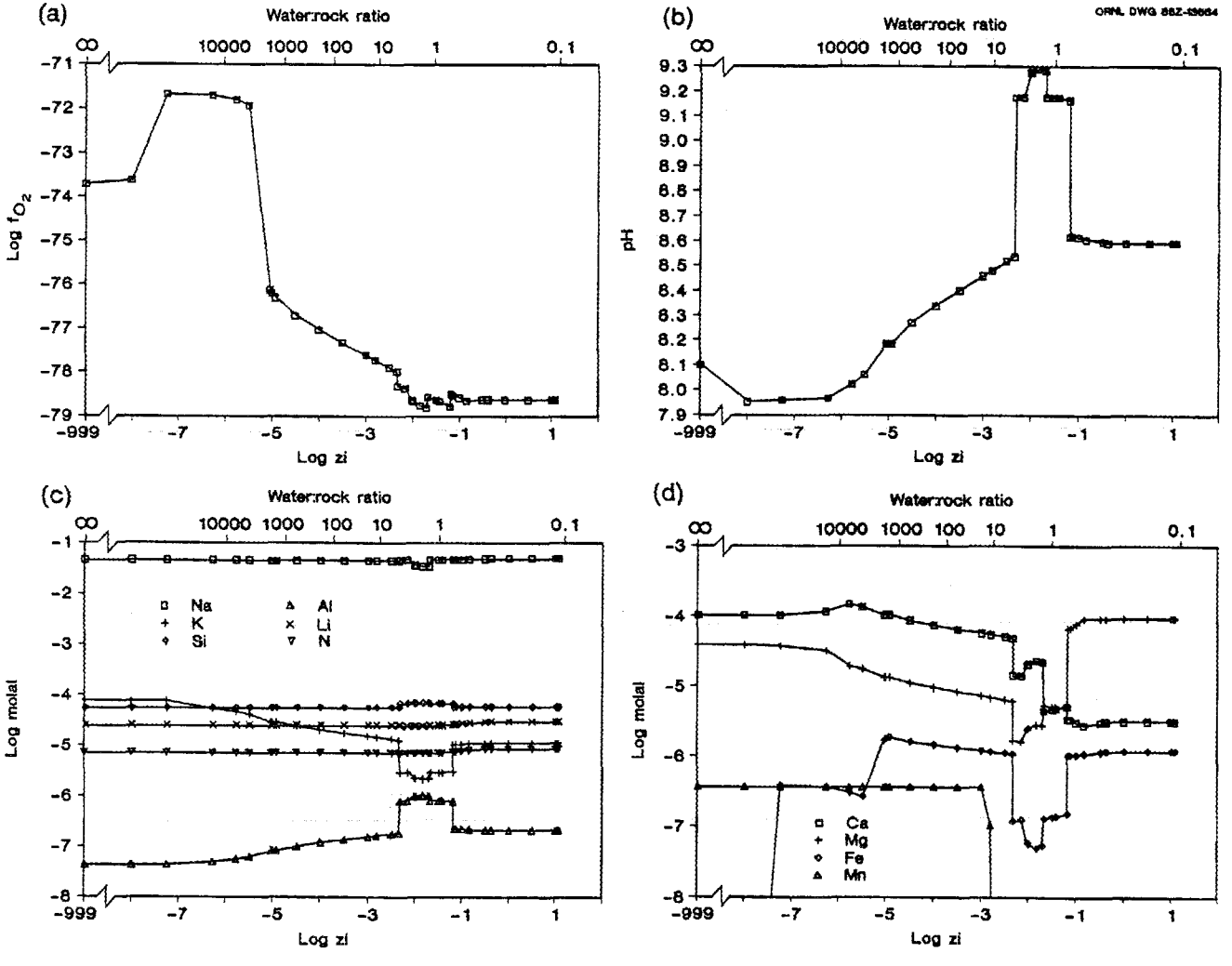

Fig. 5. Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) at T = 10.5°C: (a) Log f_{O_2}, (b) pH, (c) Na, K, Si, Al, Li, and N, (d) Ca, Mg, Fe, and Mn.

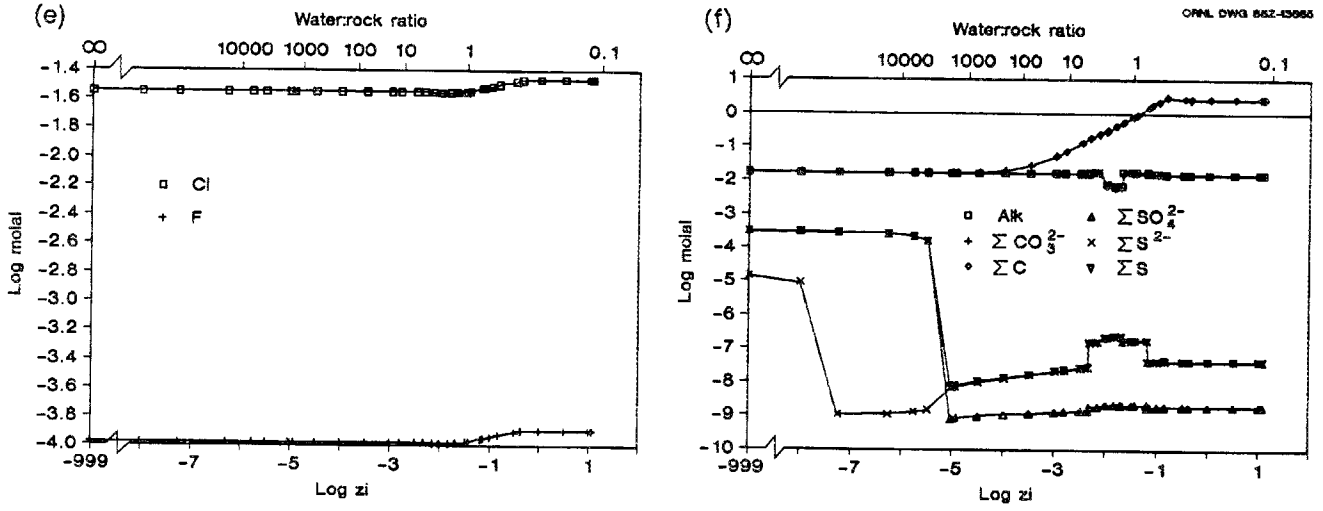

Fig. 5 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) at T = 10.5°C: (e) Cl and F, (f) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

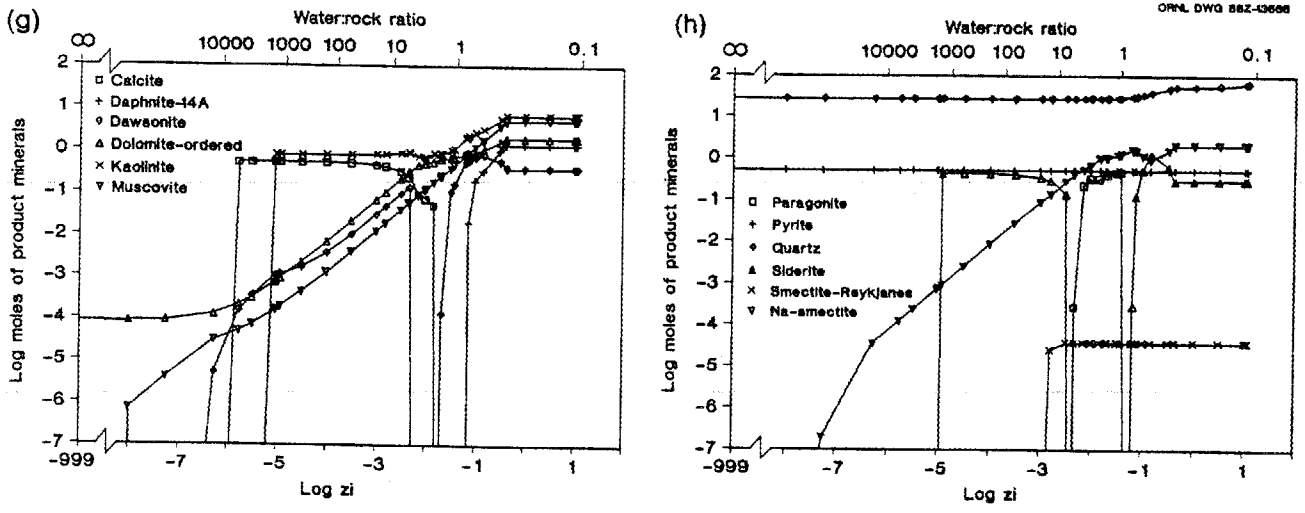

Fig. 5 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) at T = 10.5°C: (g) product minerals 1, (h) product minerals 2.

Case 6: Reaction of Bearpaw water and Pierre Shale (Schultz et al.) to T = 250°C. In this case the temperature is gradually raised from a starting value of 10.5°C to a final value of 250°C during the course of the experiment. The log f_{O_2} = -73.7 at the start of the reaction and decreases to -37.9, which is quite reducing at T = 250°C (Table 9, Fig. 6). The pH decreases from 7.9 to 6.1, however, because the neutral pH of water decreases to ~5.6 at 250°C, the water remains slightly alkaline. Alkalinity is not defined at T > 50°C in EQ6, hence no values are given for the termination of the experiment. Total carbonate, SO_4^{2-}, and H_2S increase during the course of the experiment. Among the dissolved species total Al, Fe, C, K, Na, Si, and S increase while Ca, Cl, F, Li, Mg, Mn, and N (primarily as NH_4^+) decrease. A small amount of water is produced during the course of experiment and may account for some of the small decreases observed in dissolved concentrations. CO_2(aq), CH_4(aq), and HCO_3^- are the predominant C phases, in order of abundance. Mn and Fe show the largest changes in dissolved concentrations. At the end of the reaction progress 14A-daphnite, ordered dolomite, graphite, muscovite, paragonite, pyrite, quartz, siderite, and Reykjanes-, Ca-, and Na-smectite comprise the equilibrium mineral assemblage. During the course of the reaction Mg-beidellite, low albite, calcite, dawsonite, and kaolinite are stable at various points. As in Case 5 a final water:rock ratio of 0.127 is achieved.

Case 7: Reaction of Bearpaw water and Pierre Shale (Lee et al.) at T = 10.5°C. The log f_{O_2} = -73.7 at the start of the reaction and decreases to -79.2, the temperature remaining isothermal at 10.5°C (Table 10, Fig. 7). The pH gradually increases from 7.9 to 8.2 at the end of the reaction but reaches intermediary values as high as 9.3. The alkalinity and total carbonate both decrease slightly while decreases in both total SO_4^{2-} and H_2S are larger. The total dissolved species Al, Ca, Cl, F, Fe, C, Li, Na, N (primarily as NH_4^+), and Si increase while K, Mg, Mn, and S decrease. Mn initially decreases in concentration and then begins to increase again, but remains below the

Table 9a. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Schultz et al.) at T = 250°C.
Log molal concentrations of dissolved elements.

Log zi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	N	Si	S
-999	10.5	1.01	7.95	-73.67	-0.252	-1.77	-1.76	-3.53	-4.95	-7.64	-3.99	-1.55	-3.98	-13.44	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-8	10.5	1.01	7.95	-73.63	-0.252	-1.77	-1.76	-3.53	-5.05	-7.37	-3.99	-1.55	-3.98	-13.28	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-7.2547	10.5	1.01	7.96	-71.68	-0.225	-1.77	-1.76	-3.54	-8.96	-7.36	-3.99	-1.55	-3.98	-6.42	-1.760	-4.13	-4.61	-4.43	-6.44	-1.34	-5.15	-4.27	-3.54
-6.2773	10.5	1.01	7.97	-71.70	-0.226	-1.77	-1.76	-3.57	-8.95	-7.30	-3.93	-1.55	-3.98	-6.44	-1.759	-4.28	-4.61	-4.50	-6.44	-1.34	-5.15	-4.27	-3.57
-5.7736	10.5	1.01	8.02	-71.81	-0.230	-1.77	-1.76	-3.65	-8.88	-7.25	-3.83	-1.55	-3.98	-6.52	-1.761	-4.34	-4.61	-4.71	-6.44	-1.34	-5.15	-4.27	-3.65
-5.5	10.5	1.01	8.06	-71.92	-0.234	-1.77	-1.76	-3.79	-8.82	-7.21	-3.87	-1.55	-3.98	-6.58	-1.763	-4.39	-4.61	-4.75	-6.44	-1.34	-5.15	-4.27	-3.79
-5.0345	10.5	1.01	8.19	-76.12	-0.300	-1.78	-1.77	-9.08	-8.16	-7.07	-3.98	-1.55	-3.98	-5.78	-1.771	-4.55	-4.61	-4.87	-6.44	-1.35	-5.15	-4.27	-8.11
-5	10.5	1.01	8.18	-76.19	-0.301	-1.78	-1.77	-9.07	-8.15	-7.08	-3.98	-1.55	-3.98	-5.76	-1.770	-4.54	-4.61	-4.87	-6.44	-1.35	-5.15	-4.27	-8.10
-4.9294	10.5	1.01	8.19	-76.30	-0.303	-1.78	-1.77	-9.06	-8.13	-7.07	-3.98	-1.55	-3.98	-5.73	-1.769	-4.55	-4.61	-4.87	-6.44	-1.35	-5.15	-4.27	-8.09
-4.5	10.5	1.01	8.27	-76.70	-0.313	-1.77	-1.77	-9.00	-7.99	-6.99	-4.06	-1.55	-3.98	-5.79	-1.751	-4.63	-4.61	-4.95	-6.44	-1.35	-5.15	-4.26	-7.95
-4	10.5	1.01	8.34	-77.03	-0.322	-1.77	-1.77	-8.95	-7.88	-6.92	-4.13	-1.55	-3.98	-5.84	-1.694	-4.70	-4.61	-5.02	-6.44	-1.35	-5.15	-4.26	-7.84
-3.5	10.5	1.01	8.40	-77.32	-0.329	-1.77	-1.77	-8.91	-7.77	-6.86	-4.18	-1.55	-3.98	-5.88	-1.549	-4.76	-4.61	-5.08	-6.44	-1.35	-5.15	-4.26	-7.74
-3	10.5	1.01	8.46	-77.60	-0.336	-1.77	-1.77	-8.87	-7.67	-6.80	-4.24	-1.55	-3.98	-5.92	-1.272	-4.82	-4.61	-5.14	-6.44	-1.35	-5.15	-4.26	-7.64
-2.8139	10.5	1.01	8.48	-77.70	-0.339	-1.77	-1.77	-8.85	-7.63	-6.78	-4.26	-1.55	-3.98	-5.94	-1.135	-4.84	-4.61	-5.16	-6.95	-1.35	-5.15	-4.26	-7.61
-2.5	10.6	1.01	8.52	-77.87	-0.344	-1.77	-1.77	-8.83	-7.57	-6.74	-4.30	-1.55	-3.98	-5.96	-0.875	-4.88	-4.61	-5.19	-16.51	-1.34	-5.15	-4.25	-7.55
-2.3411	10.6	1.01	8.54	-77.95	-0.346	-1.77	-1.77	-8.81	-7.54	-6.72	-4.31	-1.55	-3.98	-5.97	-0.733	-4.90	-4.61	-5.21	-21.35	-1.34	-5.15	-4.25	-7.51
-2.3238	10.6	1.01	9.17	-78.28	-0.387	-1.72	-1.76	-8.71	-6.79	-6.09	-4.84	-1.55	-3.98	-6.92	-0.721	-5.53	-4.61	-5.78	-165.31	-1.33	-5.15	-4.18	-6.79
-2.1543	10.6	1.01	9.17	-78.33	-0.388	-1.72	-1.76	-8.70	-6.78	-6.08	-4.84	-1.55	-3.98	-6.91	-0.611	-5.53	-4.62	-5.78	-165.69	-1.33	-5.15	-4.18	-6.78
-2.0246	10.7	1.01	9.27	-78.57	-0.397	-2.05	-2.09	-8.66	-6.65	-5.99	-4.69	-1.56	-3.98	-7.24	-0.531	-5.63	-4.62	-5.61	-250.44	-1.44	-5.15	-4.16	-6.65
-2	10.7	1.01	9.27	-78.59	-0.397	-2.07	-2.11	-8.65	-6.64	-5.99	-4.68	-1.56	-3.98	-7.25	-0.512	-5.64	-4.62	-5.59	-254.90	-1.44	-5.15	-4.16	-6.64
-1.8371	10.8	1.01	9.28	-78.68	-0.399	-2.15	-2.19	-8.62	-6.61	-5.98	-4.63	-1.55	-3.98	-7.31	-0.376	-5.65	-4.61	-5.54	-271.80	-1.45	-5.15	-4.16	-6.60
-1.7044	10.9	1.01	9.27	-78.68	-0.400	-2.13	-2.17	-8.62	-6.61	-5.98	-4.64	-1.55	-3.98	-7.28	-0.278	-5.64	-4.61	-5.55	-267.46	-1.45	-5.15	-4.15	-6.60
-1.6794	10.9	1.01	9.16	-78.43	-0.390	-1.72	-1.75	-8.65	-6.74	-6.08	-5.35	-1.55	-3.98	-6.89	-0.250	-5.52	-4.61	-5.27	-196.75	-1.33	-5.15	-4.17	-6.73
-1.5	11.1	1.01	9.15	-78.43	-0.391	-1.72	-1.75	-8.64	-6.73	-6.07	-5.33	-1.54	-3.97	-6.87	-0.105	-5.52	-4.61	-5.28	-196.01	-1.32	-5.14	-4.17	-6.72
-1.4363	11.2	1.01	9.15	-78.43	-0.391	-1.72	-1.75	-8.63	-6.73	-6.07	-5.33	-1.55	-3.97	-6.86	-0.053	-5.51	-4.61	-5.28	-195.05	-1.32	-5.14	-4.17	-6.72
-1.4265	11.3	1.01	9.15	-78.43	-0.391	-1.72	-1.75	-8.63	-6.73	-6.07	-5.32	-1.55	-3.97	-6.86	-0.045	-5.51	-4.61	-5.28	-194.98	-1.32	-5.14	-4.17	-6.72
-1.1954	11.8	1.01	9.12	-78.37	-0.392	-1.72	-1.75	-8.60	-6.71	-6.06	-5.30	-1.53	-3.95	-6.82	0.175	-5.49	-4.59	-5.28	-193.57	-1.31	-5.12	-4.16	-6.71
-1.1801	11.8	1.01	8.61	-78.11	-0.360	-1.75	-1.76	-8.68	-7.30	-6.57	-5.46	-1.52	-3.95	-6.05	0.190	-4.98	-4.59	-4.24	-116.31	-1.32	-5.12	-4.22	-7.28
-1.1768	11.9	1.01	8.60	-78.09	-0.359	-1.75	-1.76	-8.68	-7.32	-6.58	-5.47	-1.52	-3.95	-6.03	0.190	-4.97	-4.59	-4.21	-114.34	-1.32	-5.12	-4.22	-7.30
-1	12.5	1.01	8.58	-77.96	-0.360	-1.75	-1.75	-8.64	-7.28	-6.55	-5.54	-1.51	-3.94	-6.03	0.321	-4.96	-4.57	-4.14	-118.85	-1.31	-5.11	-4.21	-7.26
-0.8439	13.4	1.01	8.56	-77.77	-0.361	-1.74	-1.75	-8.59	-7.23	-6.52	-5.58	-1.50	-3.92	-6.03	0.472	-4.94	-4.56	-4.09	-121.68	-1.30	-5.09	-4.19	-7.21
-0.5	16.9	1.01	8.50	-76.70	-0.362	-1.69	-1.70	-8.48	-7.10	-6.36	-5.58	-1.48	-3.91	-6.09	0.416	-4.91	-4.54	-4.15	-123.12	-1.27	-5.07	-4.12	-7.08
-0.3825	18.9	1.01	8.46	-76.11	-0.363	-1.67	-1.67	-8.42	-7.03	-6.28	-5.58	-1.47	-3.89	-6.12	0.378	-4.89	-4.53	-4.18	-123.83	-1.26	-5.06	-4.09	-7.01
-0.3706	19.1	1.01	8.46	-76.04	-0.363	-1.67	-1.67	-8.41	-7.02	-6.27	-5.58	-1.47	-3.89	-6.13	0.380	-4.89	-4.53	-4.19	-123.97	-1.25	-5.06	-4.08	-7.00
0	30.8	1.01	8.29	-72.81	-0.370	-1.50	-1.51	-8.02	-6.58	-5.80	-5.63	-1.47	-3.90	-6.37	0.364	-4.82	-4.53	-4.43	-128.72	-1.18	-5.06	-3.88	-6.56
0.1603	39.9	1.01	8.18	-70.46	-0.375	-1.39	-1.39	-7.74	-6.26	-5.50	-5.66	-1.48	-3.91	-6.55	0.345	-4.78	-4.54	-4.62	-131.41	-1.13	-5.08	-3.74	-6.25
0.5	74.7	1.01	7.42	-62.59	-0.370	-999.00	-1.44	-6.66	-5.68	-5.37	-5.26	-1.49	-3.91	-6.37	0.320	-4.31	-4.55	-4.54	-127.39	-1.18	-5.08	-3.34	-5.63
0.6663	104.6	1.19	6.89	-56.98	-0.366	-999.00	-1.44	-5.70	-5.31	-5.98	-4.92	-1.49	-3.92	-6.11	0.315	-3.99	-4.55	-4.50	-121.27	-1.22	-5.08	-3.06	-5.16
0.7477	124.0	2.26	6.60	-53.81	-0.364	-999.00	-1.39	-5.17	-5.13	-6.21	-4.71	-1.49	-3.92	-5.90	0.310	-3.83	-4.55	-4.50	-116.95	-1.25	-5.09	-2.90	-4.85
0.7941	136.8	3.30	6.44	-51.80	-0.361	-999.00	-1.31	-4.87	-5.04	-6.29	-4.60	-1.50	-3.93	-5.77	0.170	-3.74	-4.57	-4.52	-114.27	-1.28	-5.10	-2.81	-4.65
0.811	141.9	3.81	6.40	-51.04	-0.362	-999.00	-1.27	-4.76	-4.99	-6.29	-4.57	-1.55	-3.98	-5.80	0.119	-3.73	-4.61	-4.60	-111.71	-1.30	-5.15	-2.77	-4.56
0.9679	199.0	15.22	6.14	-43.58	-0.383	-999.00	-0.69	-3.60	-4.48	-5.96	-4.51	-1.56	-3.99	-5.66	-0.250	-3.33	-4.62	-5.36	-106.29	-1.30	-5.16	-2.44	-3.55
1	213.5	20.44	6.12	-41.96	-0.391	-999.00	-0.53	-3.34	-4.37	-5.80	-4.53	-1.56	-3.99	-5.62	-0.252	-3.24	-4.63	-5.53	-108.12	-1.30	-5.16	-2.36	-3.30
1.0719	250.0	39.78	6.10	-38.24	-0.413	-999.00	-0.15	-2.74	-4.19	-5.35	-4.45	-1.56	-3.99	-5.43	-0.079	-3.08	-4.62	-5.89	-113.18	-1.32	-5.16	-2.20	-2.72

Table 9b. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Schultz et al.) at T = 250°C.
Log moles of product minerals.

Log zi	Albite	Beidellite -Mg	Calcite	Daphnite -14A	Dawsonite	Dolomite -ordered	Graphite	Kaolinite	Muscovite	Paragonite	Pyrite	Quartz	Siderite	Smectite-Reykjanes	Ca-Smectite	Na-smectite
-999						-4.075					-0.296	1.42				
-8						-4.070			-6.153		-0.296	1.42				
-7.2547						-4.047			-5.407		-0.296	1.42				-6.709
-6.2773					-5.295	-3.900			-4.520		-0.296	1.42				-4.443
-5.7736			-0.296		-3.830	-3.671			-4.295		-0.296	1.42				-3.905
-5.5			-0.296		-3.470	-3.507			-4.134		-0.296	1.42				-3.624
-5.0345			-0.296		-2.985	-3.149		-0.128	-3.798		-0.296	1.42				-3.135
-5			-0.296		-2.975	-3.119		-0.128	-3.774		-0.296	1.42				-3.097
-4.9294			-0.297		-2.954	-3.058		-0.128	-3.723		-0.296	1.42	-0.361			-3.021
-4.5			-0.298		-2.790	-2.664		-0.128	-3.364		-0.296	1.42	-0.363			-2.579
-4			-0.301		-2.450	-2.180		-0.126	-2.901		-0.296	1.42	-0.369			-2.066
-3.5			-0.312		-2.011	-1.685		-0.122	-2.414		-0.296	1.42	-0.391			-1.559
-3			-0.350		-1.532	-1.186		-0.111	-1.919		-0.296	1.42	-0.467			-1.055
-2.8139			-0.383		-1.350	-1.001		-0.102	-1.733		-0.296	1.42	-0.538	-4.60		-0.868
-2.5			-0.499		-1.040	-0.687		-0.077	-1.420		-0.296	1.42	-0.673	-4.44		-0.552
-2.3411			-0.631		-0.883	-0.528		-0.056	-1.261		-0.296	1.42		-4.44		-0.393
-2.3238	-3.508		-0.643		-0.905	-0.517		-0.071	-1.244		-0.296	1.42		-4.44		-0.346
-2.1543	-0.643		-1.032			-0.346		-0.035	-1.075		-0.296	1.42		-4.44		-0.270
-2.0246	-0.479		-1.139			-0.316		-0.006	-0.945		-0.296	1.42		-4.44		-0.167
-2	-0.480		-1.155			-0.311		0.001	-0.921		-0.296	1.42		-4.44		-0.146
-1.8371	-0.490		-1.313			-0.272		0.053	-0.758		-0.296	1.42		-4.44		-0.005
-1.7044	-0.397					-0.214		0.087	-0.625		-0.296	1.42		-4.44		0.016
-1.6794	-0.393				-3.888	-0.210		0.096	-0.600		-0.296	1.42		-4.44		0.023
-1.5	-0.347				-0.996	-0.172		0.155	-0.421		-0.296	1.43		-4.44		0.078
-1.4363					-0.831	-0.155		0.018	-0.357	-0.327	-0.296	1.46		-4.44		0.101
-1.4265					-0.808	-0.152		0.022	-0.347	-0.323	-0.296	1.46		-4.44		0.105
-1.1954					-0.293	-0.102		0.282	-0.116		-0.296	1.47		-4.44		0.216
-1.1801				-2.5411	-0.2662	-0.0974		0.3149	-0.1009		-0.2957	1.48		-4.44		0.1899
-1.1768				-1.6271	-0.2516	-0.0965		0.3144	-0.0975		-0.2957	1.48	-2.7992	-4.44		0.1739
-1				-0.592	-0.1382	-0.0405		0.394	0.0792		-0.2957	1.53	-0.311	-4.44		-0.0059
-0.8439				-0.4151	-0.1015	0.0228		0.4953	0.2353		-0.2957	1.58	0.0682	-4.44		-0.1006
-0.5				0.0675	-0.1754	0.2107		0.725	0.5792		-0.2957	1.69	-0.2476	-4.44		0.0665
-0.3825				0.2077	-0.2249	0.2898		0.8157	0.6967		-0.2957	1.74	-0.6503	-4.44		0.1405
-0.3706				0.2034	-0.2407	0.2898		0.8199	0.7086		-0.2957	1.74	-0.6264	-4.44		0.1601
0				0.2357	-0.1807	0.2898		0.8108	0.7086		-0.2957	1.75	-0.6615	-4.44		0.0657
0.1603				0.2104		0.2898		0.7678	0.7086	-0.1765	-0.2957	1.75	-0.0497	-4.44		0.0477
0.5				0.2423		0.2898		0.7499	0.7086	-0.0993	-0.2957	1.77	-0.0069	-4.44		-0.1308
0.6663				0.2476		0.2898		0.7412	0.7086	-0.1024	-0.2957	1.78	-0.0002	-4.44		-0.1115
0.7477				0.25		0.2898	-1.4993	0.7335	0.7086	-0.1184	-0.2957	1.79	-0.0072	-4.44		-0.0602
0.7941				0.2526		0.2436	-0.027	0.6693	0.7086	0.0212	-0.2957	1.79	-0.0397	-4.44	0.0764	
0.811		0.6446		0.2685		0.2725	-0.0077		0.7086	0.0204	-0.2957	1.76	-0.188	-4.44	-0.3366	
0.9679				0.21		-0.0035	0.4651		0.7086	0.0197	-0.2958	1.76	0.0819	-4.44	0.7633	
1				0.2189		-0.0023	0.4934		0.7085	0.0196	-0.2959	1.77	0.0036	-4.44	0.7621	
1.0719				0.2449		0.0015	0.5333		0.7085	0.0205	-0.2966	1.78	-0.3887	-4.44	0.7581	

Table 9c. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Schultz et al.) at T = 10.5°C.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	Plagioclase	Siderite	Ca-Smectite	Calcite	Kaolinite	Ripidolite -14A	Cristobalite	Clinoptilite -na	Graphite	g^bDes^c	g^bCre^d	g^bNet	cm^{3a}Des^c	cm^{3a}Cre^d	cm^{3a}Net	Water:Rock Ratio
-999	-999	-999.000	-999	-999.000	-999.00	-999.000	-999.00	-999.00	-999.000	-999.000	-999.000	-999.000	0.000	1641	1641	0.000	597	597	
-8	-999	-6.699	-999	-6.699	-6.00	-6.699	-6.00	-6.70	-6.699	-8.000	-6.699	-6.398	0.001	1641	1641	0.000	597	597	1269680.041
-7.2547	-999	-5.954	-999	-5.954	-5.25	-5.954	-5.25	-5.95	-5.954	-7.255	-5.954	-5.653	0.004	1641	1641	0.001	597	597	228258.388
-6.2773	-999	-4.976	-999	-4.976	-4.28	-4.976	-4.28	-4.98	-4.976	-6.277	-4.976	-4.675	0.042	1641	1641	0.006	597	597	24038.462
-5.7736	-999	-4.473	-999	-4.473	-3.77	-4.473	-3.77	-4.47	-4.473	-5.774	-4.473	-4.172	0.133	1692	1692	0.020	615	615	7535.795
-5.5	-999	-4.199	-999	-4.199	-3.50	-4.199	-3.77	-4.20	-4.199	-5.500	-4.199	-3.898	0.234	1692	1692	0.032	615	615	4268.032
-5.0345	-999	-3.734	-999	-3.734	-3.03	-3.734	-3.77	-3.73	-3.734	-5.035	-3.734	-3.433	0.652	1885	1884	0.080	690	690	1533.978
-5	-999	-3.699	-999	-3.699	-3.00	-3.699	-3.77	-3.73	-3.699	-5.000	-3.699	-3.398	0.701	1885	1884	0.085	690	690	1427.552
-4.9294	-999	-3.628	-999	-3.628	-2.93	-3.628	-3.77	-3.73	-3.628	-4.929	-3.628	-3.327	0.813	1935	1934	0.095	690	690	1230.618
-4.5	-999	-3.199	-999	-3.199	-2.93	-3.199	-3.77	-3.73	-3.199	-4.500	-3.199	-2.898	1.845	1936	1934	0.215	690	690	542.005
-4	-999	-2.699	-999	-2.699	-2.93	-2.699	-3.77	-3.73	-2.699	-4.000	-2.699	-2.398	5.401	1940	1934	0.625	691	690	185.151
-3.5	-999	-2.199	-999	-2.199	-2.93	-2.199	-3.77	-3.73	-2.199	-3.500	-2.199	-1.898	16.650	1951	1934	1.924	693	691	60.060
-3	-999	-1.699	-999	-1.699	-2.93	-1.699	-3.77	-3.73	-1.699	-3.000	-1.699	-1.398	52.210	1986	1933	6.030	700	694	19.153
-2.8139	-999	-1.513	-999	-1.513	-2.93	-1.513	-3.77	-3.73	-1.513	-2.814	-1.513	-1.212	80.020	2013	1933	9.242	706	697	12.497
-2.5	-999	-1.199	-999	-1.199	-2.93	-1.199	-3.77	-3.73	-1.199	-2.500	-1.199	-0.898	164.700	2096	1932	19.020	723	704	6.072
-2.3411	-999	-1.040	-999	-1.040	-2.93	-1.040	-3.77	-3.73	-1.040	-2.341	-1.040	-0.739	237.300	2168	1930	27.410	738	710	4.214
-2.3238	-999	-1.023	-999	-1.023	-2.93	-1.023	-3.77	-3.73	-1.023	-2.324	-1.023	-0.722	247.000	2176	1929	28.520	739	711	4.049
-2.1543	-999	-0.853	-999	-0.853	-2.93	-0.853	-3.77	-3.73	-0.853	-2.154	-0.853	-0.552	364.800	2286	1921	42.120	769	726	2.741
-2.0266	-999	-0.724	-999	-0.724	-2.93	-0.724	-3.77	-3.73	-0.724	-2.025	-0.724	-0.423	491.700	2408	1916	56.780	802	745	2.034
-2	-999	-0.699	-999	-0.699	-2.93	-0.699	-3.77	-3.73	-0.699	-2.000	-0.724	-0.398	510.300	2427	1917	60.080	806	746	1.960
-1.8371	-999	-0.536	-999	-0.536	-2.93	-0.536	-3.77	-3.73	-0.536	-1.837	-0.724	-0.235	664.200	2584	1920	87.410	841	754	1.506
-1.7044	-999	-0.403	-999	-0.403	-2.93	-0.403	-3.77	-3.73	-0.536	-1.704	-0.724	-0.102	775.800	2699	1923	118.700	875	756	1.289
-1.6796	-999	-0.378	-999	-0.378	-2.93	-0.378	-3.77	-3.73	-0.536	-1.679	-0.724	-0.077	800.900	2724	1923	125.700	882	757	1.249
-1.5	-999	-0.199	-999	-0.199	-2.93	-0.199	-3.77	-3.73	-0.536	-1.500	-0.724	0.102	1030.000	2964	1933	189.900	953	763	0.971
-1.4363	-999	-0.135	-999	-0.135	-2.93	-0.135	-3.77	-3.73	-0.536	-1.436	-0.724	0.166	1137.000	3067	1929	219.900	976	756	0.880
-1.4265	-999	-0.126	-999	-0.126	-2.93	-0.126	-3.77	-3.73	-0.536	-1.427	-0.724	0.176	1155.000	3085	1930	224.900	982	757	0.866
-1.1954	-999	0.106	-999	-0.126	-2.93	0.106	-3.77	-3.73	-0.536	-1.195	-0.724	0.407	1581.000	3544	1963	330.100	1114	784	0.633
-1.1801	-999	0.121	-999	-0.126	-2.93	0.121	-3.77	-3.73	-0.536	-1.180	-0.724	0.422	1618.000	3585	1967	339.200	1127	788	0.618
-1.1768	-999	0.124	-999	-0.126	-2.93	0.124	-3.77	-3.73	-0.536	-1.177	-0.724	0.425	1626.000	3594	1968	341.300	1132	791	0.615
-1	-999	0.301	-999	-0.126	-2.93	0.301	-3.77	-3.73	-0.536	-1.000	-0.724	0.602	2167.000	4153	1986	474.900	1331	856	0.461
-0.8439	-999	0.457	-999	-0.126	-2.93	0.457	-3.77	-3.73	-0.536	-0.844	-0.724	0.758	2867.000	4875	2008	647.700	1567	919	0.349
-0.5	-999	0.801	-999	-0.126	-2.93	0.801	-3.77	-3.73	-0.536	-0.500	-0.724	0.758	5581.000	7633	2052	1339.000	2369	1030	0.179
-0.3825	-999	0.919	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	-0.383	-0.724	0.758	7123.000	9200	2077	1732.000	2825	1093	0.140
-0.3706	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	-0.371	-0.724	0.758	7212.000	9289	2077	1764.000	2855	1091	0.139
0	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.000	-0.724	0.758	7247.000	9322	2076	1779.000	2883	1104	0.138
0.1603	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.160	-0.724	0.758	7273.000	9318	2045	1790.000	2881	1090	0.137
0.5	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.500	-0.724	0.758	7377.000	9416	2039	1834.000	2935	1101	0.136
0.6663	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.666	-0.724	0.758	7465.000	9502	2037	1872.000	2970	1098	0.134
0.7477	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.748	-0.724	0.758	7523.000	9558	2035	1897.000	2991	1094	0.133
0.7961	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.796	-0.724	0.758	7561.000	9571	2011	1913.000	2984	1070	0.132
0.811	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.811	-0.724	0.758	7575.000	9488	1912	1920.000	2907	987	0.132
0.9679	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	0.968	-0.724	0.758	7745.000	9632	1887	1992.000	2942	950	0.129
1	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	1.000	-0.724	0.758	7787.000	9671	1883	2010.000	2953	943	0.128
1.0719	-999	0.930	-999	-0.126	-2.93	0.919	-3.77	-3.73	-0.536	1.072	-0.724	0.758	7896.000	9764	1868	2057.000	2980	923	0.127

[1] cm^3 = cubic centimeters
[2] g = grams
[3] Des = Destroyed
[4] Cre = Created

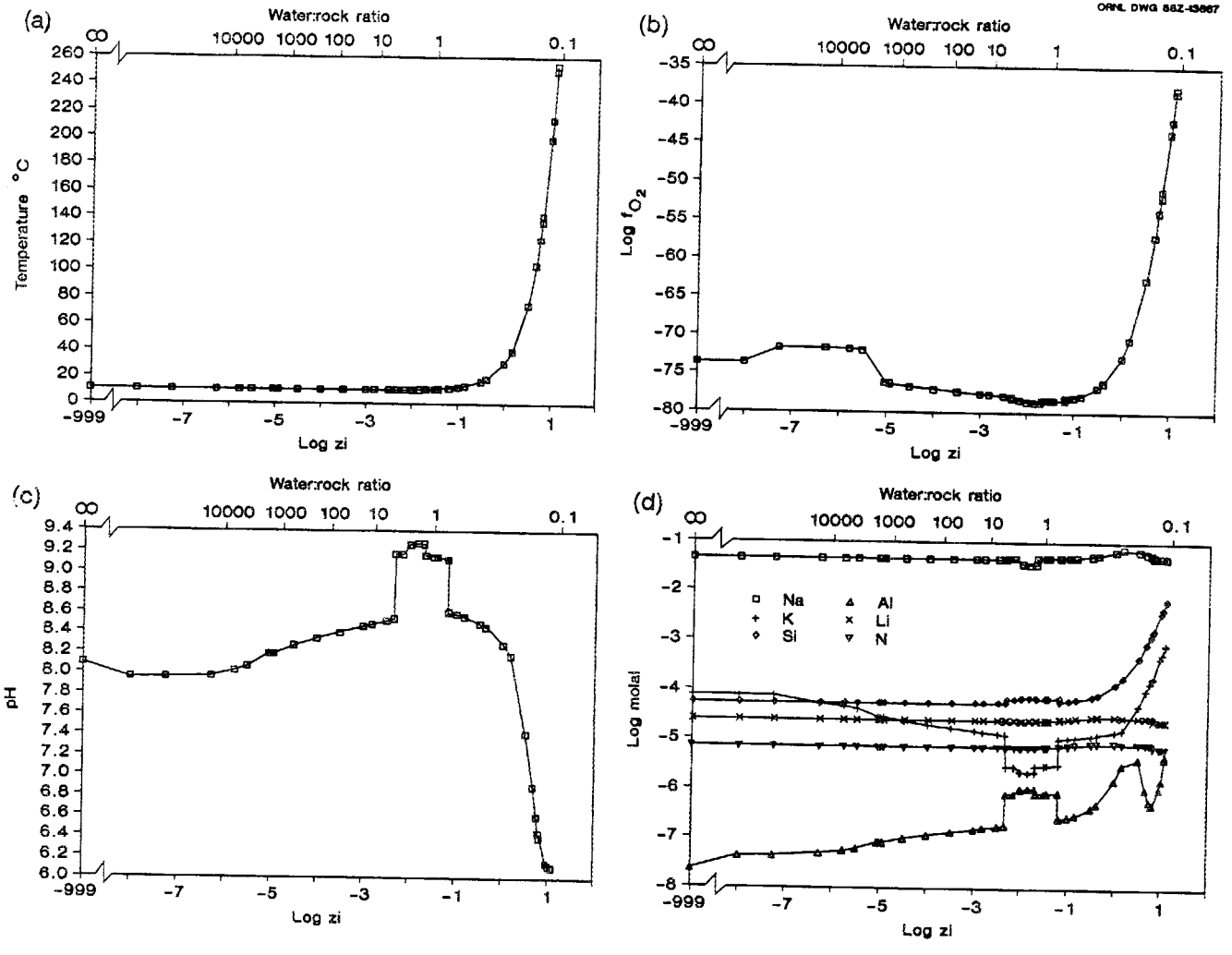

Fig. 6. Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) to T = 250°C: (a) Temperature, (b) Log f_{O_2}, (c) pH, (d) Na, K, Si, Al, Li, and N.

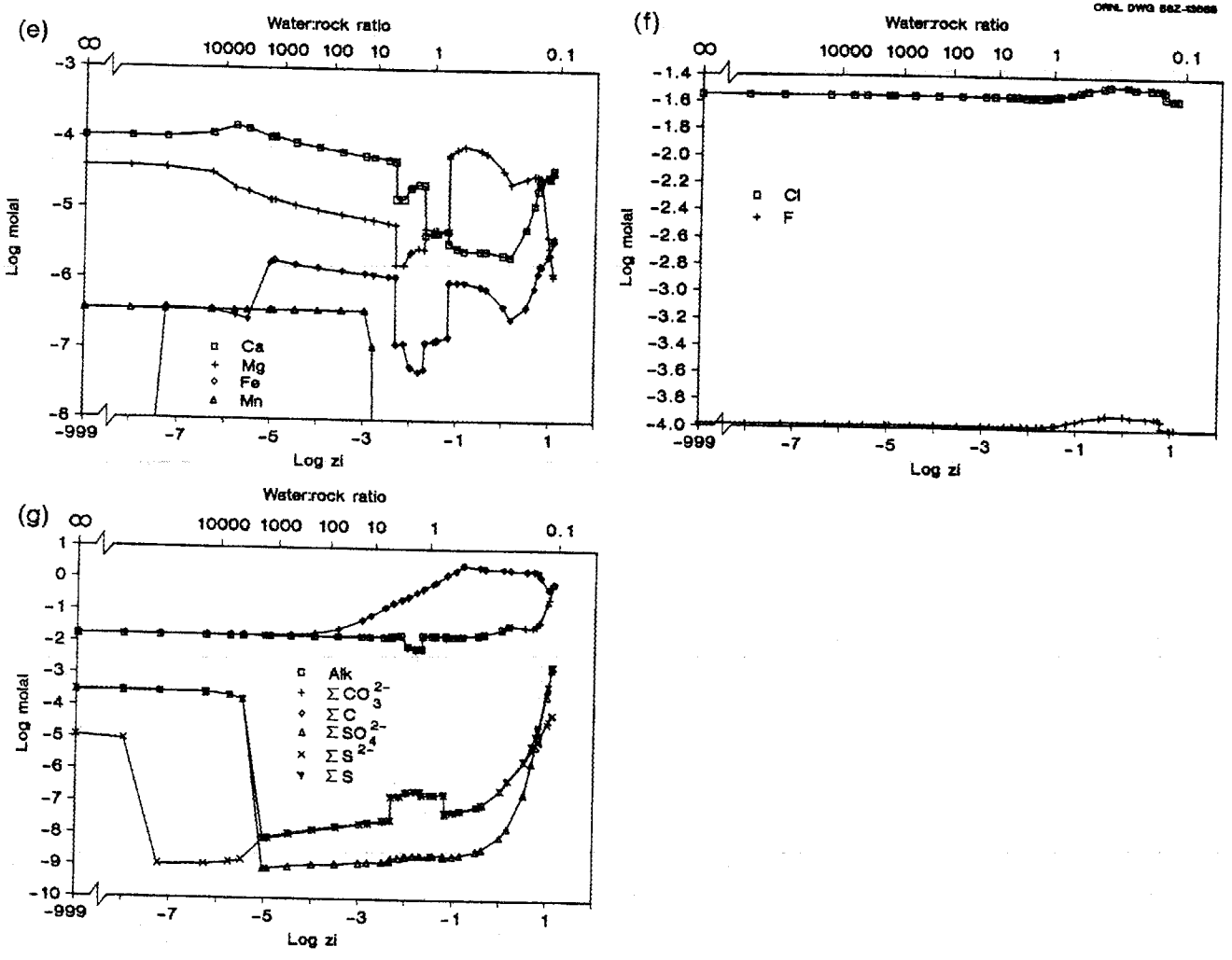

Fig. 6 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) to T = 250°C: (e) Ca, Mg, Fe, and Mn, (f) Cl and F, (g) Alkalinity, ΣCO_3^{2-}, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

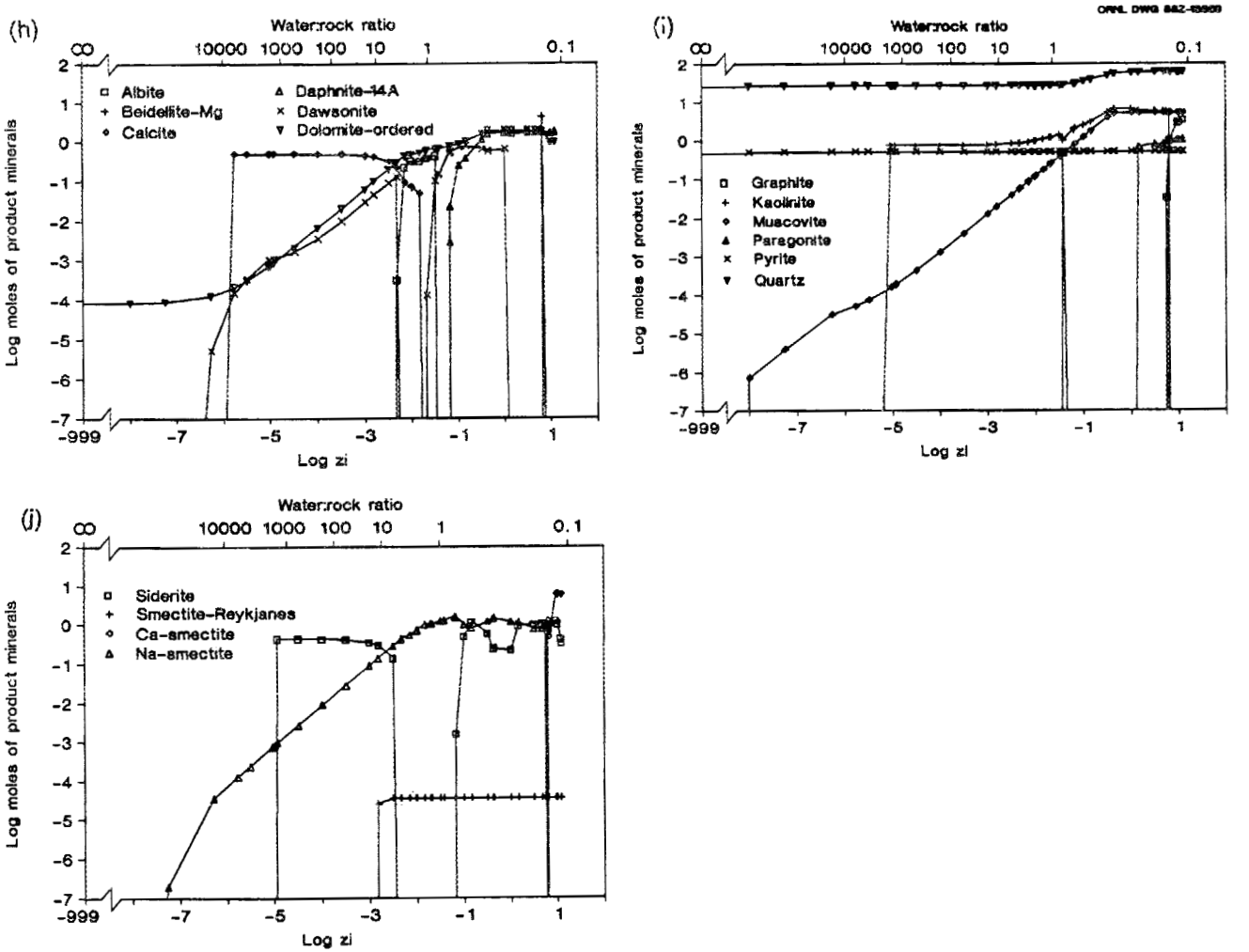

Fig. 6 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Schultz et al.) to T = 250°C: (h) product minerals 1, (i) product minerals 2, (j) product minerals 3.

Table 10a. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Lee et al.) at T = 10.5°C.
Log molal concentrations of dissolved elements.

Log zi	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	N	Si	S
-999	10.5	1.01	7.95	-73.67	-0.252	-1.77	-1.76	-3.53	-4.95	-7.64	-3.99	-1.55	-3.98	-13.44	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-8	10.5	1.01	7.95	-73.65	-0.252	-1.77	-1.76	-3.53	-5.01	-7.37	-3.99	-1.55	-3.98	-13.35	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-7.0339	10.5	1.01	7.97	-71.68	-0.225	-1.77	-1.76	-3.54	-8.96	-7.35	-3.99	-1.55	-3.98	-6.43	-1.761	-4.13	-4.61	-4.44	-6.44	-1.34	-5.15	-4.27	-3.54
-5.8928	10.5	1.01	8.06	-71.82	-0.232	-1.77	-1.76	-3.60	-8.83	-7.21	-3.94	-1.55	-3.98	-6.60	-1.763	-4.38	-4.61	-4.67	-6.44	-1.34	-5.15	-4.27	-3.60
-5.7406	10.5	1.01	8.12	-71.90	-0.237	-1.77	-1.76	-3.62	-8.76	-7.16	-3.91	-1.55	-3.98	-6.69	-1.764	-4.43	-4.61	-4.80	-6.44	-1.34	-5.15	-4.27	-3.62
-5.5	10.5	1.01	8.24	-72.07	-0.246	-1.77	-1.77	-3.70	-8.61	-7.03	-4.03	-1.55	-3.98	-6.88	-1.769	-4.57	-4.61	-4.92	-6.44	-1.34	-5.15	-4.27	-3.70
-5.246	10.5	1.01	8.49	-72.46	-0.266	-1.77	-1.78	-3.90	-8.28	-6.77	-4.26	-1.55	-3.98	-7.26	-1.776	-4.85	-4.61	-5.16	-6.44	-1.34	-5.15	-4.26	-3.90
-5.1149	10.5	1.01	8.66	-72.80	-0.280	-1.77	-1.77	-4.17	-8.05	-6.60	-4.42	-1.55	-3.98	-7.48	-1.775	-5.02	-4.61	-5.32	-6.54	-1.34	-5.15	-4.25	-4.17
-5	10.5	1.01	8.80	-73.88	-0.303	-1.76	-1.78	-5.91	-7.76	-6.47	-4.54	-1.55	-3.98	-7.45	-1.777	-5.16	-4.61	-5.45	-46.83	-1.34	-5.15	-4.23	-5.90
-4.6866	10.5	1.01	9.19	-76.95	-0.368	-1.77	-1.80	-8.88	-6.95	-6.08	-4.83	-1.55	-3.98	-7.31	-1.795	-5.55	-4.61	-5.76	-165.17	-1.34	-5.15	-4.18	-6.95
-4.5	10.5	1.01	9.20	-77.12	-0.371	-1.79	-1.83	-8.86	-6.92	-6.07	-4.82	-1.55	-3.98	-7.30	-1.813	-5.56	-4.61	-5.75	-173.61	-1.35	-5.15	-4.17	-6.92
-4	10.5	1.01	9.25	-77.56	-0.380	-1.99	-2.03	-8.80	-6.81	-6.02	-4.72	-1.55	-3.98	-7.42	-1.930	-5.62	-4.61	-5.64	-226.19	-1.42	-5.15	-4.17	-6.81
-3.5	10.5	1.01	9.30	-77.95	-0.388	-2.20	-2.25	-8.72	-6.70	-5.98	-4.59	-1.55	-3.98	-7.59	-1.854	-5.66	-4.61	-5.50	-275.77	-1.46	-5.15	-4.16	-6.69
-3.2235	10.5	1.01	9.30	-78.11	-0.391	-2.23	-2.27	-8.69	-6.66	-5.98	-4.58	-1.55	-3.98	-7.59	-1.671	-5.67	-4.61	-5.48	-281.54	-1.47	-5.15	-4.16	-6.66
-3	10.5	1.01	8.71	-78.27	-0.360	-2.98	-2.99	-8.74	-7.30	-6.57	-3.39	-1.55	-3.98	-6.64	-1.553	-5.08	-4.61	-4.26	-286.09	-1.55	-5.15	-4.24	-7.29
-2.9422	10.5	1.01	8.52	-78.31	-0.350	-3.19	-3.20	-8.75	-7.50	-6.75	-2.99	-1.55	-3.98	-6.25	-1.502	-4.90	-4.61	-3.86	-287.03	-1.57	-5.15	-4.25	-7.48
-2.5	10.5	1.01	8.53	-78.53	-0.353	-3.20	-3.21	-8.72	-7.47	-6.75	-2.99	-1.55	-3.98	-6.20	-1.062	-4.90	-4.61	-3.86	-289.67	-1.57	-5.14	-4.25	-7.44
-2.4227	10.5	1.01	8.53	-78.57	-0.354	-3.20	-3.21	-8.71	-7.46	-6.75	-2.99	-1.55	-3.98	-6.19	-0.986	-4.90	-4.61	-3.86	-290.18	-1.57	-5.14	-4.25	-7.44
-2.0969	10.5	1.01	8.54	-78.72	-0.357	-3.21	-3.23	-8.68	-7.41	-6.74	-2.99	-1.55	-3.97	-6.22	-0.727	-4.91	-4.61	-3.86	-295.71	-1.57	-5.14	-4.25	-7.39
-2	10.5	1.01	8.54	-78.75	-0.357	-3.22	-3.23	-8.67	-7.40	-6.73	-2.99	-1.55	-3.97	-6.22	-0.663	-4.92	-4.61	-3.86	-296.71	-1.57	-5.14	-4.25	-7.38
-1.7394	10.5	1.01	8.57	-78.86	-0.360	-3.20	-3.21	-8.64	-7.35	-6.71	-3.03	-1.54	-3.97	-6.27	-0.458	-4.94	-4.60	-3.90	-298.93	-1.56	-5.14	-4.25	-7.33
-1.7328	10.5	1.01	8.58	-78.86	-0.361	-3.19	-3.20	-8.64	-7.34	-6.70	-3.05	-1.54	-3.97	-6.28	-0.452	-4.95	-4.60	-3.91	-298.86	-1.56	-5.14	-4.25	-7.32
-1.5842	10.5	1.01	8.59	-78.93	-0.362	-3.19	-3.20	-8.63	-7.31	-6.69	-3.05	-1.54	-3.97	-6.29	-0.331	-4.96	-4.60	-3.92	-300.07	-1.56	-5.14	-4.25	-7.29
-1.5	10.5	1.01	8.61	-78.97	-0.364	-3.17	-3.18	-8.62	-7.28	-6.67	-3.10	-1.54	-3.97	-6.33	-0.257	-4.98	-4.60	-3.96	-300.49	-1.55	-5.13	-4.25	-7.26
-1.3799	10.5	1.01	8.63	-79.02	-0.366	-3.14	-3.15	-8.60	-7.24	-6.64	-3.15	-1.54	-3.96	-6.38	-0.149	-5.00	-4.60	-4.02	-301.14	-1.55	-5.13	-4.25	-7.23
-1.1062	10.5	1.01	9.27	-79.05	-0.402	-2.18	-2.22	-8.60	-6.59	-6.00	-4.58	-1.52	-3.95	-7.23	0.161	-5.64	-4.58	-5.49	-276.98	-1.44	-5.12	-4.16	-6.59
-1.0589	10.5	1.01	9.23	-78.92	-0.398	-1.96	-1.99	-8.63	-6.67	-6.04	-4.72	-1.52	-3.95	-7.02	0.181	-5.59	-4.58	-5.64	-225.10	-1.39	-5.12	-4.17	-6.66
-1.0583	10.5	1.01	9.21	-78.88	-0.396	-1.89	-1.92	-8.64	-6.69	-6.06	-4.75	-1.52	-3.95	-6.94	0.183	-5.57	-4.58	-5.68	-208.12	-1.37	-5.12	-4.17	-6.69
-1.0327	10.5	1.01	9.19	-78.87	-0.395	-1.83	-1.86	-8.64	-6.71	-6.08	-4.78	-1.52	-3.94	-6.87	0.247	-5.55	-4.58	-5.71	-193.27	-1.34	-5.11	-4.18	-6.71
-1.0286	10.5	1.01	9.00	-78.73	-0.383	-1.76	-1.78	-8.67	-6.94	-6.27	-4.69	-1.52	-3.94	-6.55	0.253	-5.36	-4.58	-5.61	-132.82	-1.32	-5.11	-4.21	-6.93
-1.0122	10.5	1.01	8.86	-78.65	-0.374	-1.77	-1.78	-8.69	-7.09	-6.41	-4.58	-1.52	-3.94	-6.35	0.239	-5.22	-4.58	-5.49	-100.76	-1.32	-5.11	-4.23	-7.08
-1.0121	10.5	1.01	8.62	-78.53	-0.358	-1.78	-1.79	-8.73	-7.37	-6.65	-4.36	-1.52	-3.94	-5.98	0.239	-4.97	-4.58	-5.26	-44.71	-1.33	-5.11	-4.25	-7.35
-1	10.5	1.01	8.61	-78.54	-0.358	-1.78	-1.79	-8.72	-7.37	-6.65	-4.36	-1.51	-3.94	-5.98	0.253	-4.97	-4.58	-5.26	-44.64	-1.33	-5.11	-4.25	-7.35
-0.5	10.5	1.01	8.57	-78.84	-0.360	-1.81	-1.81	-8.65	-7.33	-6.69	-4.27	-1.43	-3.86	-5.88	0.848	-4.93	-4.49	-5.17	-41.95	-1.28	-5.03	-4.25	-7.31
-0.1518	10.5	1.01	8.45	-79.11	-0.357	-1.91	-1.89	-8.58	-7.38	-6.80	-3.99	-1.23	-3.66	-5.54	1.401	-4.79	-4.29	-4.91	-39.32	-1.15	-4.83	-4.26	-7.35
-0.0141	10.5	1.01	8.33	-79.28	-0.352	-1.99	-1.95	-8.54	-7.45	-6.91	-3.71	-1.07	-3.50	-5.16	1.722	-4.66	-4.13	-4.64	-37.24	-1.02	-4.66	-4.26	-7.41
-0.0141	10.5	1.01	8.23	-79.23	-0.347	-1.99	-1.95	-8.50	-7.50	-7.00	-3.62	-1.07	-3.50	-5.07	1.722	-4.56	-4.13	-4.54	-9.73	-1.02	-4.66	-4.27	-7.46

Table 10b. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Lee et al.) at T = 10.5°C.
Log moles of product minerals.

Log zi	Albite	Calcite	Daphnite -14A	Dawsonite	Dolomite -ordered	Kaolinite	Muscovite	Paragonite	Pyrite	Quartz	Siderite	Smectite-Reykjanes	Ca-Smectite	Na-smectite
-999					-4.075				0.223	1.22				
-8					-4.069		-6.178		0.223	1.22				
-7.0339					-4.022		-5.209		0.223	1.22				-7.010
-5.8928				-5.291	-3.665		-4.122		0.223	1.22				-4.273
-5.7406		1.18		-4.480	-3.570		-4.008		0.223	1.22				-4.109
-5.5		1.18		-3.950	-3.406		-3.821		0.223	1.22				-3.854
-5.246		1.18		-3.737	-3.207	-0.412	-3.612		0.223	1.22				-3.584
-5.1149		1.18			-3.101	-0.412	-3.505		0.223	1.22		-5.12		-3.447
-5		1.18			-3.017	-0.412	-3.410		0.223	1.22		-4.44		-3.333
-4.6866	-4.82	1.18			-2.724	-0.412	-3.136		0.223	1.22		-4.44		-2.946
-4.5	-3.03	1.18			-2.544	-0.413	-2.965		0.223	1.22		-4.44		-2.744
-4	-2.22	1.18			-2.081	-0.415	-2.485		0.223	1.22		-4.44		-2.210
-3.5	-2.24	1.18			-1.927	-0.414	-1.992		0.223	1.22		-4.44		-1.592
-3.2235		1.18			-1.921	-0.412	-1.717		0.223	1.22		-4.44		-1.278
-3		1.18			-1.783	-0.402	-1.494		0.223	1.22		-4.44		-1.085
-2.9422		1.18			-1.757	-0.398	-1.436		0.223	1.22		-4.44	-3.201	-1.036
-2.5		1.18			-1.466	-0.376	-0.995		0.223	1.21		-4.44	-0.964	-0.815
-2.4227		1.18	-3.116		-1.404	-0.369	-0.917		0.223	1.21		-4.44	-0.856	-0.765
-2.0969		1.18	-1.289		-1.083	-0.339	-0.592		0.223	1.21		-4.44	-0.652	-0.523
-2		1.18	-1.117		-1.006	-0.342	-0.495		0.223	1.21		-4.44	-0.764	-0.443
-1.7394		1.18	-0.776		-0.786	-0.351	-0.234		0.223	1.23		-4.44		-0.215
-1.7328		1.18	-0.773		-0.781	-0.351	-0.228		0.223	1.23		-4.44		-0.210
-1.5842		1.17	-0.581		-0.477	-0.479	-0.079		0.223	1.25		-4.44		-0.210
-1.5		1.17	-0.483		-0.342	-0.653	-0.025		0.223	1.26		-4.44		-0.210
-1.3799		1.17	-0.348		-0.170	-1.589	0.059		0.223	1.28		-4.44		-0.211
-1.1062		1.15	-0.258		0.129	-0.475	0.059	-2.137	0.223	1.32		-4.44		-0.242
-1.0589		1.14	-0.130		0.207	-0.738	0.059	-0.717	0.223	1.36		-4.44		
-1.0583		1.14	-0.130		0.207	-0.725	0.059	-0.724	0.223	1.36		-4.44		-2.401
-1.0327		1.14	-0.236		0.204	-0.303	0.059		0.223	1.34		-4.44		-0.243
-1.0286		1.14	-0.236	-3.071	0.207	-0.281	0.059		0.223	1.34		-4.44		-0.251
-1.0122		1.14	-0.106	-0.729	0.207	-0.339	0.059		0.223	1.37		-4.44		
-1.0121		1.14	-0.106	-0.728	0.207	-0.339	0.059		0.223	1.37	-5.351	-4.44		
-1		1.14	-0.105	-0.728	0.207	-0.308	0.059		0.223	1.37	-1.273	-4.44		
-0.5		1.16	-0.055	-0.720	0.207	0.491	0.059		0.223	1.53	0.628	-4.44		
-0.1518		1.20	0.022	-0.707	0.207	0.891	0.059		0.223	1.72	1.072	-4.44		
-0.0141		1.20	-0.701		0.207	0.946	0.059		0.223	1.73	1.232	-4.44		
-0.0141		1.20	-0.701		0.207	0.946	0.059		0.223	1.73	1.232	-4.44		

Table 10c. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Lee et al.) at T = 10.5°C.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	Plagioclase	Biotite	Ca-Smectite	Calcite	Kaolinite	Ripidolite -14a	Graphite	g[b]Des[c]	g[b]Cre[d]	g[b]Net	cm[3a]Des[c]	cm[3a]Cre[d]	cm[3a]Net	Water:Rock Ratio
-999	-999	-999.000	-999	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	-999.000	0.000	1198	1198	0.000	377	377	
-8	-999	-6.699	-999	-6.699	-6.699	-6.699	-6.00	-6.70	-6.699	-6.398	0.001	1198	1198	0.000	377	377	1708525.542
-7.0339	-999	-5.733	-999	-5.733	-5.733	-5.733	-5.03	-5.73	-5.733	-5.432	0.005	1198	1198	0.001	377	377	184706.317
-5.8928	-999	-4.592	-999	-4.592	-4.592	-4.592	-3.89	-4.59	-4.592	-4.291	0.075	1198	1198	0.016	377	377	13347.571
-5.7406	-999	-4.440	-999	-4.440	-4.440	-4.440	-3.74	-4.44	-4.440	-4.139	0.106	2699	2699	0.023	931	931	9398.496
-5.5	-999	-4.199	-999	-4.199	-4.199	-4.199	-3.74	-4.20	-4.199	-3.898	0.172	2699	2699	0.036	931	931	5827.506
-5.246	-999	-3.945	-999	-3.945	-3.945	-3.945	-3.74	-3.95	-3.945	-3.644	0.294	2799	2799	0.059	969	969	3405.995
-5.1149	-999	-3.814	-999	-3.814	-3.814	-3.814	-3.74	-3.95	-3.814	-3.513	0.380	2799	2799	0.073	969	969	2629.503
-5	-999	-3.699	-999	-3.699	-3.699	-3.699	-3.74	-3.95	-3.699	-3.398	0.481	2799	2799	0.090	969	969	2078.570
-4.6866	-999	-3.386	-999	-3.386	-3.386	-3.386	-3.74	-3.95	-3.386	-3.085	0.940	2800	2799	0.166	969	969	1064.169
-4.5	-999	-3.199	-999	-3.199	-3.199	-3.199	-3.74	-3.95	-3.199	-2.898	1.419	2801	2799	0.245	970	969	704.722
-4	-999	-2.699	-999	-2.699	-2.699	-2.699	-3.74	-3.95	-2.699	-2.398	4.383	2804	2799	0.736	970	969	228.154
-3.5	-999	-2.199	-999	-2.199	-2.199	-2.199	-3.74	-3.95	-2.199	-1.898	13.760	2814	2800	2.289	972	970	72.674
-3.2235	-999	-1.922	-999	-1.922	-1.922	-1.922	-3.74	-3.95	-1.922	-1.621	25.970	2826	2800	4.310	974	970	38.506
-3	-999	-1.699	-999	-1.699	-1.699	-1.699	-3.74	-3.95	-1.699	-1.398	43.410	2844	2801	7.198	978	971	23.036
-2.9422	-999	-1.641	-999	-1.641	-1.641	-1.641	-3.74	-3.95	-1.641	-1.340	49.580	2851	2801	8.220	979	971	20.169
-2.5	-999	-1.199	-999	-1.199	-1.199	-1.199	-3.74	-3.95	-1.199	-0.898	137.200	2939	2802	22.720	995	973	7.289
-2.4227	-999	-1.122	-999	-1.122	-1.122	-1.122	-3.74	-3.95	-1.122	-0.821	163.900	2967	2803	27.150	1000	973	6.101
-2.0969	-999	-0.796	-999	-0.796	-0.796	-0.796	-3.74	-3.95	-0.796	-0.495	346.900	3152	2805	57.460	1041	984	2.863
-2	-999	-0.699	-999	-0.699	-0.699	-0.699	-3.74	-3.95	-0.796	-0.398	408.900	3216	2807	71.820	1059	987	2.446
-1.7394	-999	-0.438	-999	-0.438	-0.438	-0.438	-3.74	-3.95	-0.796	-0.137	663.700	3478	2814	130.900	1128	997	1.507
-1.7328	-999	-0.432	-999	-0.432	-0.432	-0.432	-3.74	-3.95	-0.796	-0.131	672.200	3487	2815	132.800	1130	997	1.488
-1.5842	-999	-0.283	-999	-0.432	-0.283	-0.283	-3.74	-3.95	-0.796	0.018	865.300	3682	2817	171.900	1178	1006	1.156
-1.5	-999	-0.283	-999	-0.432	-0.199	-0.199	-3.74	-3.95	-0.796	0.102	965.000	3783	2818	185.200	1197	1012	1.036
-1.3799	-999	-0.283	-999	-0.432	-0.079	-0.079	-3.74	-3.95	-0.796	0.222	1145.000	3966	2821	209.300	1232	1023	0.873
-1.1062	-999	-0.283	-999	-0.432	-0.079	0.195	-3.74	-3.95	-0.796	0.496	1454.000	4293	2839	252.900	1305	1052	0.688
-1.0589	-999	-0.283	-999	-0.432	-0.079	0.242	-3.74	-3.95	-0.796	0.543	1530.000	4368	2837	263.600	1340	1077	0.654
-1.0583	-999	-0.283	-999	-0.432	-0.079	0.243	-3.74	-3.95	-0.796	0.544	1531.000	4369	2837	263.800	1341	1077	0.653
-1.0327	-999	-0.283	-999	-0.432	-0.079	0.268	-3.74	-3.95	-0.796	0.569	1576.000	4422	2846	270.100	1332	1062	0.635
-1.0286	-999	-0.283	-999	-0.432	-0.079	0.272	-3.74	-3.95	-0.796	0.574	1583.000	4430	2847	271.100	1334	1063	0.632
-1.0122	-999	-0.283	-999	-0.432	-0.079	0.289	-3.74	-3.95	-0.796	0.590	1614.000	4464	2850	275.400	1369	1093	0.620
-1.0121	-999	-0.283	-999	-0.432	-0.079	0.289	-3.74	-3.95	-0.796	0.590	1614.000	4464	2850	275.500	1369	1093	0.620
-1	-999	-0.283	-999	-0.432	-0.079	0.301	-3.74	-3.95	-0.796	0.602	1637.000	4488	2851	278.700	1375	1097	0.611
-0.5	-999	-0.283	-999	-0.432	-0.079	0.801	-3.74	-3.95	-0.796	1.102	3461.000	6410	2949	536.400	1897	1360	0.289
-0.1518	-999	-0.283	-999	-0.432	-0.079	1.149	-3.74	-3.95	-0.796	1.450	6740.000	9865	3125	999.700	2834	1834	0.148
-0.0141	-999	-0.283	-999	-0.432	-0.079	1.149	-3.74	-3.95	-0.796	1.588	6867.000	10060	3192	999.700	2963	1963	0.146
-0.0141	-999	-0.283	-999	-0.432	-0.079	1.149	-3.74	-3.95	-0.796	1.588	6867.000	10060	3192	999.700	2963	1963	0.146

[1]cm3 = cubic centimeters
[2]g = grams
[3]Des = Destroyed
[4]Cre = Created

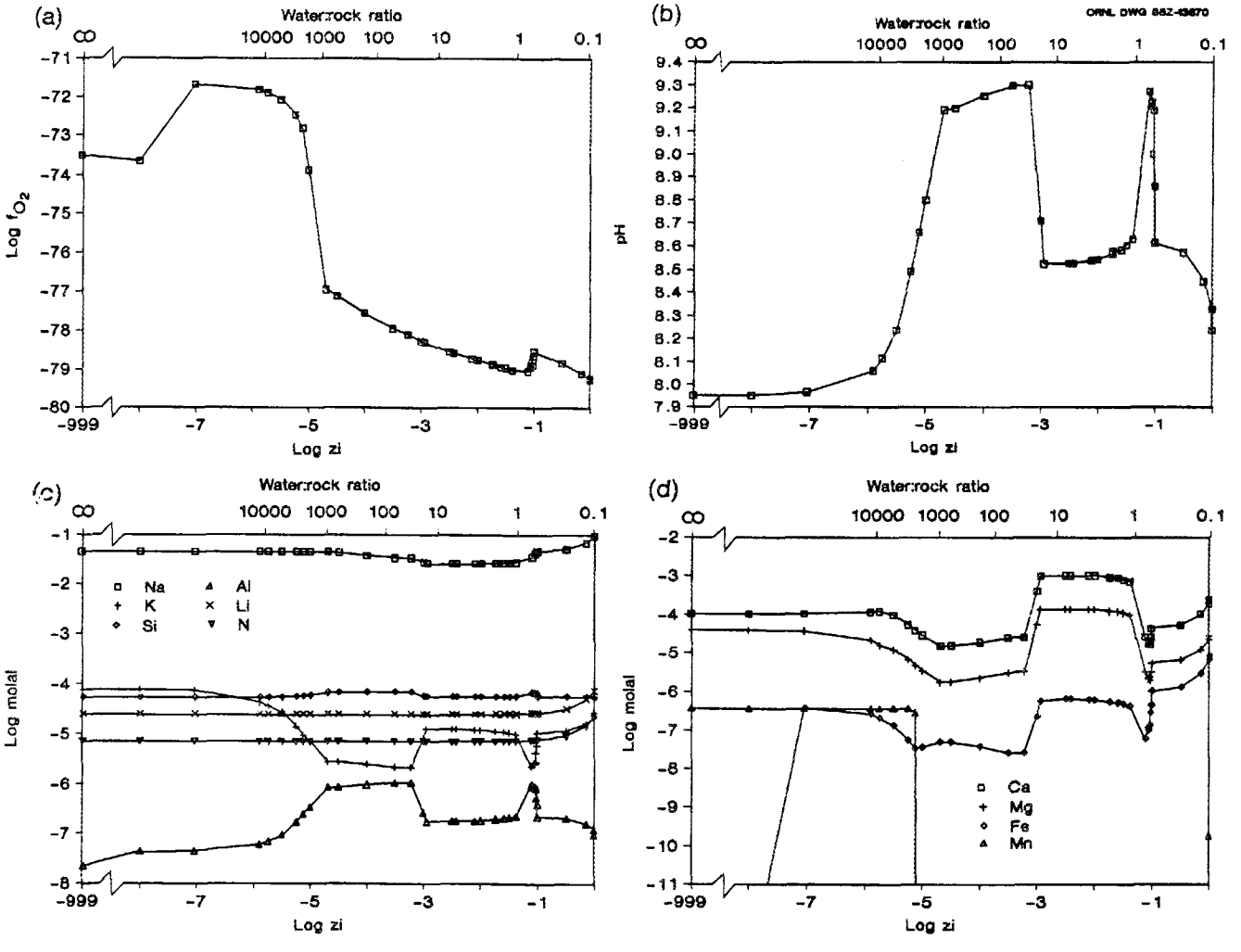

Fig. 7. Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) at T = 10.5°C: (a) Log f_{O_2}, (b) pH, (c) Na, K, Si, Al, Li, and N, (d) Ca, Mg, Fe, and Mn.

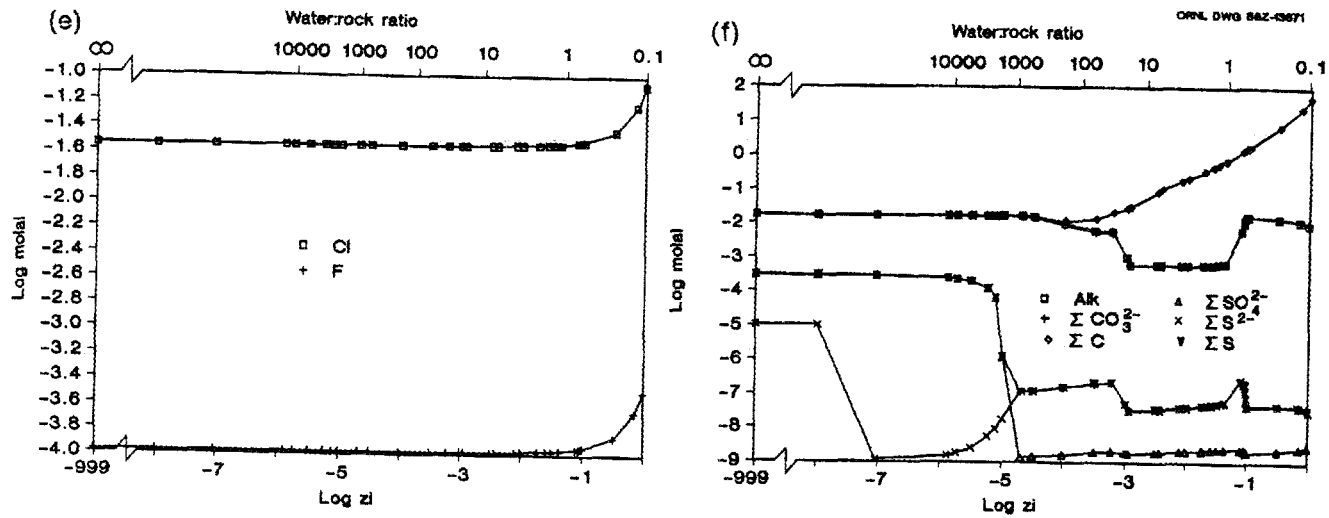

Fig. 7 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) at T = 10.5°C: (e) Cl and F, (f) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

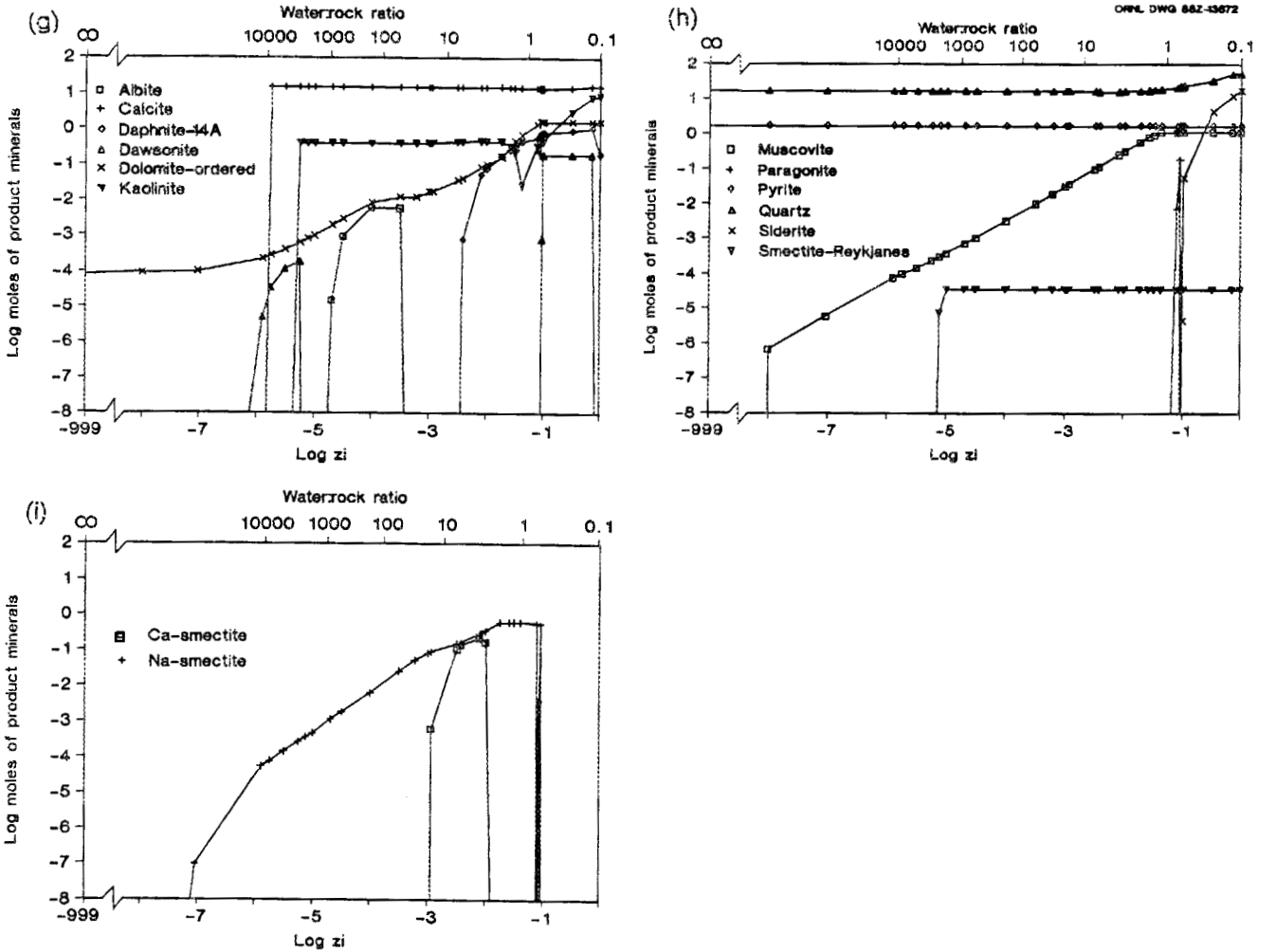

Fig. 7 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) at T = 10.5°C: (g) product minerals 1, (h) product minerals 2, (i) product minerals 3.

starting value. The largest changes are seen in Fe, C (CH_4(aq) is the predominant species), Mn, and S. A substantial amount of water is removed from the solution during the course of the reaction. At the end of the reaction progress calcite, 14A-daphnite, ordered dolomite, kaolinite, muscovite, pyrite, quartz, siderite and Reykjanes-smectite comprise the stable mineral assemblage while low albite, dawsonite, paragonite, and Ca- and Na-smectite are stable at various times during the reaction progress. The final water:rock ratio is 0.15, again slightly higher than the goal of 0.1 due to saturations of initial minerals during the reaction progress.

Case 8: Reaction of Bearpaw water with Pierre Shale (Lee et al.) to T = 250°C. In this case, as in that of Case 6, the temperature is gradually increased from 10.5 to 250°C during the experiment and the log f_{O_2} increases from -73.7 to -38.2, which is reducing under these conditions (Table 11, Fig. 8). The pH decreases from 7.9 to 6.1, and thus remains slightly alkaline. Alkalinity increases during the early phase of the experiment but is undefined in EQ6 at temperatures above 50°C. Total carbonate increases as does total SO_4^{2-} and H_2S. Total dissolved Al, Cl, F, Fe, C, K, Li, Na, N (primarily as NH_3 and NH_4^+), Si, and S increase while Ca, Mg, and Mn decrease. A small amount of H_2O is consumed during the course of the reaction. Total dissolved Mn, Fe, Al, Si, and C (primarily as CO_2(aq), CH_4(aq) and HCO_3^-) show the largest changes. Calcite, 14A-daphnite, ordered dolomite, graphite, muscovite, paragonite, pyrite, quartz, siderite, and Reykjanes- and Ca-smectite comprise the final equilibrium mineral assemblage while low albite, dawsonite, kaolinite, and Na-smectite are also part of the equilibrium assemblage during the course of the reaction. The final water:rock ratio achieved is 0.15.

Table 11a. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Lee et al.) at T = 250°C.
Log molal concentrations of dissolved elements.

Log ξ	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	N	Si	S
-999	10.5	1.01	7.95	-73.7	-0.252	-1.77	-1.76	-3.53	-4.95	-7.64	-3.99	-1.55	-3.98	-13.44	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-8	10.5	1.01	7.95	-73.6	-0.252	-1.77	-1.76	-3.53	-5.01	-7.37	-3.99	-1.55	-3.98	-13.35	-1.760	-4.12	-4.61	-4.41	-6.44	-1.34	-5.15	-4.27	-3.52
-7.0339	10.5	1.01	7.97	-71.7	-0.225	-1.77	-1.76	-3.54	-8.96	-7.35	-3.99	-1.55	-3.98	-6.43	-1.761	-4.13	-4.61	-4.44	-6.44	-1.34	-5.15	-4.27	-3.54
-5.8928	10.5	1.01	8.06	-71.8	-0.232	-1.77	-1.76	-3.60	-8.83	-7.21	-3.94	-1.55	-3.98	-6.60	-1.763	-4.38	-4.61	-4.67	-6.44	-1.34	-5.15	-4.27	-3.60
-5.7406	10.5	1.01	8.12	-71.9	-0.237	-1.77	-1.76	-3.62	-8.76	-7.16	-3.91	-1.55	-3.98	-6.69	-1.764	-4.43	-4.61	-4.80	-6.44	-1.34	-5.15	-4.27	-3.62
-5.5	10.5	1.01	8.24	-72.1	-0.246	-1.77	-1.77	-3.70	-8.61	-7.03	-4.03	-1.55	-3.98	-6.88	-1.769	-4.57	-4.61	-4.92	-6.44	-1.34	-5.15	-4.27	-3.70
-5.2577	10.5	1.01	8.48	-72.4	-0.265	-1.77	-1.78	-3.89	-8.30	-6.79	-4.25	-1.55	-3.98	-7.24	-1.776	-4.83	-4.61	-5.15	-6.44	-1.34	-5.15	-4.26	-3.89
-5.1235	10.5	1.01	8.66	-72.8	-0.280	-1.77	-1.77	-4.15	-8.05	-6.60	-4.42	-1.55	-3.98	-7.48	-1.775	-5.02	-4.61	-5.32	-6.44	-1.34	-5.15	-4.25	-4.15
-5.122	10.5	1.01	8.66	-72.8	-0.280	-1.77	-1.77	-4.15	-8.05	-6.60	-4.42	-1.55	-3.98	-7.48	-1.775	-5.02	-4.61	-5.32	-6.45	-1.34	-5.15	-4.25	-4.15
-5	10.5	1.01	8.80	-73.9	-0.303	-1.76	-1.78	-5.91	-7.76	-6.47	-4.54	-1.55	-3.98	-7.45	-1.777	-5.16	-4.61	-5.45	-46.84	-1.34	-5.15	-4.23	-5.90
-4.6865	10.5	1.01	9.19	-76.9	-0.368	-1.77	-1.80	-8.88	-6.95	-6.08	-4.83	-1.55	-3.98	-7.31	-1.795	-5.55	-4.61	-5.76	-165.18	-1.34	-5.15	-4.18	-6.95
-4.5	10.5	1.01	9.20	-77.1	-0.371	-1.79	-1.83	-8.86	-6.92	-6.07	-4.82	-1.55	-3.98	-7.30	-1.813	-5.56	-4.61	-5.75	-173.62	-1.35	-5.15	-4.17	-6.92
-4	10.5	1.01	9.25	-77.6	-0.380	-1.99	-2.03	-8.80	-6.81	-6.02	-4.72	-1.55	-3.98	-7.42	-1.930	-5.62	-4.61	-5.64	-226.22	-1.42	-5.15	-4.17	-6.81
-3.5	10.6	1.01	9.29	-77.9	-0.388	-2.20	-2.25	-8.72	-6.69	-5.98	-4.59	-1.55	-3.98	-7.59	-1.854	-5.66	-4.61	-5.50	-275.73	-1.46	-5.15	-4.16	-6.69
-3.2243	10.6	1.01	9.30	-78.1	-0.391	-2.23	-2.27	-8.69	-6.66	-5.97	-4.58	-1.55	-3.98	-7.59	-1.671	-5.67	-4.61	-5.48	-281.43	-1.47	-5.15	-4.16	-6.66
-3	10.7	1.01	8.70	-78.2	-0.360	-2.98	-2.99	-8.73	-7.30	-6.56	-3.39	-1.55	-3.98	-6.64	-1.552	-5.08	-4.61	-4.26	-285.94	-1.55	-5.15	-4.24	-7.28
-2.9437	10.8	1.01	8.52	-78.2	-0.350	-3.19	-3.20	-8.74	-7.49	-6.74	-3.00	-1.55	-3.98	-6.25	-1.503	-4.89	-4.61	-3.87	-286.83	-1.57	-5.15	-4.25	-7.47
-2.5	11.3	1.01	8.51	-78.3	-0.354	-3.18	-3.19	-8.69	-7.44	-6.71	-3.01	-1.55	-3.98	-6.21	-1.061	-4.89	-4.61	-3.88	-289.15	-1.57	-5.14	-4.24	-7.41
-2.4463	11.4	1.01	8.51	-78.3	-0.354	-3.18	-3.19	-8.69	-7.43	-6.71	-3.01	-1.55	-3.98	-6.21	-1.011	-4.89	-4.61	-3.88	-289.53	-1.57	-5.14	-4.24	-7.41
-2.0969	12.5	1.01	8.51	-78.1	-0.358	-3.17	-3.18	-8.61	-7.33	-6.64	-3.03	-1.55	-3.97	-6.26	-0.736	-4.90	-4.61	-3.91	-294.93	-1.57	-5.14	-4.21	-7.31
-2	13.0	1.01	8.51	-78.0	-0.359	-3.17	-3.18	-8.58	-7.30	-6.61	-3.04	-1.55	-3.97	-6.27	-0.673	-4.90	-4.61	-3.92	-295.66	-1.57	-5.14	-4.20	-7.28
-1.7843	14.6	1.01	8.49	-77.6	-0.361	-3.14	-3.15	-8.51	-7.20	-6.53	-3.07	-1.54	-3.97	-6.31	-0.509	-4.90	-4.60	-3.96	-296.78	-1.56	-5.14	-4.17	-7.18
-1.7328	15.1	1.01	8.55	-77.5	-0.366	-3.03	-3.05	-8.49	-7.11	-6.44	-3.24	-1.54	-3.97	-6.46	-0.455	-4.97	-4.60	-4.14	-295.96	-1.55	-5.14	-4.16	-7.09
-1.5842	16.9	1.01	8.55	-77.9	-0.369	-2.98	-2.99	-8.41	-6.99	-6.33	-3.32	-1.54	-3.97	-6.53	-0.335	-4.98	-4.60	-4.23	-295.93	-1.54	-5.14	-4.12	-6.98
-1.5	18.3	1.01	8.56	-76.6	-0.372	-2.91	-2.92	-8.35	-6.90	-6.24	-3.42	-1.54	-3.97	-6.61	-0.261	-5.00	-4.60	-4.33	-295.43	-1.53	-5.13	-4.09	-6.88
-1.3833	20.7	1.01	8.56	-76.0	-0.377	-2.82	-2.83	-8.26	-6.75	-6.09	-3.55	-1.54	-3.96	-6.73	-0.156	-5.03	-4.60	-4.48	-294.41	-1.52	-5.13	-4.05	-6.74
-1.3799	20.8	1.01	8.57	-75.9	-0.378	-2.80	-2.82	-8.26	-6.74	-6.09	-3.57	-1.54	-3.96	-6.75	-0.152	-5.00	-4.60	-4.50	-293.91	-1.52	-5.13	-4.04	-6.73
-1.3684	21.1	1.01	8.59	-75.9	-0.379	-2.77	-2.78	-8.25	-6.70	-6.04	-3.62	-1.54	-3.96	-6.79	-0.140	-5.06	-4.60	-4.56	-293.98	-1.52	-5.13	-4.04	-6.69
-1.236	24.9	1.01	8.87	-74.8	-0.401	-2.24	-2.26	-8.12	-6.22	-5.55	-4.40	-1.53	-3.96	-7.40	0.010	-5.36	-4.59	-5.37	-286.28	-1.45	-5.13	-3.93	-6.21
-1.0598	32.1	1.01	8.66	-72.9	-0.400	-2.20	-2.21	-7.87	-6.06	-5.40	-4.35	-1.52	-3.95	-7.35	0.179	-5.22	-4.58	-5.36	-272.12	-1.44	-5.12	-3.83	-6.05
-1.0532	32.4	1.01	8.42	-72.4	-0.380	-1.46	-1.47	-7.97	-6.37	-5.59	-4.67	-1.52	-3.95	-6.70	0.195	-4.97	-4.58	-5.73	-91.37	-1.19	-5.12	-3.84	-6.36
-1.0122	34.6	1.01	8.35	-71.8	-0.379	-1.44	-1.45	-7.90	-6.34	-5.56	-4.65	-1.52	-3.94	-6.67	0.244	-4.92	-4.58	-5.72	-83.26	-1.17	-5.11	-3.81	-6.32
-1.0121	34.6	1.01	8.26	-71.8	-0.372	-1.44	-1.45	-7.92	-6.44	-5.66	-4.57	-1.52	-3.94	-6.50	0.244	-4.82	-4.58	-5.64	-61.16	-1.18	-5.11	-3.82	-6.43
-1	35.2	1.01	8.25	-71.6	-0.372	-1.43	-1.44	-7.89	-6.42	-5.64	-4.57	-1.51	-3.94	-6.51	0.258	-4.82	-4.58	-5.65	-61.56	-1.17	-5.11	-3.81	-6.40
-0.9258	39.9	1.01	8.18	-70.5	-0.376	-1.38	-1.38	-7.74	-6.26	-5.50	-4.60	-1.51	-3.94	-6.58	0.339	-4.79	-4.57	-5.71	-64.24	-1.14	-5.11	-3.74	-6.24
-0.5392	78.8	1.01	7.33	-62.0	-0.372	-999.00	-1.45	-6.47	-5.58	-5.43	-4.22	-1.45	-3.88	-6.28	0.765	-4.25	-4.52	-5.48	-63.27	-1.17	-5.05	-3.30	-5.52
-0.5	88.8	1.01	7.15	-60.0	-0.370	-999.00	-1.45	-6.16	-5.46	-5.61	-4.14	-1.46	-3.89	-6.21	0.665	-4.14	-4.52	-5.44	-63.82	-1.19	-5.06	-3.20	-5.38
-0.4356	101.3	1.06	6.94	-57.7	-0.368	-999.00	-1.45	-5.76	-5.32	-5.93	-4.05	-1.47	-3.89	-6.10	0.579	-4.02	-4.53	-5.39	-64.22	-1.21	-5.06	-3.08	-5.19
-0.2603	146.4	4.32	6.33	-50.4	-0.360	-999.00	-1.24	-4.65	-4.98	-6.31	-3.81	-1.52	-3.95	-5.69	0.072	-3.69	-4.58	-5.28	-65.90	-1.30	-5.12	-2.74	-4.49
-0.1518	185.0	11.23	6.18	-45.2	-0.376	-999.00	-0.84	-3.87	-4.59	-6.10	-4.06	-1.52	-3.95	-5.65	-0.203	-3.39	-4.59	-5.60	-66.00	-1.28	-5.12	-2.51	-3.79
-0.0143	250.0	39.78	6.08	-38.2	-0.411	-999.00	-0.15	-2.74	-4.21	-5.36	-4.23	-1.53	-3.95	-5.36	-0.078	-3.06	-4.59	-6.04	-66.00	-1.31	-5.12	-2.20	-2.72

Table 11b. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Lee et al.) at T = 250°C.
Log moles of product minerals.

Log zi	Albite	Calcite	Daphnite -14A	Dawsonite	Dolomite -ordered	Graphite	Kaolinite	Muscovite	Paragonite	Pyrite	Quartz	Siderite	Smectite-Reykjanes	Ca-Smectite	Na-smectite
-999					-4.075					0.223	1.22				
-8					-4.069			-6.178		0.223	1.22				
-7.0339					-4.022			-5.209		0.223	1.22				-7.010
-5.8928				-5.292	-3.665			-4.122		0.223	1.22				-4.273
-5.7406		1.18		-4.480	-3.570			-4.008		0.223	1.22				-4.109
-5.5		1.18		-3.950	-3.406			-3.821		0.223	1.22				-3.854
-5.2577		1.18		-3.708	-3.216		-0.412	-3.622		0.223	1.22				-3.596
-5.1235		1.18			-3.103		-0.412	-3.511		0.223	1.22				-3.452
-5.122		1.18			-3.103		-0.412	-3.510		0.223	1.22		-5.89		-3.451
-5		1.18			-3.017		-0.412	-3.410		0.223	1.22		-4.44		-3.333
-4.6865	-4.80	1.18			-2.724		-0.412	-3.136		0.223	1.22		-4.44		-2.946
-4.5	-3.03	1.18			-2.544		-0.413	-2.965		0.223	1.22		-4.44		-2.744
-4	-2.22	1.18			-2.081		-0.415	-2.485		0.223	1.22		-4.44		-2.210
-3.5	-2.24	1.18			-1.927		-0.414	-1.992		0.223	1.22		-4.44		-1.592
-3.2243		1.18			-1.921		-0.412	-1.718		0.223	1.22		-4.44		-1.279
-3		1.18			-1.783		-0.402	-1.494		0.223	1.22		-4.44		-1.085
-2.9437		1.18			-1.757		-0.398	-1.438		0.223	1.22		-4.44	-3.221	-1.038
-2.5		1.18			-1.465		-0.376	-0.995		0.223	1.21		-4.44	-0.961	-0.816
-2.4463		1.18	-3.002		-1.421		-0.372	-0.941		0.223	1.21		-4.44	-0.889	-0.781
-2.0969		1.18	-1.237		-1.076		-0.343	-0.592		0.223	1.21		-4.44	-0.683	-0.524
-2		1.18	-1.075		-0.998		-0.347	-0.495		0.223	1.21		-4.44	-0.811	-0.444
-1.7843		1.18	-0.788		-0.816		-0.359	-0.279		0.223	1.23		-4.44		-0.257
-1.7328		1.18	-0.761		-0.775		-0.365	-0.228		0.223	1.23		-4.44		-0.212
-1.5842		1.17	-0.570		-0.473		-0.505	-0.079		0.223	1.25		-4.44		-0.213
-1.5		1.17	-0.472		-0.338		-0.702	-0.025		0.223	1.26		-4.44		-0.213
-1.3833		1.17	-0.341		-0.171			0.057		0.223	1.28		-4.44		-0.215
-1.3799		1.17	-0.339		-0.167			0.059		0.223	1.28		-4.44		-0.215
-1.3684		1.17	-0.334		-0.154		-2.924	0.059		0.223	1.28		-4.44		-0.215
-1.236		1.16	-0.289		-0.007		-0.982	0.059	-2.755	0.223	1.30		-4.44		-0.228
-1.0598		1.14	-0.130		0.207		-0.758	0.059	-0.707	0.223	1.36		-4.44		
-1.0532		1.14	-0.127	-3.663	0.207		-0.647	0.059	-0.770	0.223	1.36		-4.44		
-1.0122		1.14	-0.106	-0.773	0.207		-0.330	0.059		0.223	1.37		-4.44		
-1.0121		1.14	-0.106	-0.772	0.207		-0.330	0.059		0.223	1.37	-5.097	-4.44		
-1		1.14	-0.105	-0.774	0.207		-0.300	0.059		0.223	1.37	-1.273	-4.44		
-0.9258		1.15	-0.119		0.207		-0.225	0.059	-0.784	0.223	1.39	-0.237	-4.44		

Table 11c. Reaction of Bearpaw Shale Groundwater and Pierre Shale (Lee et al.) at T = 250°C.
Log moles of destroyed reactants.

Log zi	Quartz	Illite	Pyrite	Plagioclase	Biotite	Ca-Smectite	Calcite	Kaolinite	Ripidolite -14a	Graphite	g^bDes^c	g^bCre^d	g^bNet	cm^{3a}Des^c	cm^{3a}Cre^d	cm^{3a}Net	Water:Rock Ratio
-999	-999	-999.000	-999	-999.000	-999.000	-999.000	-999.00	-999.00	-999.000	-999.000	0.000	1198	1198	0.000	377	377	
-8	-999	-6.699	-999	-6.699	-6.699	-6.699	-6.00	-6.70	-6.699	-6.398	0.001	1198	1198	0.000	377	377	1708525.542
-7.0339	-999	-5.733	-999	-5.733	-5.733	-5.733	-5.03	-5.73	-5.733	-5.432	0.005	1198	1198	0.001	377	377	184706.317
-5.8928	-999	-4.592	-999	-4.592	-4.592	-4.592	-3.89	-4.59	-4.592	-4.291	0.075	1198	1198	0.016	377	377	13347.571
-5.7406	-999	-4.440	-999	-4.440	-4.440	-4.440	-3.74	-4.44	-4.440	-4.139	0.106	2699	2699	0.023	931	931	9398.496
-5.5	-999	-4.199	-999	-4.199	-4.199	-4.199	-3.74	-4.20	-4.199	-3.898	0.172	2699	2699	0.036	931	931	5827.506
-5.2577	-999	-3.957	-999	-3.957	-3.957	-3.957	-3.74	-3.96	-3.957	-3.656	0.266	2799	2799	0.057	969	969	3492.840
-5.1235	-999	-3.823	-999	-3.823	-3.823	-3.823	-3.74	-3.96	-3.823	-3.521	0.373	2799	2799	0.072	969	969	2680.965
-5.122	-999	-3.821	-999	-3.821	-3.821	-3.821	-3.74	-3.96	-3.821	-3.520	0.374	2799	2799	0.072	969	969	2673.082
-5	-999	-3.699	-999	-3.699	-3.699	-3.699	-3.74	-3.96	-3.699	-3.398	0.480	2799	2799	0.090	969	969	2082.032
-4.6865	-999	-3.385	-999	-3.385	-3.385	-3.385	-3.74	-3.96	-3.385	-3.084	0.939	2800	2799	0.166	969	969	1064.736
-4.5	-999	-3.199	-999	-3.199	-3.199	-3.199	-3.74	-3.96	-3.199	-2.898	1.418	2801	2799	0.245	970	969	705.219
-4	-999	-2.699	-999	-2.699	-2.699	-2.699	-3.74	-3.96	-2.699	-2.398	4.382	2804	2799	0.736	970	969	228.206
-3.5	-999	-2.199	-999	-2.199	-2.199	-2.199	-3.74	-3.96	-2.199	-1.898	13.760	2814	2800	2.288	972	970	72.674
-3.2243	-999	-1.923	-999	-1.923	-1.923	-1.923	-3.74	-3.96	-1.923	-1.622	25.920	2826	2800	4.302	974	970	38.580
-3	-999	-1.699	-999	-1.699	-1.699	-1.699	-3.74	-3.96	-1.699	-1.398	43.400	2844	2801	7.198	978	971	23.041
-2.9437	-999	-1.643	-999	-1.643	-1.643	-1.643	-3.74	-3.96	-1.643	-1.342	49.400	2850	2801	8.191	979	971	20.243
-2.5	-999	-1.199	-999	-1.199	-1.199	-1.199	-3.74	-3.96	-1.199	-0.898	137.200	2939	2802	22.720	995	973	7.289
-2.4463	-999	-1.145	-999	-1.145	-1.145	-1.145	-3.74	-3.96	-1.145	-0.844	155.200	2958	2803	25.710	999	973	6.443
-2.0969	-999	-0.796	-999	-0.796	-0.796	-0.796	-3.74	-3.96	-0.796	-0.495	346.900	3152	2805	57.460	1042	985	2.883
-2	-999	-0.699	-999	-0.699	-0.699	-0.699	-3.74	-3.96	-0.796	-0.398	408.900	3216	2807	71.820	1060	988	2.446
-1.7843	-999	-0.483	-999	-0.483	-0.483	-0.483	-3.74	-3.96	-0.796	-0.182	608.100	3421	2813	118.000	1115	997	1.644
-1.7328	-999	-0.432	-999	-0.432	-0.432	-0.432	-3.74	-3.96	-0.796	-0.131	672.200	3487	2814	132.800	1131	998	1.488
-1.5842	-999	-0.283	-999	-0.432	-0.283	-0.283	-3.74	-3.96	-0.796	0.018	865.300	3682	2817	171.900	1179	1007	1.156
-1.5	-999	-0.283	-999	-0.432	-0.199	-0.199	-3.74	-3.96	-0.796	0.102	965.000	3783	2818	185.200	1198	1013	1.036
-1.3833	-999	-0.283	-999	-0.432	-0.082	-0.082	-3.74	-3.96	-0.796	0.219	1140.000	3960	2820	208.500	1232	1023	0.877
-1.3799	-999	-0.283	-999	-0.432	-0.079	-0.079	-3.74	-3.96	-0.796	0.222	1145.000	3966	2820	209.300	1233	1024	0.873
-1.3684	-999	-0.283	-999	-0.432	-0.079	-0.067	-3.74	-3.96	-0.796	0.234	1155.000	3975	2821	210.600	1235	1025	0.866
-1.236	-999	-0.283	-999	-0.432	-0.079	0.065	-3.74	-3.96	-0.796	0.366	1284.000	4111	2827	228.800	1266	1037	0.779
-1.0598	-999	-0.283	-999	-0.432	-0.079	0.241	-3.74	-3.96	-0.796	0.542	1529.000	4366	2837	263.400	1340	1077	0.654
-1.0532	-999	-0.283	-999	-0.432	-0.079	0.248	-3.74	-3.96	-0.796	0.549	1540.000	4377	2837	265.000	1343	1078	0.649
-1.0122	-999	-0.283	-999	-0.432	-0.079	0.289	-3.74	-3.96	-0.796	0.590	1614.000	4462	2848	275.400	1368	1093	0.620
-1.0121	-999	-0.283	-999	-0.432	-0.079	0.289	-3.74	-3.96	-0.796	0.590	1614.000	4462	2848	275.400	1368	1093	0.620
-1	-999	-0.283	-999	-0.432	-0.079	0.301	-3.74	-3.96	-0.796	0.602	1637.000	4487	2850	278.700	1375	1096	0.611
-0.9258	-999	-0.283	-999	-0.432	-0.079	0.375	-3.74	-3.96	-0.796	0.676	1794.000	4645	2851	300.900	1416	1115	0.557
-0.5592	-999	-0.283	-999	-0.432	-0.079	0.742	-3.74	-3.96	-0.796	1.043	3121.000	6410	3289	488.400	1794	1305	0.320
-0.5	-999	-0.283	-999	-0.432	-0.079	0.801	-3.74	-3.96	-0.796	1.043	3442.000	6728	3287	536.400	1852	1316	0.291
-0.4356	-999	-0.283	-999	-0.432	-0.079	0.865	-3.74	-3.96	-0.796	1.043	3844.000	7133	3290	596.600	1937	1340	0.260
-0.2603	-999	-0.283	-999	-0.432	-0.079	1.041	-3.74	-3.96	-0.796	1.043	5294.000	8507	3213	813.900	2166	1352	0.189
-0.1518	-999	-0.283	-999	-0.432	-0.079	1.149	-3.74	-3.96	-0.796	1.043	6534.000	9744	3210	999.700	2435	1435	0.153
-0.0143	-999	-0.283	-999	-0.432	-0.079	1.149	-3.74	-3.96	-0.796	1.043	6534.000	9721	3187	999.700	2416	1417	0.153

[1] cm3 = cubic centimeters
[2] g = grams
[3] Des = Destroyed
[4] Cre = Created

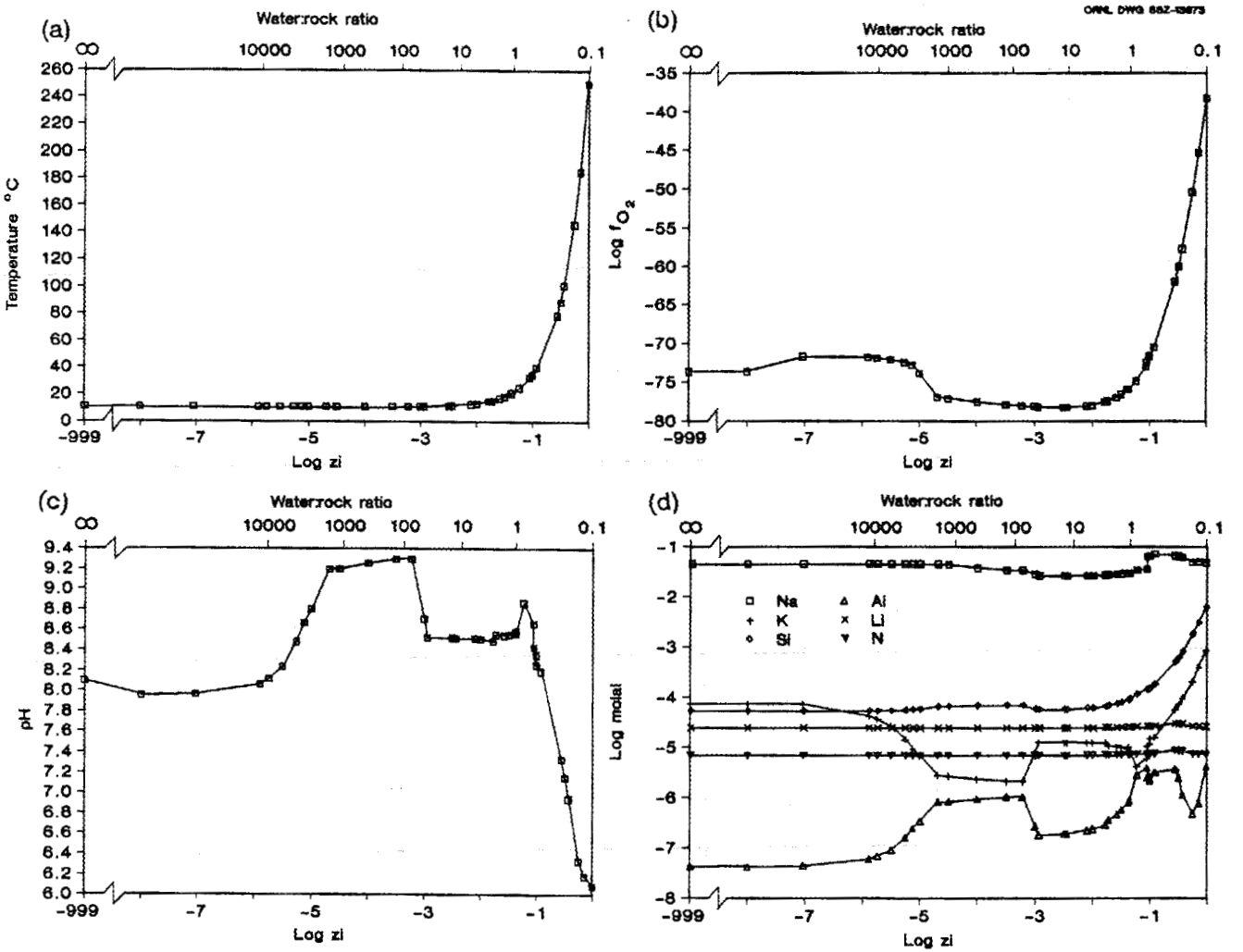

Fig. 8. Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) to T = 250°C: (a) Temperature, (b) Log f_{O_2}, (c) pH, (d) Na, K, Si, Al, Li, and N.

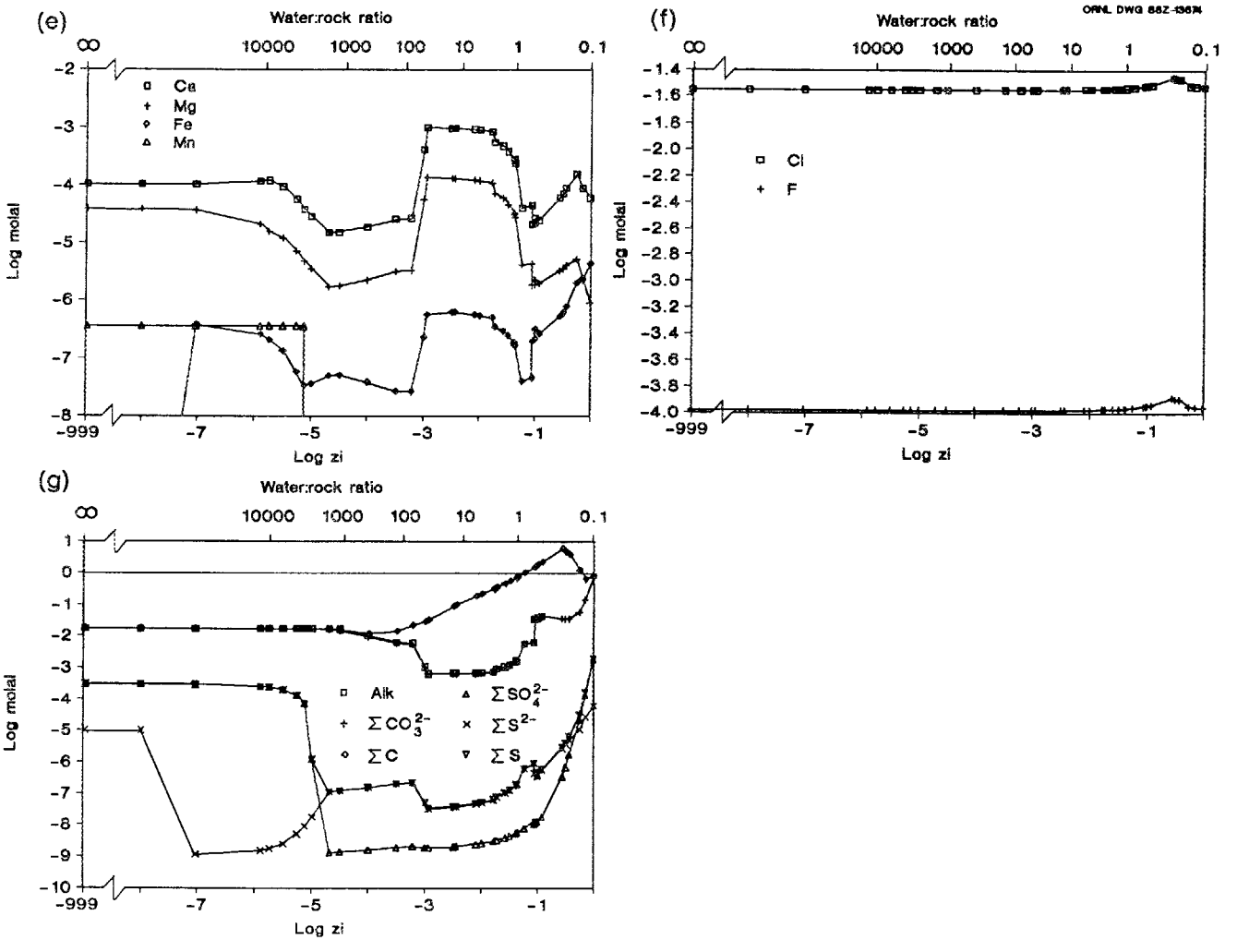

Fig. 8 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) to T = 250°C: (e) Ca, Mg, Fe, and Mn, (f) Cl and F, (g) Alkalinity, ΣCO_3^{2-}, ΣC, ΣSO_4^{2-}, ΣS^{2-}, and ΣS.

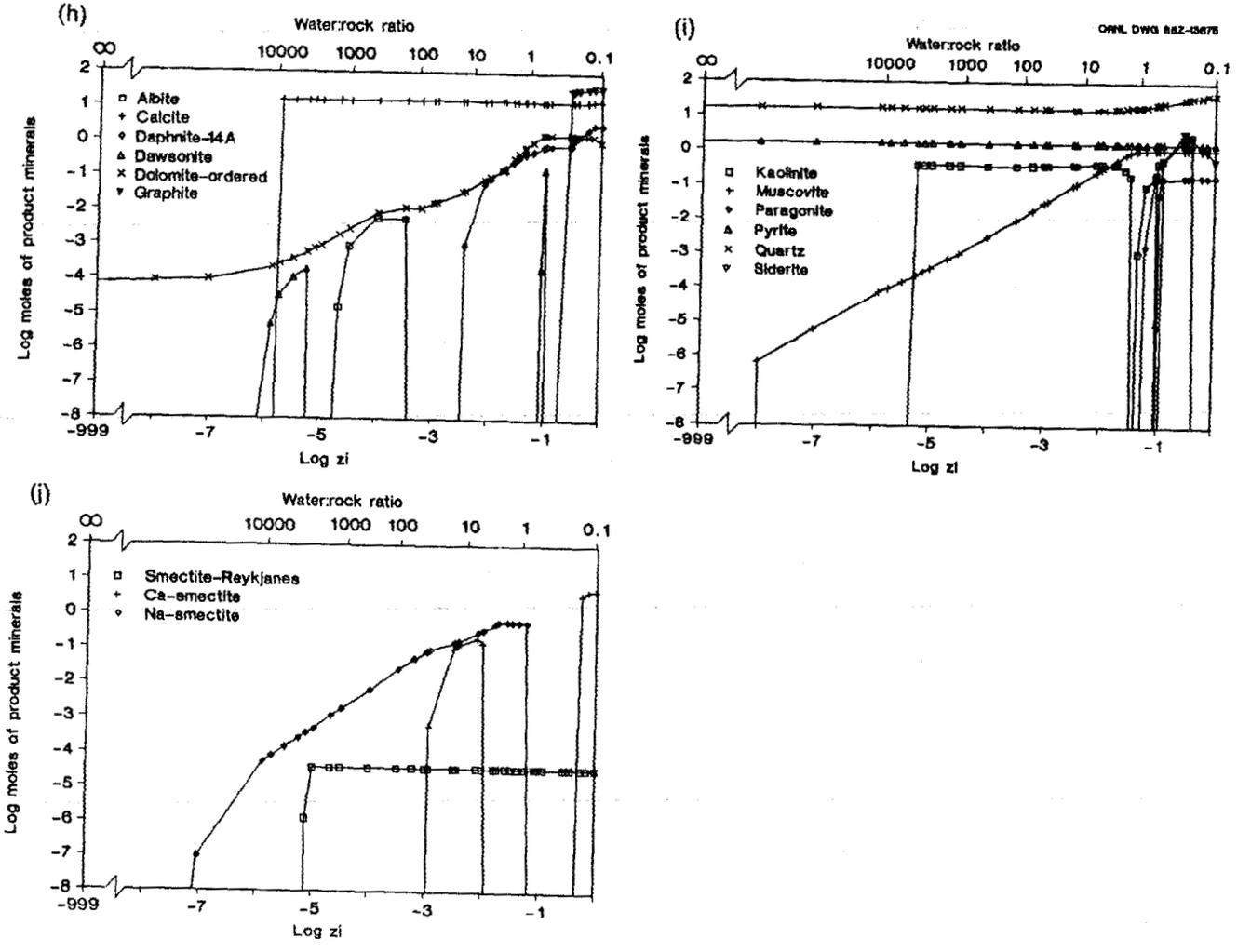

Fig. 8 (continued). Reaction of Bearpaw Shale water and Pierre Shale (Lee et al.) to T = 250°C: (h) product minerals 1, (i) product minerals 2, (j) product minerals 3.

DISCUSSION

Table 12 provides a summary of the composition of the aqueous phase at the end of the reaction progress, i.e., the final step from the previous tables, when the water:rock ratio reaches its minimum value. Table 13 provides a summary of the final equilibrium mineralogy. In general, regardless of mineralogy, total dissolved CO_3^{2-}, SO_4^{2-}, S^{2-}, Al and Si are higher in the elevated temperature cases than in the lower temperature cases. Graphite is present in the final equilibrium mineral assemblage for every higher temperature case, regardless of starting mineralogy, but is never present at lower temperature.

Comparison of Illitic Cases

In the two low temperature cases with pyrite present, significant CH_3COO^- is present in the case with CH_4 suppression. The presence or absence of CH_3COO^- is of particular interest as it is a potentially important ligand for metals, and may increase their transport in a repository setting. These results suggest it may be present in significant quantities (approaching molal concentrations), as the production of CH_4 is kinetically slow. This is a result that must be resolved by laboratory or field studies, as kinetics and organic matter speciation are not adequately addressed in EQ6.

The water in the 250°C case, compared to the 13.5°C case is more acidic, has higher total H_2S, carbonate, and F which suggests that it is a more aggressive solution and may be better able to transport metals as indicated by the higher Fe content. The main differences in the mineralogies are that albite is stable at the end of the 250°C experiment while fluorite, kaolinite, and laumontite are not. Laumontite is a potentially important phase to have present as it is a zeolite and these minerals are strong scavengers of many radionuclides. However, laumontite and, in addition, heulandite are stable at higher water:rock ratios at the higher temperature conditions. Hence their

Table 12. Summary of Log Molal Concentrations of Dissolved Elements for all Cases Examined, at Termination of Reaction Progress.

Case	Rock Type	Temp°C	Press (bars)	pH	Log f_{O_2}	Eh	Log alk	Log tot CO_3^{2-}	Log tot SO_4^{2-}	Log tot S^{2-}	Al	Br	Ca	Cl	F	Fe	C	K	Li	Mg	Mn	Na	N	Si	S	Sr	Water:Rock Ratio
1a	PVS	13.50	1.01	8.52	-81.0	-0.405	-3.56	-3.29	-7.78	-6.36	-6.48	-2.79	-2.79	-0.783	-0.275	-4.463	-5.94	-3.295	-4.80	-3.66	-408.956	-0.693		-4.20	-6.34	-3.91	0.157
1b	PVS	13.50	1.01	8.52	-78.7	-0.373	-4.43	-4.60	-8.32	-6.89	-6.48	-2.79	-2.79	-0.783	-0.274	-4.464	-6.01	-0.747	-4.80	-3.70	-0.693	-4.204		-6.88	-3.91	-3.89	0.156
2	PVS	249.98	39.76	5.46	-38.6	-0.355		-0.48	-2.68	-4.61	-4.08	-2.81	-2.81	-2.540	-0.299	-3.001	-2.96	-0.683	-2.02	-4.13	-156.679	-0.310		-2.26	-2.68	-3.72	0.156
3	PVS	13.50	1.01	8.44	-78.9	-0.370	-4.37	-4.49	-8.31	-6.97	-6.56	-2.77	-2.77	-0.810	-0.256	-4.449	-5.78	-0.215	-4.72	-3.52	-409.194	-0.609		-4.21	-6.95	-3.94	0.156
4	PVS	249.98	39.76	5.46	-38.5	-0.353		-0.46	-2.69	-4.62	-4.07	-2.81	-2.81	-2.550	-0.296	-2.998	-2.94	-0.244	-2.02	-4.12	-154.887	-0.307		-2.26	-2.68	-3.72	0.156
5	Pierre (Shultz)	10.50	1.01	8.59	-78.6	-0.358	-1.80	-1.81	-8.70	-7.37	-6.67		-5.50	-1.465	-3.893	-5.929	0.412	-4.95	-4.526	-4.02	-118.79	-1.301	-5.062	-4.25	-7.35		0.127
6	Pierre (Shultz)	250.00	39.78	6.10	-38.2	-0.413		-0.15	-2.74	-4.19	-5.35		-4.45	-1.563	-3.991	-5.431	-0.079	-3.08	-4.625	-5.89	-113.18	-1.321	-5.160	-2.20	-2.72		0.127
7	Pierre (Lee)	10.50	1.01	8.23	-79.2	-0.347	-1.99	-1.95	-8.50	-7.50	-7.00		-3.62	-1.867	-3.495	-5.068	1.722	-4.56	-4.129	-4.54	-9.73	-1.020	-4.664	-4.27	-7.46		0.146
8	Pierre (Lee)	250.00	39.78	6.08	-38.2	-0.411		-0.15	-2.74	-4.21	-5.36		-4.23	-1.526	-3.954	-5.363	-0.078	-3.06	-4.588	-6.04	-66.00	-1.308	-5.123	-2.20	-2.72		0.153

Table 13. Summary of Log Moles of Product Minerals for all Cases Examined, at Termination of Reaction Process.

Case	Rock Type	Albite	Calcite	Daphnite-14A	Dawsonite	Dolomite-ordered	Fluorite	Kaolinite	Laumontite	Graphite	Muscovite	Paragonite	Pyrite	Quartz	Siderite	Smectite-Reykjanes	Strontianite	Ca-smectite	Na-smectite	Water:Rock Ratio
1a	PVS		1.000	-0.531		*	-3.28	0.432	-3.80		0.9768	0.2034	-0.0747	1.64		-2.22	-2.89	0.3871	*	0.156
1b	PVS		0.991			*	-3.28	0.417	-1.52		0.9768	0.2034	-0.0747	1.62		-2.22	-2.89	0.5279	*	0.156
2	PVS	0.105	0.975	-0.823		*	*	*	*	-0.745	0.9764	*	-0.0752	1.55		-2.22	-2.92	0.827	*	0.156
3	PVS		1.010			*	-3.28	0.585			0.9768	-0.073	-2.0936	1.62		-2.22	-2.89	0.0528	0.338	0.156
4	PVS	0.105	0.966	-0.827		-0.6808	*	*		-0.270	0.9764	*	-2.1589	1.55		-2.22	-2.92	0.8234	*	0.156
5	Pierre (Shultz)		*	0.130	-0.427	0.2898		0.834			0.7086	*	-0.2957	1.81	-0.531	-4.44			0.316	0.127
6	Pierre (Shultz)	*	*	0.245	*	0.0015		*		0.533	0.7085	0.0205	-0.2967	1.78	-0.389	-4.44		0.7581	*	0.127
7	Pierre (Lee)	*	1.201	-0.701	*	0.2071		0.946			0.0594	*	0.2228	1.73	1.232	-4.44		*	*	0.146
8	Pierre (Lee)	*	1.192	0.498	*	0.0362		*		1.575	0.0591	-0.7354	0.2225	1.63	-0.267	-4.44		0.7162	*	0.153

[a]Celestite, hematite, and pyrolusite are also present during the reaction progress, but are absent from the final equilibrium mineral assemblage in Cases 1a, 1b, 2, 3 and 4. Heulandite is present during the reaction progress, but is absent from the final equilibrium mineral assemblage in Cases 2 and 4. Mg-beidellite is present during the reaction progress, but is absent from the final equilibrium mineral assemblage in Case 6.

[b]*=mineral is present during the reaction progress, but is absent from the final equilibrium mineral assemblage.

presence or absence is not a simple function of temperature but a complex combination of temperature and water:rock ratio.

A comparison of the lower temperature cases, with graphite replacing pyrite shows that the waters are similar in almost all properties including pH and log f_{O_2}. Total C is significantly higher in the graphitic case than in the lower temperature pyritic case with CH_4 suppressed, but is lower than the pyritic case in which CH_4 is permitted. The mineralogy shows additional differences, Na-smectite being present in the graphitic case, but absent in the two low temperature pyritic cases, 14A-daphnite being present only in the pyritic case with CH_4 suppression, and laumontite being absent in the graphitic case.

A comparison of the lower to higher temperature graphitic case shows that the waters are more acidic, and have higher total carbonate, total SO_4^{2-}, total H_2S, Al, Fe, K, Na, Si, and lower Ca, and F, in the higher temperature case. Minerals present in the final assemblage in the high temperature case that are absent in the final mineral assemblage from the low temperature case are albite, 14A-daphnite, ordered dolomite, and graphite (albite and graphite are never part of the lower temperature equilibrium mineral assemblage) while fluorite, kaolinite, paragonite, and Na-smectite are all present at higher water:rock ratios in the higher temperature case but are not present at the end of the experiment as they are in the lower temperature case.

A comparison of the higher temperature pyritic to graphitic case shows that all the dissolved species, including the pH and log f_{O_2}, are almost identical, with a small additional amount of C being present in the graphitic case.

These results show that while the presence of a very reduced mineral has an important influence on the chemistry of the system, quickly creating reducing conditions in the groundwaters, the form of the mineral itself, at least for the case of pyrite versus graphite, is not very important to the overall chemistry of the groundwaters. The temperature will however play an extremely important role in determining pH and other properties in the groundwaters. The mineralogy observed throughout the reaction progress is quite similar with the exception of a few phases, but the final mineral assemblage at

the same water:rock ratio differs for the two temperature cases. This is especially apparent for some of the zeolitic phases, which are of particular usefulness in retarding radionuclide transport.

Comparison of Smectitic Cases

A comparison of the low temperature to the high temperature case based on the Schultz et al. (1980) mineralogy shows that both waters are alkaline and reducing, and that the higher temperature waters have higher total carbonate, total SO_4^{2-}, total H_2S, Al, Ca, Fe, K, Li, N, and Si, and lower Cl, C, F, and Mg. The final equilibrium mineral assemblage in the higher temperature case includes graphite, paragonite, and Ca-smectite which are not stable at the end of the lower temperature reaction, but does not include dawsonite and kaolinite, which are stable for the lower temperature case. It is unclear if the higher temperature case would be more effective at transporting radionuclides.

A comparison of the lower temperature to the higher temperature case based on the Lee et al. (1987) mineralogy shows that both groundwaters are again alkaline and reducing, with the higher temperature case having higher total carbonate, total SO_4^{2-}, total H_2S, Al, K, and Si, and lower Ca, Cl, F, Fe, C, Li, Mg, Mn, Na, and N. In the higher temperature case the final equilibrium mineral assemblage contains graphite, paragonite, and Ca-smectite which are not present in the final assemblage at the lower temperature; but kaolinite which is present at the lower temperatures is absent from the higher temperature final assemblage.

A comparison of the two low temperature cases shows that both are alkaline and reducing, while the Schultz et al. (1980) mineralogy results in more Al, and Mg in solution and less Ca, Cl, F, Fe, C, K, Li, Mn (a very large amount less), Na, and N. Regarding the final mineralogy the Schultz et al. (1980) case has dawsonite and Na-smectite

but is lacking calcite compared to the Lee et al. (1987) case. Different phases are also present during the reaction progress.

A comparison of the two higher temperature cases shows that the two cases are similar in most dissolved species including pH and log f_{O_2}, while the Schultz et al. (1980) case has higher C, and Mg, and lower Ca, and Mn. In general these differences are quite small. The only difference in the final mineral assemblages is the presence of calcite in the Lee et al. (1987) case. This suggests that the mineralogy observed by Lee et al. (1987) would have more buffering capacity and would therefore be able to keep the groundwaters more alkaline in the case of oxidation reactions. The Lee et al. (1987) mineralogy does initially contain much more calcite than that observed by Schultz et al. (1980) (Table 7).

Comparison of Illitic to Smectitic Cases

A potential advantage of the illitic mineralogy is the predicted formation of zeolites during the reaction progress which may help to remove radionuclides from the groundwaters. A significant disadvantage of the illitic cases, however, is that the groundwaters appear to become acid at elevated temperatures while the smectitic cases do not. This may be a result of several differences between the two cases: (1) the illitic groundwaters used in the calculations were acidic initially while the smectitic ones were initially alkaline, and (2) the illitic waters were initially oxic which resulted in the oxidation of reducing minerals and the production of protons, while the smectitic waters were initially reducing. Calcite, which can be an important mineral for buffering the pH, was present in the final mineral assemblage of the high temperature illitic cases. In spite of this, the pH of the groundwaters remained acid, demonstrating that an acid pH is not simply the result of the consumption of all the calcite. Calcite also exerts an important mineralogical control on the carbon speciation in the waters. The total carbonate is limited by calcite solubility, which is a function of pH. Dawsonite, siderite, and dolomite are other carbonate minerals present in some cases but are usually not as abundant as calcite. Total carbonate in solution can continue to decrease, after the initial saturation with calcite is

reached, due to additional input of calcium to the dissolved phase. Once calcite saturation is reached, increases in the total carbon present in solution (which are not accompanied by decreases in calcium) are a result of increasing non-carbonate carbon (e.g., CH_4, CH_3COOH).

Illite never appears in a final equilibrium mineral assemblage but muscovite is present in every case. Illite and muscovite are quite similar and muscovite may be serving as a proxy for illite as a result of thermodynamic limitations. Illite is another mineral phase which can be important in sorbing radionuclides. The concentration of potassium in solution is not a simple function of the conversion of smectite to illite or muscovite, but appears to also be related to the temperature and pH. Dissolved potassium is higher in all of the illitic cases than in the smectitic cases.

Smectites were also included in all the final mineral assemblages, although the type varied between Reykjanes-, Ca-, and Na-smectite or a combination of them. The thermodynamic data for Reykjanes smectite is highly uncertain and is based on the hydrothermal alteration of basalt; hence, it is probably unlikely to form in a sedimentary system. The Na-smectite will swell more and hence has better physical properties for aiding the isolation of waste and is probably also a better sorber or ion exchanger than the Ca form (Deer et al. 1966). Na-smectites are present in the final mineral assemblage only in the illitic, graphitic, low temperature case and in both the high and low temperature smectitic cases based on the mineralogy of Schultz et al. (1980). Na-smectites are, however, found in all cases during some part of the reaction progress, usually at somewhat higher water:rock ratios. Smectites can also be important sorbers of radionuclides and other ions and have been suggested as backfill material for an HLW repository.

Dawsonite and siderite are present in every smectitic case, but never appear in the illitic cases, although the species required for their formation are present. Laumontite and heulandite (zeolites) are only present in the illitic cases. In addition, fluorite, strontianite, celestite, hematite and pyrolusite are only present in the illitic cases but their absence from the smectitic cases is a result either of the needed species not being present or of the initial oxidizing conditions.

CONCLUSIONS

The model calculations conducted suggest that there may be important differences in the final groundwater compositions and equilibrium mineral assemblages depending on the starting mineral, whether illitic or smectitic. There are advantages and disadvantages to both, hence neither appears to have a distinct advantage on the basis of this study. The results suggest that although the presence of a reducing mineral, in even very small amounts, is important in controlling the redox state of the groundwaters, its form (e.g., graphite or pyrite) does not appear to be of major importance. An uncertainty in the "alteration" of the organic matter exists that cannot be resolved with a modeling approach related to the formation (or lack thereof) of CH_4, CH_3COOH, and other organic species. These observations relating to reducing minerals and organic speciation also relate to the use of carbonaceous shales, which were not specifically modeled in this study. The presence or absence of carbonate minerals was shown to have an important effect on buffering the pH in the experimental study of Von Damm and Johnson (1987). Their system was, however, oxidizing. In the model cases where the groundwaters remain reducing, the importance of carbonate minerals in buffering the pH is less clear. Calcite concentrations varied among the starting mineralogies, but the final pHs show no clear relationship to the starting concentrations or the abundance of carbonate mineral at the termination of the modeling experiments. Finally, elevated temperatures are shown to have a potentially large effect on the solution chemistry, although they tend to reduce the observed differences in final mineralogies created from different initial mineral assemblages.

Further work may include (1) modeling of similar ionic strength solutions in both illitic and smectitic mineralogies to see if and how this parameter changes in a relative sense, (2) modeling of groundwaters which have the same and varying initial redox states to evaluate how this parameter may effect the final pH, (3) modeling of groundwaters with varying initial pH's to see how this effects the final pH, (4) addition of large amounts of calcite to further examine

its potential as a pH buffer, (5) suppression of unlikely mineral phases such as muscovite and Reykjanes smectite in an attempt to produce the (probably) more realistic illite and Ca- and Na-smectites, respectively, (6) use of the open system option to better represent reactions along a groundwater flow path, (7) inclusion of radionuclide species of interest, where reliable thermodynamic data are available, to better assess their behavior under a variety of conditions, and (8) experimental validation of the model results.

ACKNOWLEDGMENTS

This work was supported by the Sedimentary Rock Program (SERP) through the Repository Technology Program, Office of Civilian Radioactive Waste Management (OCRWM), U.S. Department of Energy. A. J. VandenBrook was a participant in the Oak Ridge Associated Universities Professional Internship Program. This report was improved by reviews by P. M. Baxter, G. K. Jacobs, and C. R. Olsen. T. Prandini prepared the tables.

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APPENDIX A
MINERAL NAMES AND CHEMICAL FORMULAS

Mineral names and their chemical formulas as included in the EQ3NR/EQ6 data base, in alphabetical order.

NAME	FORMULA	COMMENTS
Albite	$NaAlSi_3O_8$	
Anorthite	$CaAl_2Si_2O_8$	
Mg-beidellite	$Mg_{.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	
Biotite		solid solution
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	
Pd-oxyannite	$KFe_3AlSi_3O_{12}H_{-1}$	
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	
Calcite	$CaCO_3$	
Celestite	$SrSO_4$	
Na-clinoptilolite	$Na_2Al_2Si_{10}O_{24}\bullet 8H_2O$	
Cristobalite	SiO_2	
14A-daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$	a chlorite
Dawsonite	$NaAlCO_3(OH)_2$	
Ordered dolomite	$CaMg(CO_3)_2$	
K-feldspar	$KAlSi_3O_8$	
Fluorite	$CaF_2(c)$	
Graphite	C	
Hematite	Fe_2O_3	
Heulandite	$CaAl_2Si_7O_{18}\bullet 6H_2O$	a zeolite
Illite	$K_{.6}Mg_{.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	
Kaolinite	$Al_2Si_2O_5(OH)_4$	
Laumontite	$CaAl_2Si_4O_{12}\bullet 4H_2O$	a zeolite
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	
Paragonite	$NaAl_3Si_3O_{10}(OH)_2$	
Plagioclase		solid solution
Albite	$NaAlSi_3O_8$	
Anorthite	$CaAl_2Si_2O_8$	
Pyrite	FeS_2	
Pyrolusite	MnO_2	
Quartz	SiO_2	
14A-ripidolite	$MgFe_3Al_2Si_3O_{10}(OH)_8$	
Siderite	$FeCO_3(c)$	
Ca-smectite		solid solution
Ca-beidellite	$Ca_{.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	
Ca-nontronite	$Ca_{.165}Fe_2Al_{.33}Si_{3.67}O_{10}(OH)_2$	
Ca-saponite	$Ca_{.165}Mg_3Al_{.33}Si_{3.67}O_{10}(OH)_2$	
Na-smectite		solid solution
Na-beidellite	$Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	
Na-nontronite	$Na_{.33}Fe_2Al_{.33}Si_{3.67}O_{10}(OH)_2$	
Na-saponite	$Na_{.33}Mg_3Al_{.33}Si_{3.67}O_{10}(OH)_2$	
Reykjanes-smectite	$Fe_{.68}Na_{.33}Mn_{.01}K_{.3}Ca_{.66}Mg_{1.29}Al_{1.11}Si_{3.17}O_{10}(OH)_2$	
Strontianite	$SrCO_3$	

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