

K.L. Von Damm
 Environmental Sciences Division
 Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

ABSTRACT: The chemistry of groundwaters is one of the most important parameters in determining the mobility of species within a rock formation. A three pronged approach was used to determine the composition of, and geochemical controls, on groundwaters specifically within shale formations: (1) available data were collected from the literature, the U. S. Geological Survey WATSTORE data base, and field sampling, (2) the geochemical modeling code EQ3/6 was used to simulate interaction of various shales and groundwaters, and (3) several types of shale were reacted with synthetic groundwaters in the laboratory. The comparison of model results to field and laboratory data provide a means of validating the models, as well as a means of deconvoluting complex field interactions. Results suggest that groundwaters in shales have a wide range in composition and are primarily of the Na-Cl-HCO₃- type. The constancy of the Na:Cl (molar) ratio at 1:1 and the Ca:Mg ratio from 3:1 to 1:1 suggests the importance of halite and carbonates in controlling groundwater compositions. In agreement with the reaction path modeling, most of the groundwaters are neutral to slightly alkaline at low temperatures. Model and experimental results suggest that reaction (1) at elevated temperatures, or (2) in the presence of oxygen will lead to more acidic conditions. Some acetate was found to be produced in the experiments; depending on the constraints applied, large amounts of acetate were produced in the model results.

1 INTRODUCTION

Although groundwaters comprise a relatively small volumetric proportion of the hydrologic reservoir, they are a particularly important component for several reasons. (1) The large rock:water ratio and often long residence time of water in these subsurface systems provide conditions which are favorable for extensive reaction between the rocks and waters, which may cause large changes in the chemistry of the waters.

Groundwaters often contain much larger concentrations of solutes than river waters. (2) Recent estimates (COSOD II, 1987) suggest that direct groundwater input from the continents to the oceans may be larger than previously believed, and may thus influence not only the continental but also the oceanic environment.

(3) Subsurface disposal of wastes has become a common practice and the groundwater chemistry is a critical factor in the migration of contaminant species. It is therefore important to understand the geochemical controls on the chemistry of groundwaters.

One of the problems in understanding groundwater chemistry has been the relative inaccessibility of these systems and the sampling artifacts associated with the collection of data. To overcome some of these problems we took a three pronged approach: (1) collection of reported data from the literature, the U. S. Geological Survey's WATSTORE data base of groundwater data, and some field sampling on the Oak Ridge Reservation, (2) experimental interaction of rock with synthetic groundwater in the laboratory, and

(3) use of the geochemical modeling code EQ3/6 (Wolery, 1983) to simulate the interaction of various groundwater and rock compositions. The three approaches are complementary, and help to identify deficiencies in all three individual approaches. Use of EQ3/6 to model systems where both the groundwater and rock compositions are known provides a means of validating the code, thereby increasing its utility in the study of other systems.

In this particular study we concentrated on groundwaters from shale formations. Shales have a wide range in composition, but for this study were divided into four idealized endmember compositions: illitic, smectitic, organic matter rich, and carbonate rich. Although shales are probably the single most abundant rock type on the continents, few data have been reported for the chemistry of their groundwaters as shales are generally deemed to be relatively impermeable and contain little water. For this reason shales have been, and are being considered as host formations for various wastes. Increasing awareness of the importance of fracture flow in the subsurface suggests that shales are not as impermeable as was once thought, requiring an improved understanding of the groundwaters in these systems.

2 RESULTS

Although much has been written regarding the controls on shale groundwater composition (Graf et al., 1966;

by either probable chemical artifacts (e.g., sulfide oxidation) or poor identification of the source formation. Many of the papers discuss a model in which shales, particularly in shale-sandstone sequences, are thought to behave as semipermeable membranes, preferentially retarding certain chemical species.

2.1 WATSTORE data

Due to the paucity of published data, the U.S. Geological Survey WATSTORE (national WATER data STORAGE and RETRIEVAL system) data base was used to obtain most of the data on shale groundwater chemistry for this study. WATSTORE contains chemical data for groundwaters in the United States from specific wells, which can be retrieved on a formation specific basis. Limitations of this approach include: (1) detailed sampling information is not available (e.g., whether a packer was used), (2) the exact depth of sampling is not always given, (3) no data were obtained for interlayered shale-sandstone sequences, and (4) all chemical species of interest are not always reported. An advantage of this approach is that a large amount of high quality chemical data are available. Even though interpretation of depth related trends is limited, the large amount of chemical data for a variety of shale formations provides for the first time a general insight into the geochemical processes occurring in shale formations.

From the several thousand analyses recovered from WATSTORE, the data were edited to include only those which (1) were from greater than 61 m (200 ft) to avoid recent meteoric influence, (2) included a complete set of major element analyses, and (3) had a reported charge imbalance of less than 20% (in fact, most were better than 5%). Table 1 summarizes the data obtained for shale formations. Some of the differences in groundwater chemistries between different formations may reflect reactions with differing mineralogies as, for example, the Green River Shale is more carbonate-rich and relatively clay-poor compared to the others.

Based on the data obtained from WATSTORE, several general statements can be made regarding the chemistry of groundwaters within shale formations. (1) Most of these waters are of the Na-Cl-HCO₃- type, and secondarily Na-HCO₃-Cl, rather than sulfate-rich as was suggested in several previous studies (Schmidt, 1973). (2) Shale waters are not limited to being relatively dilute as previously suggested, but rather cover a wide range in total ionic strength. (3) The Na:Cl (molar) ratio is close to 1:1 suggesting halite as the major source of these two elements and that the abundance of halite in these formations is greater than previously recognized. (4) The Ca:Mg (molar) ratio is within the range 3:1 to 1:1, suggesting a carbonate source. However, in some samples from the Green River Shale formation, which contains many unusual carbonate minerals, Mg>Ca. (5) Within the constraints of the limited depth data, no depth related trends emerge. (6) The explanation of the observed data does not require invoking shale membrane filtration.

2.2 Experimental data

Experimental interaction of various shale mineralogies with synthetic groundwaters provides a means of gaining additional insights into the reactions occurring in the actual groundwater systems, as well as a way of examining expected conditions that do not presently occur, and obtaining data on species of interest (e.g., dissolved organics, redox couples) not reported by other workers. To date only a few preliminary experiments have reacted illitic, smectitic, organic matter and pyrite rich, and carbonate rich shales with distilled water at room temperature and 100°C (Von Damm and Johnson, 1987). In contrast to the WATSTORE results, the dominant anion in the experimental solutions was sulfate. This result suggests that the efforts to limit oxygen in the experiments were inadequate and that significant oxidation of pyrite,

Table 1. Summary of groundwater data obtained from WATSTORE.

	Gulf Coast	Pierre & Bearpaw	Green River	Mid-Continent
Maximum Depth (m)	1834.9	701.0	3627.1	1895.9
Number of Samples	114	54	249	5
pH	5.9 - 9.4	7.0 - 8.7	7.3 - 10.9	7.2 - 7.7
Ca ¹	0.0250 - 49.9	0.0973 - 17.2	0.0175 - 37.4	0.125 - 15.2
Mg	0.00823 - 23.0	0.0535 - 6.58	0.00823 - 15.2	0.946 - 3.25
Na	0.0783 - 3175	2.74 - 783	3.39 - 870	0.409 - 65.2
K	0.00512 - 6.65	0.0512 - 5.63	0.00767 - 8.95	0.0332 - 1.59
Cl	0.0197 - 3385	0.166 - 790	0.0310 - 959	0.220 - 5.36
Alkalinity	0.0300 - 23.6	5.89 - 20.0	2.88 - 304	2.20 - 6.15
SO ₄	0.00208 - 27.1	0.00833 - 20.8	0.0312 - 56.2	0.0687 - 30.2
SiO ₂	0.00333 - 0.932	0.0666 - 0.716	0.0383 - 0.466	0.200 - 0.216

¹All units are mmoles/l except alkalinity which is meq/l.

present in at least trace amounts in most of the shales, occurred especially at 100°C where the solutions also went quite acid (25°C pH as low as 3.4). Only those shales containing a significant amount of carbonate did not produce acid waters. Several of the waters produced in the 100°C experiments contained measurable acetate (~100 umoles/l), however the highest acetate concentrations did not correlate strictly with the percent organic carbon in the starting shale.

2.3 Modeling results

The geochemical modeling code EQ3/6 was used to simulate reaction of various types of shale with groundwaters of appropriate composition. Reaction path modeling was limited to an illitic shale (typified by the Pumpkin Valley Shale, Oak Ridge, Tennessee, USA) and a smectitic shale (typified by the Pierre Shale, North and South Dakota, USA), as the thermodynamic data base does not contain many organic species which would be important in an organic rich shale such as the Chattanooga Shale (Tennessee, USA), or many of the unusual carbonate minerals found in the Green River Shale (Utah, USA). The initial focus of the modeling was to use an observed mineral and groundwater composition for the Pumpkin Valley and Pierre Shales, to let them react to equilibrium at a very low water:rock mass ratio at their observed temperatures (<15°C), and to see how different the predicted water composition and mineralogy was from the starting values. Observed differences between the model results and the field data could be the result of (1) sampling artifacts and hence incorrect field data, (2) errors in the model, primarily as inaccuracies or omissions of important species in the thermodynamic data base, or (3) lack of attainment of equilibrium between the groundwater and rock in the field setting. In general, the agreement between the observed and model predicted mineralogies is quite good, and the agreement for many of the aqueous species is good as well (Von Damm and VandenBrook, 1988).

Besides the model simulations which replicated observed field conditions as much as possible, simulations were also done with the formation of methane suppressed, the inclusion of graphite as a proxy for organic matter, and with the temperature increased to 250°C to simulate conditions relevant to radioactive waste disposal and hydrothermal systems. Although these results have not yet been verified by experimental data they suggest several interesting results. (1) Even a very small amount of a reducing mineral (e.g., 1 wt. % pyrite) has a large influence on the redox state of the groundwaters. (2) Aside from small differences in the dissolved concentrations of C, Fe, and S the replacement of pyrite by graphite produces essentially the same results. (3) When methane is suppressed, the next most reduced carbon species which can form is acetate, based on what is available in the thermodynamic data base. The amounts formed are similar to the experimental values and are in agreement with the recent hypothesis and data presented by Shock

the illitic shales produced acid waters and zeolites, while the smectitic cases remained alkaline. These results need to be examined further in light of the initial conditions of the model runs.

3 CONCLUSIONS

Three complementary approaches using available field data, laboratory experiments and computer simulation of rock-water interaction have been used to elucidate controls on groundwater chemistry, as applied specifically to shale formations. Each approach has its limitations, but taken together they can help to decipher the geochemical processes occurring in these systems. Groundwaters in shales are strongly influenced by the presence of the minerals halite, carbonates, and pyrite or other reduced phases such as organic matter. Experimental results strongly suggest that the sulfate-rich waters suggested by previous workers as typical of shales are probably experimental artifacts. Where comparable, the model simulations give similar results to the field data. Additional experimental work is needed to validate the model results under other conditions of interest, such as higher temperatures, and to better understand the role of various organic species which cannot be adequately modeled at the present time.

ACKNOWLEDGMENTS

This work was supported by the Geoscience Technology Support Program, Oak Ridge National Laboratory, through the Repository Technology Program, Office of Civilian Radioactive Waste Management, U.S. Department of Energy. Contribution number 3297 from the Environmental Sciences Division, Oak Ridge National Laboratory, which is operated by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400 from the U.S. Department of Energy.

REFERENCES

- Carpenter, A.B. 1978. Origin and chemical evolution of brines in sedimentary basins. *Oklahoma Geol. Surv. Circ.* 79:60-77.
- COSOD II (Report of the Second Conference on Scientific Ocean Drilling) 1987. Strasbourg, 6-8 July 1987. European Science Foundation and Joint Oceanographic Institutions for Deep Earth Sampling.
- Graf, D.L. 1982. Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. *Geochim. Cosmochim. Acta* 46:1431-1448.
- Graf, D.L., W.F. Meents, I. Friedman, & N.F. Shrimp 1966. The origin of saline formation waters, III: calcium chloride waters. *Illinois State Geol. Surv. Circ.* 397:1-58.
- Hitchon, B., G.K. Billings, & J.E. Klován 1971. Geochemistry and origin of formation waters in the

The geochemical modeling code EQ3/6 was used to simulate reaction of various types of shale with groundwaters of appropriate composition. Reaction path modeling was limited to an illitic shale (typified by the Pumpkin Valley Shale, Oak Ridge, Tennessee, USA) and a smectitic shale (typified by the Pierre Shale, North and South Dakota, USA), as the thermodynamic data base does not contain many organic species which would be important in an organic rich shale such as the Chattanooga Shale (Tennessee, USA), or many of the unusual carbonate minerals found in the Green River Shale (Utah, USA). The initial focus of the modeling was to use an observed mineral and groundwater composition for the Pumpkin Valley and Pierre Shales, to let them react to equilibrium at a very low water:rock mass ratio at their observed temperatures (<15°C), and to see how different the predicted water composition and mineralogy was from the starting values. Observed differences between the model results and the field data could be the result of (1) sampling artifacts and hence incorrect field data, (2) errors in the model, primarily as inaccuracies or omissions of important species in the thermodynamic data base, or (3) lack of attainment of equilibrium between the groundwater and rock in the field setting. In general, the agreement between the observed and model predicted mineralogies is quite good, and the agreement for many of the aqueous species is good as well (Von Damm and VandenBrook, 1988).

Besides the model simulations which replicated observed field conditions as much as possible, simulations were also done with the formation of methane suppressed, the inclusion of graphite as a proxy for organic matter, and with the temperature increased to 250°C to simulate conditions relevant to radioactive waste disposal and hydrothermal systems. Although these results have not yet been verified by experimental data they suggest several interesting results. (1) Even a very small amount of a reducing mineral (e.g., 1 wt. % pyrite) has a large influence on the redox state of the groundwaters. (2) Aside from small differences in the dissolved concentrations of C, Fe, and S the replacement of pyrite by graphite produces essentially the same results. (3) When methane is suppressed, the next most reduced carbon species which can form is acetate, based on what is available in the thermodynamic data base. The amounts formed are similar to the experimental values and are in agreement with the recent hypothesis and data presented by Shock (1988) that suggests the stable form of organic acids (e.g., acetate) in a sedimentary system may be in redox equilibrium with carbon dioxide rather than with methane. (4) At elevated temperatures reactions with

specimens to shale formations. Each approach has its limitations, but taken together they can help to decipher the geochemical processes occurring in these systems. Groundwaters in shales are strongly influenced by the presence of the minerals halite, carbonates, and pyrite or other reduced phases such as organic matter. Experimental results strongly suggest that the sulfate-rich waters suggested by previous workers as typical of shales are probably experimental artifacts. Where comparable, the model simulations give similar results to the field data. Additional experimental work is needed to validate the model results under other conditions of interest, such as higher temperatures, and to better understand the role of various organic species which cannot be adequately modeled at the present time.

ACKNOWLEDGMENTS

This work was supported by the Geoscience Technology Support Program, Oak Ridge National Laboratory, through the Repository Technology Program, Office of Civilian Radioactive Waste Management, U.S. Department of Energy. Contribution number 3297 from the Environmental Sciences Division, Oak Ridge National Laboratory, which is operated by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400 from the U.S. Department of Energy.

REFERENCES

- Carpenter, A.B. 1978. Origin and chemical evolution of brines in sedimentary basins. *Oklahoma Geol. Surv. Circ. 79:60-77.*
- COSOD II (Report of the Second Conference on Scientific Ocean Drilling) 1987. Strasbourg, 6-8 July 1987. European Science Foundation and Joint Oceanographic Institutions for Deep Earth Sampling.
- Graf, D.L. 1982. Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. *Geochim. Cosmochim. Acta 46:1431-1448.*
- Graf, D.L., W.F. Meents, I. Friedman, & N.F. Shrimp 1966. The origin of saline formation waters, III: calcium chloride waters. *Illinois State Geol. Surv. Circ. 397:1-58.*
- Hitchon, B., G.K. Billings, & J.E. Klován 1971. Geochemistry and origin of formation waters in the western Canada sedimentary basin, III. Factors controlling chemical composition. *Geochim. Cosmochim. Acta 35:567-598.*

- Kharaka, Y.K. & F.A.F. Berry 1974. The influence of geological membranes on the geochemistry of subsurface waters from Miocene sediments at Kettleman North Dome in California. *Water Res. Res.* 10:313-327.
- Schmidt, G.W. 1973. Interstitial water composition and geochemistry of deep Gulf Coast shales and sandstones. *Am. Assoc. Petrol. Geol.* 57:321-337.
- Shock, E. 1988. Organic acid metastability in sedimentary basins. *Geology* 16:886-890.
- Von Damm, K.L. 1987. Geochemistry of shale groundwaters: survey of available data and postulated mineralogic controls on composition. ORNL/TM-10488, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Von Damm, K.L. & K.O. Johnson 1987. Geochemistry of shale groundwaters: results of preliminary laboratory leaching experiments. ORNL/TM-10535, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Von Damm, K.L. & A.J. VandenBrook 1988. Geochemical controls on shale groundwaters: results of reaction path modeling. ORNL/TM-10944, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Wallace, C.A. 1976. Diagenetic replacement of feldspar by quartz in the Uinta Mountain Group, Utah and its geochemical implications. *J. Sediment. Petrol.* 46:847-861.
- Wolery, T.J. 1983. EQ3NR a computer program for geochemical aqueous speciation-solubility calculations: user's guide and documentation. UCRL-53414, Lawrence Livermore National Laboratory, Livermore, California, USA.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.