Geochemical Modeling and Nuclide/Rock/Groundwater
Interaction Studies

Computed Solid Phases Limiting the Concentration of Dissolved Constituents in Basalt Aquifers of the Columbia Plateau in Eastern Washington

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EXECUTIVE SUMMARY

A speciation-solubility geochemical model, WATEQ2, was used to analyze geographically-diverse, ground-water samples from the aquifers of the Columbia Plateau basalts in eastern Washington. The ground-water samples compute to be at equilibrium with calcite, which provides both a solubility control for dissolved calcium and a pH buffer. Amorphous ferric hydroxide, $\text{Fe}(\text{OH})_3(\text{A})$, is at saturation or modestly oversaturated in the few water samples with measured redox potentials. Most of the ground-water samples compute to be at equilibrium with amorphous silica (glass) and wairakite, a zeolite, and are saturated to oversaturated with respect to allophane, an amorphous aluminosilicate. The water samples are saturated to undersaturated with halloysite, a clay, and are variably oversaturated with regard to other secondary clay minerals. Equilibrium between the ground water and amorphous silica presumably results from the dissolution of the glassy matrix of the basalt. The oversaturation of the clay minerals other than halloysite indicates that their rate of formation lags the dissolution rate of the basaltic glass. The modeling results indicate that metastable amorphous solids limit the concentration of dissolved silicon and suggest the same possibility for aluminum and iron. The results also suggest that the processes of dissolution of basaltic glass and formation of metastable secondary minerals are continuing even though the basalts are of Miocene age and presumably have undergone a long history of contact with ground waters. The computed solubility relations are found to agree with the known assemblages of alteration minerals in the basalt fractures and vesicles, if account is taken of both the difficulty of identifying amorphous phases and the slow rate of formation of clay minerals at low temperatures.

Because the chemical reactivity of the bedrock will influence the transport of solutes in ground water, the observed solubility equilibria are important factors with regard to chemical-retention processes associated with the possible migration of nuclear waste stored in the earth's crust. Specifically, the occurrence of secondary minerals will enhance the sorption of dissolved radionuclides. Speciation-solubility geochemical models provide an important means of determining these solubility-equilibria relationships.

INTRODUCTION

One option for disposal of nuclear waste is to bury it in deep, mined repositories. The U.S. Department of Energy through its National Waste Terminal Storage Program is identifying and characterizing candidate sites for mined repositories. The U.S. Department of Energy is also developing techniques to evaluate the expected performance of the candidate sites with respect to long-term isolation of nuclear waste.

An important element in characterizing and evaluating a site is its geochemistry. Geochemical effects would result from the chemical interactions between ground water (the most likely transport mechanism) and the waste form and with the barrier materials surrounding the waste. Dissolved radionuclides in the ground water may be removed by precipitation or sorption onto the bedrock. Thus, geochemical characterization of the candidate site should include the chemistry of the ground water and the primary and secondary mineralogy of the bedrock.

Data for the ground-water chemistry can be used to determine solubility equilibria which are important because the precipitation and dissolution of minerals and amorphous solids [i.e., "amorphous-like" but in practice those that have a minimal X-ray diffraction pattern (Jenne, 1972; 1977)] control, in part, the concentrations of major solute species in the ground water. In addition, secondary solid phases can serve as important sorption substrates. Both of these processes can influence the migration of radionuclides in an aquifer system. It is, therefore, important that the characterization and evaluation of a repository site accurately identify the solubility-limiting phases present. The purpose of this study is to utilize geochemical modeling to interpret solubility controls for major ions in aquifers in the Columbia Plateau basalts in eastern Washington. Interpretation of solubility controls for trace elements must await the availability of appropriate chemical analyses of these waters.

The Columbia Plateau basalts were chosen for the modeling exercise because: 1) they are a candidate site for a nuclear waste repository (Deju et al., 1977); and 2) the ground-water and mineralogical data for the basalts

are readily accessible. The results discussed in this paper are based on speciation-solubility modeling, whereby the analytical data for ground-water samples are used to identify the solid phases which may be limiting or controlling the dissolved constituents in the ground-water system. Reaction path modeling for this basalt system (Benson et al., 1978; 1979) simulated the incremental dissolution and precipitation, i.e., the mass transfer, of basaltic minerals and other solids. Their preliminary results have shown that mass transfer modeling produced an assemblage of minerals and ground-water compositions qualitatively similar to those identified in the basalt aquifers.

CONCLUSIONS

The ion-speciation/solubility WATEQ2 model is a useful tool for determining the solid phases which limit the concentrations of dissolved constituents in ground waters. An extensive thermodynamic data base, as well as accurate and comprehensive analytical data for the ground waters, are necessary prerequisites to the successful application of geochemical models to diverse aqueous systems. Without the inclusion of solubility data for amorphous solids and metastable minerals, identification of permissive solubility controls would be limited.

Based on the results of this modeling study, calcite is at equilibrium with the basalt ground waters. In addition, zeolites and amorphous phases, such as ferric hydroxide, allophane, and SiO_2 (A,gl), apparently play an important role at ambient temperatures in limiting the maximum concentration of dissolved Fe, Al, and Si in the ground waters. Detailed mineralogical studies are needed to ascertain if certain of the solid crystalline phases (dolomite, sepiolite and MnHPO_4), which similarly compute to be in equilibrium with these water samples, are in fact present as secondary minerals of the altered Columbia Plateau basalt.

SITE DESCRIPTION AND MODELING

The Columbia Plateau is located in the states of Washington, Oregon, and Idaho. [See Myers and Price (1979) for geologic information for this region.] The Plateau consists of a layered sequence of flood basalts with the first layer deposited in early Miocene time, approximately 14 million years ago. Volcanism on the Columbia Plateau was a periodic event over the ensuing 10 million years. This volcanic activity resulted in a heterogeneous sequence of individual basalt flows and sedimentary interbeds that are capped in some areas by an alluvial cover.

The segment of the Plateau selected for this study is that portion of eastern Washington shown in Figure 1. The ground-water hydrology of this region has been studied by Gephart et al. (1979) and Dove et al. (1982). Direct recharge of the basalt aquifers occurs principally as a result of rainfall infiltration through the weathered basalt surface in the northeast portion of the study area where rainfall is relatively high. In addition to direct recharge, the basalt aquifers may be recharged by percolation from alluvial aquifers that, in turn, are recharged by infiltration from rainfall and irrigation water. The irrigation water is derived principally from the Columbia Basin Irrigation Project (Figure 1). Ground-water flow through the basalt tends to parallel the flow units because the most permeable portion of the flows are generally along the fractured, contact zones between flows (Newcomb, 1976). In the northeastern portion of the study area, ground-water flow is generally in a southwestward direction; whereas along the southwestern border, ground water is recharged along the uplands and moves generally in an eastwardly direction toward the central region of the Hanford Reservation (Figure 1). The Hanford Reservation is located in the Pasco Basin which is a topographic low for the region.

MINERAL CHEMISTRY OF BASALT AQUIFERS

The continental basalts of the Columbia Plateau have been extensively characterized with respect to their mineralogy and bulk chemical composition. Subtle differences in the mineralogy and bulk compositions, as well as down-hole logs and magnetic-polarity stratigraphy, are used to differentiate between

FIGURE 1. Location of Study Area

the various basalt units. The primary basaltic minerals consist principally of plagioclase feldspar with compositions that range between labradorite and andesine, pyroxenes generally with augite and subcalcic augite compositions, and minor iron-titanium oxides with compositions in the ilmenite-magnetite solid solution (Ames, 1980). The accessory minerals include apatite, occasional olivine, a minor Fe-Co-Ni sulfide, and an unidentified Fe-rich mineraloid (Ames, 1980). The primary and secondary minerals are contained within a groundmass of basaltic glass.

Fractures and vesicles in the basalts contain a complex series of alteration products (Table 1) that have been identified in core samples with petrographic microscopy, X-ray diffraction, electron microprobe analysis, and scanning electron microscopy (Ames, 1980; Benson et al., 1978; Benson and Teague, 1979; Basalt Waste Isolation Project and Colorado School of Mines Staff, 1979; and Teague, 1980). Because these fractures and vesicles are the primary

TABLE 1. Solid Phases Calculated by WATEQ2 to be in Equilibrium with the Ground Waters or Identified to be Alteration Products of the Columbia Plateau Basalts

Solid Phases	Calculated Equilibrium Phases ^(a) This Study	Ames (1980)	Benson et al. (1978)	Benson and Teague (1979)	BWIP & CSM Staff (1979)	Teague (1980)
<u>Minerals</u>						
Analcime	X		X	X		X
Calcite	X	X		X		
Chabazite		X		X		
Chlorite		X				
Clinoptilolite ^(b)		X	X	X	X	X
Cristobalite ^(b)		X	X	X	X	X
Dolomite	X					
Erionite		X	X	X		
Gmelinite		X				
Gypsum		X		X		
Halloysite	X					
Harmotome		X				
Heulandite		X			X	
Illite (celadonite)			X	X		X
Laumontite		X				
Mordenite		X	X	X	X	X
Opal ^(c)		X	X	X		X
Phillipsite		X		X		
Pyrite		X	X	X	X	X
Quartz ^(b)		X		X	X	X
Sepiolite	X					
Smectite Clay ^(b)	X	X	X	X	X	X
Tridymite			X	X		X
Vermiculite		X	X	X		
Wairakite	X		X	X		
<u>Other Solids</u>						
Allophane	X					
Ferric Hydroxide (amorphous)	X					
Iron Oxides		X				
MnHPO ₄	X					
SiO ₂ (A,gl)	X					

(a) Rhodocrosite and fluorite calculated to be at equilibrium solubility in a very limited number of samples.

(b) Major solid phases reported.

(c) Opal: poorly-ordered cristobalite and tridymite.

conduits for ground-water flow in the basalt aquifers, the mineralogy and chemistry of these alteration products may have an important effect on the composition of the ground water. Of the minerals listed in Table 1, iron-rich smectite and clinoptilolite are the predominant secondary minerals followed in relative abundance by polymorphic silica minerals (quartz, cristobalite, and tridymite), with the remaining minerals present only in minor amounts. In addition to the mineralogical characterization, Benson and Teague (1979) chemically extracted easily-dissolvable Fe and Al from "clay" scraped from four fractures of a basalt core. Although there was no significant reduction in Al-content of the "clay" following extraction, an appreciable amount of extractable Fe was observed in all cases, suggesting the presence of an amorphous iron component in the "clay".

A distinction has been noted by Benson and Teague (1979, p. 7) between the secondary minerals found in the vesicles and along fractures in their basalt cores. They state "vesicles exhibit a more complex mineralogical assemblage than fractures. Other than clinoptilolite, smectite, and silica, the only minerals found in fractures are illite (an iron-rich variety) and pyrite. Vesicles, on the other hand, were found to contain minor amounts of a variety of secondary phases such as erionite, chabazite, analcime, vermiculite, phillipsite, gypsum, and calcite." Ames (1980) similarly found a greater diversity of secondary minerals in vesicles than on fractures, but also identified calcite in some of the sampled basalt fracture surfaces. The presence of less common secondary minerals in some vesicles may be due to isolation of the vesicle from the moving ground water, at which point diffusive mass transport processes would become more important than advective processes. This change in processes might be reflected in the minerals subsequently formed (Benson et al., 1978), and, in fact, chabazite and erionite, two of the zeolites found in the vesicles, are not characteristic of zeolites formed in open ground-water systems (Hay and Sheppard, 1977). An understanding of how permeability has changed as the ground water reacts with the basalt over time may provide insight into the occurrence of the various assemblages of basalt alteration products.

GROUND-WATER DATA

Ground-water analyses used in this modeling study consisted of 118 sets of chemical data published by the state of Washington (Van Denburgh and Santos, 1965), the U.S. Geological Survey (La Sala and Doty, 1971; La Sala et al., 1973) and in Hanford area reports (Apps et al., 1979). The analyses selected were from wells (shown in Figure 1) described by the original authors as being completed in basalt aquifers. The majority of the water samples came from shallow wells screened in more than one interval. However, a few data sets (Apps et al. 1979) were available from the deep (>1000 m) aquifer system in the Pasco Basin, and these samples exhibit a distinctive chemistry and corresponding equilibrium mineral assemblage. The fact that samples came from more than one transmissive unit in the basalt limits stratigraphic interpretations of the modeling results. Except for differentiating between the shallow and deep aquifer samples, no attempt has been made to relate the modeling results to particular units in the sequence of basalt flows. The ground-water samples used in this study are listed in the Appendix.

The analytical data reported from the well-sampling programs include temperature, pH, and major element concentrations; a few of the analyses also list concentrations for Al, Mn, Sr, Li, F, and B. In nine wells sampled by La Sala et al. (1973), the carbon-14 content of the ground water was determined. The ground-water ages based on these radiocarbon contents range from 13,000 to >41,000 years and generally increase with distance from the presumed recharge zones around the periphery of the plateau. Measurements of E^H are available for only four of the water samples used in this study; one of which (No. 5468, Appendix) was relatively high in tritium, suggesting that it has a component of recent meteoric water. Thus, the E^H of this sample may in general not be representative of the basalt aquifer water. [The E^H notation, with accompanying subscripts, will be used to differentiate between different analytical sources of the E^H value, e.g., E_{Pt}^H for the platinum electrode and $E_{Fe^{2+}/Fe^{3+}}^H$ for the Fe^{2+}/Fe^{3+} redox couple.]

Using a similar data set, Gephart et al. (1979) have noted definite trends in the ground-water composition relative to distance from the northeast and

southwest recharge zones. As a function of distance and, consequently, residence time in the basalt aquifers (supported by the ground-water ages of La Sala et al., 1973), these trends include: 1) an increase in concentration of Na, K, Cl, and F; and 2) a decrease in Ca and Mg. Gephart et al. (1979) attribute the changes in chemical composition of the ground water to the processes of cation exchange and mineral equilibria controls.

GEOCHEMICAL MODELING

The speciation-solubility WATEQ2 geochemical model was selected to determine the solubility constraints for the published water analyses because: 1) its data base contains thermodynamic data for trace elements and thermodynamically stable solids as well as those phases considered metastable at 25°C and 1 atmosphere pressure; 2) it is the best documented of the available models; and 3) it may have the most thoroughly evaluated thermodynamic data base (Truesdell and Jones, 1973; Plummer et al., 1976; Ball et al., 1979; 1980; 1981). The quality of the data base of a geochemical model is extremely important in that it plays a major part in conclusions drawn concerning solubility equilibrium. The comprehensive documentation of WATEQ2 facilitates its use for validation and application studies. Analytical data required as input to the computerized model include the concentrations of dissolved constituents, temperature, pH, and E^H . The aqueous speciation is computed by an iterative process using equilibrium constants based on the Gibbs free energy of reaction, a Davies or extended Debye-Huckel equation for activity coefficients, and either analytical expressions or the Van't Hoff relation to adjust the equilibrium constants to the temperature of the water sample.

Solubility-equilibrium hypotheses are then tested by first computing ion activity products (AP) from the activities of the uncomplexed ions based on the stoichiometries of the minerals and other solids in the WATEQ2 data base. These activity products are then compared to the solubility products (K) for the same solid phases to test the assumption that certain of the dissolved constituents in the ground water are in equilibrium with particular minerals and amorphous solids. Disequilibrium indices ($\log AP/K$) are calculated to

determine if the water is at thermodynamic equilibrium ($\log AP/K \approx 0$), over-saturated ($\log AP/K > 0$), or undersaturated ($\log AP/K < 0$) with respect to a certain solid phase.

EVALUATION OF ANALYTICAL DATA

Aqueous speciation, hence the testing of solubility hypotheses, is only reliable if the quality of the chemical analyses is adequate. A large cation/anion imbalance is indicative of a poor quality chemical analysis or the lack of analysis for an important constituent. As an operating constraint, the WATEQ2 geochemical model does not attempt to model a water analysis with a cation/anion imbalance of >30%. The cation/anion balance is calculated using Equation 1:

$$\text{Cation/Anion Balance (\%)} = \frac{\text{Cations (equiv. L}^{-1}\text{)} - \text{Anions (equiv. L}^{-1}\text{)}}{[\text{Cations (equiv. L}^{-1}\text{)} + \text{Anions (equiv. L}^{-1}\text{)}]/2} \times 100\% \quad (1)$$

The cation/anion balances computed for the modeled analyses are included in the tabulation of samples in the Appendix. The cation/anion imbalance of the unspicated input data exceeds 5% in only six of the samples modeled.

The pH of a solution is an important variable in mineral solubility calculations. The pH ranges from 7 to 9 for the majority of the basalt ground waters sampled. Within this pH range the pH of ground water is primarily a function of its CO₂ content. The partial pressure of carbon dioxide in ground waters of confined aquifers commonly varies from that for equilibrium with the atmosphere (Pearson et al., 1978) and, as a consequence, CO₂ may be gained or lost during sampling unless special techniques are employed. A change in CO₂ content will affect the measured pH of the water which, if used, will result in erroneous calculations of mineral equilibria. The calculation of calcite equilibrium in ground water will be particularly affected due to the dependency of speciation of the carbonate complexes on pH. In ground waters in contact with calcite, field measurements of pH can be verified by estimating the pH value at which calcite is at equilibrium with the water. After the present modeling results indicated that the sampled waters were

generally in equilibrium with calcite, several ground-water analyses were remodeled using selected pH values to interpolate the required pH for equilibrium with calcite. The disequilibrium indices calculated from these arbitrary pH values generally fall along a straight line when plotted versus pH. The intersection of this line and the $\log AP/K = 0$ line is the pH at which calcite is at equilibrium with this water.

Figure 2 shows the results of these estimates for four water analyses. A comparison of measured pH values versus these interpolated pH values for equilibrium with calcite are given in Table 2 for a subset of the analyses. The difference between a measured and calculated pH may be due to: 1) non-equilibrium with calcite; 2) incorrect measurement of pH, Ca or alkalinity ($\text{HCO}_3 + \text{CO}_3$); or 3) addition of atmospheric CO_2 before analysis which would lower the pH. Because calcite is generally present and most pH values calculated from calcite equilibria are 0.1 to 0.3 pH units higher than the measured values, we consider it likely that CO_2 addition has occurred, thus lowering measured pH values. It is presumed that the CO_2 content of these basaltic ground waters is less than that in equilibrium with the atmosphere because of the precipitation of carbonates. We suspect that the significantly higher pH values calculated for Nos. 5055 and 5060 are not due to CO_2 addition, but rather, they indicate errors in the water analyses. All actual calculations of disequilibrium indices used measured pH values.

The measurement or calculation of accurate, in situ E^H values is necessary in order to calculate the speciation, hence predict the mobility, of redox-sensitive elements that may be present or introduced into the ground-water regime. Four ground-water samples, the only ones for which E^H values were reported, were computed to be near equilibrium or oversaturated with amorphous ferric hydroxide, $\text{Fe}(\text{OH})_3(\text{A})$ ("A" refers to an amorphous solid). This is not surprising in light of the fact that various investigators (see later section on iron solubility controls) have found that amorphous ferric oxyhydroxide, or an Fe compound with similar solubility properties, forms readily under a variety of field and laboratory conditions. The assumption of $\text{Fe}(\text{OH})_3(\text{A})$ equilibrium can be used to estimate maximum E^H values in a similar manner to that used to estimate pH by assuming calcite equilibrium. The

FIGURE 2. Selected Calcite Disequilibrium Indices Plotted vs. pH

results of these E^H calculations for a subset of the data are also given in Table 2. The $E^H_{Fe(OH)_3(A)}$ values show a range from approximately -0.2 to 0.0 V.

Smith et al. (1980) use a different approach to estimate redox conditions in the aquifer. They compute a theoretical E^H based on a stable mineral assemblage for a basalt system that is poised (E^H buffered) by the quartz-fayalite-magnetite (QFM) assemblage. At a pH of 9.4, they calculate that the QFM assemblage will poise the ground-water system at an E^H value of close to -0.5 V, which is 0.3 to 0.5 V more negative than the maximum value estimated assuming equilibrium with $Fe(OH)_3(A)$. This difference is significant for the mobility of several redox-sensitive, actinide elements because the low valence forms tend to be cationic and, hence, more strongly adsorbed than higher

TABLE 2. Comparison of Measured pH Values with Those Calculated for Ground Water at Equilibrium with Calcite. E^H Calculated Assuming Equilibrium with Amorphous Ferric Hydroxide $[\text{Fe}(\text{OH})_3(\text{A})]$ and Using Measured pH Values

Sample Number	pH		ΔpH (measured - calculated)	E^H $\text{Fe}(\text{OH})_3(\text{A})$ (V)
	Measured	Calculated		
5053	9.0	9.0	0	-0.14
5055	8.8	9.4	-0.6	-0.22
5061	8.8	8.8	0	-0.12
5054	8.6	8.8	-0.2	-0.12
5059	8.6	8.9	-0.3	-0.16
5060	8.6	9.5	-0.9	-0.23
5062	8.4	8.2	+0.2	-0.03
5063	8.2	8.4	-0.2	-0.03
5050	8.1	8.4	-0.3	-0.05
5058	8.1	7.9	+0.2	+0.01
5057	8.0	7.9	+0.1	+0.01
5070	8.0	8.0	0	+0.01
5051	7.9	8.3	-0.4	+0.01
5064	7.9	8.1	-0.2	-0.03

valence ionic forms. As a consequence of the large difference in equilibrium E^H values calculated with respect to $\text{Fe}(\text{OH})_3(\text{A})$ and the QFM assemblages, both systems could not be poisoning the E^H simultaneously. Smith et al. (1980) show that the assemblage pyrite, magnetite, and siderite would poise the E^H of the basalt system at a value similar to that of the QFM assemblage and they consider the reported presence of these minerals in the Columbia Plateau basalts as verification of their theoretical E^H . However, we find no published evidence for the occurrence of siderite in these basalts. In order to serve as a poisoning material, these minerals must be shown to be both present, in significant amounts, throughout the aquifer and reactive with the ground water. The presence of a more reactive, redox-sensitive phase, such as $\text{Fe}(\text{OH})_3(\text{A})$, must also be collaborated by mineral characterization studies.

Methane, a redox-sensitive constituent, has been shown to be present in the basalt ground water (Apps et al., 1979; Gephart et al. 1979). Under equilibrium conditions, methane becomes stable relative to carbon dioxide when the E^H of the environment drops below -0.3 V at a pH of 8 (Lindsay, 1979). If methane production is occurring in the basalt aquifers, the methane/carbon-dioxide equilibrium relationship would provide both a means of poisoning the system and another method for determining the redox state of this environment. An alternative to production of methane in the basalt aquifers would be its generation by thermal alteration of organic matter in underlying formations and subsequent movement into the basalts.

MINERAL EQUILIBRIA

Disequilibrium indices ($\log AP/K$) were calculated by the WATEQ2 geochemical model for those minerals and other solids stored in the model's data bank for which their dissolved constituents are reported in the ground-water analyses. Jenne et al. (1980) observed in previous studies that the variance in disequilibrium indices about the zero value for waters in apparent equilibrium with that mineral increases with the magnitude of the solubility value for that solid. They determined that a value of $1/20$ of the log of the solid's solubility product ($\pm 5\% \times \log K$) represented a useful error band for permissive equilibrium with the solid. All plots of disequilibrium indices which follow in this paper indicate this error band by a dashed line on each side of the equilibrium line ($\log AP/K = 0$).

The numerous possible sources of error in the course of sampling, storage, and analysis of the ground waters require that several samples must be modeled to draw meaningful conclusions concerning solubility-limiting phases. Therefore, it is useful to display the modeling results in the form of disequilibrium indices plotted against pH, conductivity, or other variables, or against the disequilibrium indices for a second solid phase. Where relatively few of the calculated values of $\log AP/K$ fall outside of the error band for a particular solid, then that phase must be considered as a permissible solubility-limiting phase. Moreover, the occurrence of several undersaturated values does not necessarily indicate that a particular solid is not a solubility-limiting phase.

CALCIUM AND MAGNESIUM SOLUBILITY CONTROLS

The disequilibrium indices for end-member calcite, CaCO_3 , indicate that calcite is a principal solubility control for dissolved calcium (Figure 3). This agrees with site studies that show calcite as a common secondary mineral in the basalt (Table 1). Several ground-water analyses show undersaturation with respect to calcite, but there is no obvious geographic pattern to these particular water samples. Moreover, depth correlations for these same samples are not possible due to the sparsity and unreliability of the reported depth data.

FIGURE 3. Calcite Disequilibrium Indices Plotted vs. Calcium Concentration

Calcite equilibrium can be a function of structural substitution, of Mg^{2+} , Mn^{2+} , Fe^{2+} , and Sr^{2+} for Ca^{2+} , in natural calcites which is common and well documented (Deer et al., 1967). The range of solid solution for most of these constituents is fairly restricted to near end-member CaCO_3 , but the substitution of Mg^{2+} for Ca^{2+} in natural and laboratory-precipitated calcites can exist over the compositional range from end-member CaCO_3 (0 mol% MgCO_3 component) to approximately 30 mol% MgCO_3 (Garrels and Wollast, 1978). The calcites found in the basalt cores from the Hanford Reservation, based on the electron microprobe analyses of Ames (1980, Tables 26 and 35), contain appreciable Mg, Mn, and Fe in solid solution. Although the Mg-contents remain fairly constant between 2.0 and 7.5 atom%, the substituted cation totals for Mg, Mn, and Fe in the Hanford calcites range from 2.6 to 21.1 atom% (Ames, 1980).

The solubility of magnesian calcites has been shown to be significantly different from the solubility of end-member calcite. Based on the results of Plummer and Mackenzie (1974), the log K values calculated by Thorstenson and Plummer (1977) for end-member calcite and their most Mg-rich calcite, 26.7 mol% MgCO_3 , are respectively -8.426 and -7.29, which represents more than a 10-fold greater solubility for the magnesian calcite. A Gibbs free energy of formation value experimentally determined for a high magnesian calcite with 13.2 mol% MgCO_3 reported in a recent abstract by Lafon (1981) is in excellent agreement with the free energy values calculated by Thorstenson and Plummer (1977).

The activities for the species Mg^{2+} , Ca^{2+} , and CO_3^{2-} calculated by the WATEQ2 model were used with the data presented in Thorstenson and Plummer (1977, Figure 4) to estimate the Mg content for calcites in equilibrium (or "stoichiometric saturation") with these modeled ground waters. Because the ratio of dissolved Mg/Ca is fairly constant between 0.5 and 1 (Figure 4), the major variation in the Mg content of the calcites will be due to the amount of oversaturation of the waters with calcite. The maximum oversaturations with calcite were computed for water sample No. 5289 and 5268, which had log AP/K (calcite) values of 0.85 and 0.50, respectively. The estimated, maximum Mg-component for calcites in contact with these waters is 12 mol% MgCO_3 for sample No. 5289 and 8 mol% MgCO_3 for sample No. 5268. Because the majority of ground waters are at equilibrium with respect to pure end-member calcite, the maximum Mg concentration of calcites calculated to be in equilibrium with the ground waters is expected to be closer to 5 mol% or less. These estimates are in reasonable agreement with the Mg contents of the calcites analyzed by Ames (1980), but considerably less than the observed range in the substituted cation totals for Mg, Mn, and Fe. Unfortunately, it is not certain if the substituted Mn and Fe can be treated in an equally analogous fashion to the magnesian calcites. The fact that substituted cations total >5 mol% in the analyzed calcites might reflect the precipitation of calcite from aqueous solutions that differ in chemistry and temperature from present ground waters.

The disequilibrium indices for dolomite, $\text{CaMg}(\text{CO}_3)_2$ (Figure 5), show an apparent equilibrium saturation of these waters with respect to dolomite. However, the disequilibrium indices tend to increase somewhat with the Mg

FIGURE 4. Calcium and Magnesium Concentrations for Basalt Ground Waters

concentration of the water samples suggesting that dolomite is not serving as an effective solubility-limiting phase. Additionally, this mineral has not been reported as a secondary mineral in the Columbia Plateau basalts (Table 1). Further, dolomite is not known to form by direct precipitation except in "warm" hypersaline lagoons with high molal Mg/Ca ratios (~3 to 100) and mildly alkaline pH values (Skinner, 1963; and other studies summarized by Hanshaw et al., 1971). The modern formation of dolomite has also been reported by Hanshaw et al. (1971) in Tertiary limestone aquifer systems of the Florida and Yucatan Peninsulas. Although they have shown that Mg/Ca activity ratio of 1 in the water is necessary for the three-phase equilibrium between calcite, dolomite, and aqueous solution, dolomitization in dynamic ground-water systems requires a sufficient source of dissolved Mg^{2+} and Mg/Ca ratios >1 to enhance the

FIGURE 5. Dolomite Disequilibrium Indices Plotted vs. Magnesium Concentration

kinetics of the process (Hanshaw et al., 1971). Except in a few instances, the molal Mg/Ca ratios for these basalt ground waters are ≤ 1 (Figure 4). Therefore, it would appear unlikely that there is currently any active precipitation of dolomite or dolomitization of calcite in the basalt aquifers.

The results computed for fluorite, CaF_2 , generally indicate that the ground water is undersaturated throughout the region where F concentrations typically average 1 mg L^{-1} . However, in deep ($>1000 \text{ m}$) wells where F values are 20 to 30 mg L^{-1} , fluorite is at apparent saturation and may play a role in limiting Ca and/or F in these cases.

The disequilibrium indices (data not shown) for crystalline sepiolite $[\text{Mg}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \cdot 3\text{H}_2\text{O}]$, a chain-lattice clay mineral, compute to be in the lower half (less saturated) of the error band, suggesting that: 1) the sepiolite,

if forming in this environment, is less soluble than that for which the thermodynamic data in WATEQ2 was derived; or 2) a solid phase other than sepiolite limits Mg concentrations in the ground water. Sepiolite has not been reported in these basalt aquifers. It is known to form authigenically from marine and lacustrine waters (Bigham et al., 1980) and as a product of the weathering of ultramafic rocks (MacKenzie et al., 1969). Low concentrations of dissolved Al and moderately alkaline pH values are common chemical features for these environments. The relatively few Al values available for the ground water in the basalt aquifers are not particularly low (0.1 to 1.1 mg L⁻¹). The apparent equilibrium based on the computed disequilibrium indices could, therefore, be simply coincidental.

SILICON AND ALUMINUM SOLUBILITY CONTROLS

Based on the calculated disequilibrium indices (Figure 6), nearly all of the ground-water samples for the basalt aquifers are in equilibrium with a form of amorphous silica, SiO₂ (A,gl), whose Gibbs free energy of formation is equivalent to that for SiO₂ glass, as originally compiled by Robie and Waldbaum (1968). This silica phase is less soluble than the fine-grained, "amorphous" silica reported by Morey et al. (1964), but is more soluble than chalcedony, cristobalite and quartz based on the log K values computed by Truesdell and Jones (1973). The silica phase which computes to be at equilibrium with the basalt ground waters will be termed "amorphous silica (glass)" in this paper due to its intermediate solubility between the "amorphous" silica (precipitate) and the crystalline SiO₂ polymorphs.

Oehler (1976) proposed that metastable forms of silica convert through initial crystallization to "opal-CT" [nomenclature from Jones and Segnit (1971) for disordered cristobalite-tridymite stacking sequences with poor crystallinity] and, on recrystallization of the opal, to more stable spherulitic quartz and finally to microcrystalline quartz. As shown in Table 1, investigators have identified opal, cristobalite, tridymite, and quartz in basalt fractures and vesicles. These observed crystalline phases are more easily identified than an amorphous phase using standard characterization techniques. The

FIGURE 6. SiO_2 (A,gl) Disequilibrium Indices Plotted vs. Total Dissolved Solids

identified minerals may be forming according to Oehler's crystallization sequence by aging of an initial amorphous precipitate that is limiting silica concentration in the ground water.

Clays and zeolites are the common basalt alteration products reported in the study area. The solubility relationships of these aluminosilicates must be determined. Unfortunately, concentrations of dissolved Al are reported in only eighteen of the ground-water samples. Eleven of these samples were taken from segregated intervals in a single well and the remainder are from wells located principally in the southwestern section of the study area. As a consequence, the results of the solubility calculations for aluminosilicates do not represent the regional, basalt system. Furthermore, because Al is a major constituent of many rock-forming minerals, Al determinations are influenced by the presence of suspended particulates not removed by filtration before analysis of the water sample.

Wairakite, $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$, is a zeolite that computes to be at or near equilibrium (Figure 7). Analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, also computes to be in equilibrium with some of the ground waters sampled. The formation of zeolites, in general, requires an alkaline pH and high silica activity (Hay, 1966, p. 81; Hay and Shephard, 1977). Wairakite has been identified in a single vesicle in the basalts of this study (Table 1), which suggests that its formation is not an active process throughout the aquifer system. The occurrence of analcime is also rare in these basalts. However, the zeolite clinoptilolite, with an ideal formula of $(\text{K},\text{Na})\text{AlSi}_5\text{O}_{12} \cdot 3.5 \text{H}_2\text{O}$, has been reported as a major component of the secondary mineral assemblage. The formation of clinoptilolite may limit Al and Si activities in the ground water to values in apparent equilibrium with wairakite and analcime. Unfortunately, thermodynamic data for clinoptilolite are not currently available and consequently determination of its solubility equilibria cannot be made.

FIGURE 7. Disequilibrium Indices of Wairakite Plotted vs. pH

Certain clays, allophane and halloysite, which are in equilibrium with the water under conditions of high pH and high SiO_2 activity, may also be important solubility constraints. The disequilibrium indices of allophane, an amorphous aluminosilicate, $(\text{Al}(\text{OH})_3)_{2-x}(\text{SiO}_2)_x$, whose Al/Si ratio varies with the pH of the water from which it precipitates (Paces, 1973), are plotted in Figure 8. Six of the samples are oversaturated with allophane, which suggests possible contamination of the water samples with sediment. Because the indices for allophane show considerable scatter, it is not certain that allophane is a solubility control for dissolved Al. Halloysite is a 1:1 clay mineral that forms easily, particularly when volcanic glass is present, and is a potential solubility-limiting phase in the basalt aquifers. A number of the calculated disequilibrium indices for halloysite (Figure 9) indicate equilibrium although

FIGURE 8. Disequilibrium Indices of Allophane Plotted vs. pH

FIGURE 9. Disequilibrium Indices of Halloysite Plotted vs. pH

the majority fall below the halloysite equilibrium region, suggesting that Al and Si activities in the ground water are not generally high enough to be in equilibrium with this mineral.

The fact that zeolites and amorphous clays are in apparent equilibrium with the basalt ground waters implies that the omnipresent crystalline clays identified in the basalts (Benson and Teague, 1979) are not in equilibrium with the ground water. In general, the clay minerals, except halloysite, are oversaturated with respect to the ground water, and the montmorillonite plot (Figure 10) displays this trend. Three of the samples at high pH which fall within the equilibrium error band represent analyses of water from the bottom of a deep ($\approx 1,000$ m) borehole which has an ambient temperature of $>40^{\circ}\text{C}$. These elevated temperatures may be responsible for equilibrium of the water with crystalline clays. In most cases, however, it does not appear that clays are effective solubility-limiting phases.

FIGURE 10. Disequilibrium Indices of Montmorillonite Plotted vs. pH

IRON AND MANGANESE SOLUBILITY CONTROLS

The geochemistry of Fe in the ground water of basalt aquifers is particularly important because: 1) Fe is a major constituent of the clay minerals in the altered basalts (Ames, 1980); 2) Fe oxyhydroxide precipitates are known to be strong sorbers for ions in solution (Jenne, 1968, 1977; Koons et al., 1980); and 3) the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is important in ground water under reduced oxygen fugacities because it may control the E^H of the ground waters. Because Fe is so sensitive to redox conditions, the concentrations of Fe(II) and Fe(III) in the water must be determined analytically and/or the redox potential must be accurately measured to model the two valence states of Fe and, hence, its various complexes.

The concentrations of Fe(II) and Fe(III) in the ground water were not reported for any of the samples used in this study; however, E^H_{pt} values of

-0.05, -0.03, +0.09, and +0.15 V were measured in four cases (Apps et al., 1979). Using the analytically determined concentrations of total Fe and these E_{pt}^H values, the computed Fe(II)/Fe(III) ratios are $10^{-4.3}$, $10^{-3.5}$, 5.4, and 0.57, respectively for these water samples. These ratios do not vary linearly with E^H because pH affects the hydrolysis of Fe(II) and Fe(III), hence the activity of Fe^{2+} and Fe^{3+} . The Fe(II)/Fe(III) ratios for the ground water can be compared to the same ratio for the basaltic rock. Swanson (1967, p. 1093, analysis 3) and Waters (1961, p. 594, analysis 2) report the chemical composition of Columbia River Basalt and, using their weight percentages for FeO and Fe_2O_3 , an Fe(II)/Fe(III) ratio of 3.5 can be calculated for this basalt. This value reflects the ratio of the two valence states for the bulk rock which may not precisely represent the most soluble phase in the basalt, e.g. the glassy groundmass. However, if this Fe(II)/Fe(III) ratio is reasonably accurate and representative of that released to the ground water by the ongoing dissolution of the basalt, then Fe(II)-containing solids should be precipitating from solution at a faster rate than Fe(III) solids, to obtain the Fe(II)/Fe(III) ratios calculated for the waters having measured E^H values. As an alternative to the precipitation of Fe(II) compounds, the decrease of Fe(II)/Fe(III) from 3.5 to less than 1 could result from the oxidation of Fe(II) by traces of O_2 in the recharge water, including leakage from the overlying alluvial aquifer.

No solubility-limiting solid was identified for Fe(II) based on these modeling results. This could be due to: 1) the absence of the necessary analytical data on the water as input to WATEQ2; 2) Fe(II) may be coprecipitating as a minor constituent in other minerals such as calcite; and/or 3) Fe(II) is being oxidized by O_2 to Fe(III), which is solubility limited. One of these explanations must hold, or the concentration of dissolved Fe would otherwise increase down the flow gradient which is not supported by ground-water analyses based on their geographic locations. WATEQ2 will not calculate the activity of reduced sulfur species from an analytical sulfate value because of the gross redox disequilibrium commonly observed between dissolved sulfide and sulfate. Several Fe sulfide minerals [e.g., pyrite (FeS_2), mackinawite (FeS), and greigite (Fe_3S_4)] are potential Fe(II)-limiting phases; consequently the lack of measured dissolved sulfide values may affect the determination of

an important solubility-limiting phase for Fe(II). A sulfide concentration (6.2 mg L^{-1} as HS^-) is reported for only one water sample (No. 5468). For this case, pyrite ($\log \text{AP/K} = 15.9$) and greigite ($\log \text{AP/K} = 5.5$) are oversaturated whereas mackinawite ($\log \text{AP/K} = -1.3$) is undersaturated, and none of the disequilibrium indices for these minerals are within their respective equilibrium error bands. Pyrite is reported as an alteration phase of the basalts, but, whether or not it is in equilibrium with the present-day ground water, cannot be determined due to the limited analytical data for the basalt ground water.

The disequilibrium indices for siderite, FeCO_3 (data not shown), compute to be undersaturated in the majority of the cases. Siderite has not been reported in the mineralogical studies compiled in Table 1, which, in agreement with the modeling results, indicates that siderite is probably not a solubility-limiting phase. Significantly, electron microprobe analyses indicate that the calcite on the fracture surfaces of the basalt contains about 3 wt% total Fe, or a Ca/Fe(total) mole ratio of 16 (Ames, 1980). Thus, the solid solution of Fe in the calcites appears to be one of the processes removing Fe(II) from the ground water. This process may be occurring and limiting Fe(II) in the ground water along with the oxidation of Fe(II) by O_2 and the precipitation of, yet to be identified, Fe(II)-bearing minerals.

Fe(III) forms very insoluble oxides and hydroxides, and, as is found elsewhere, the crystalline Fe oxides generally show supersaturation in the basalt ground waters. An Fe(III)-rich smectite [termed nontronite by Ames (1980)] occurs widely as an alteration product of the Columbia Plateau basalts. This particular mineral was not in the thermodynamic data base of WATEQ2 when this study was done, therefore the EQ3 code (Wolery, 1979) was used to test for ground-water equilibrium with end-member compositions of nontronite. In order to compute a $\log \text{AP/K}$ for nontronite both E_{pt}^{H} and Al concentration must be specified. These two parameters were not reported jointly in any one sample, therefore, we assumed an Al concentration for one of the samples (No. 5468) which had a measured E_{pt}^{H} . Using a very low Al concentration of 10^{-9} molar ($2.7 \times 10^{-5} \text{ mg L}^{-1}$), the calculated $\log \text{AP/K}$ for nontronite

is 8 units above the equilibrium error band. It appears that nontronite is not a solubility-limiting phase based on the available data and an assumed minimum Al concentration.

Amorphous ferric hydroxide, $\text{Fe}(\text{OH})_3(\text{A})$, is the $\text{Fe}(\text{III})$ phase calculated to be at equilibrium in two of the four cases where E_{pt}^{H} values are given. The value of the Gibbs free energy used in WATEQ2 for this compound was taken from Langmuir (1969), and, for simplicity, its composition has been considered to be $\text{Fe}(\text{OH})_3(\text{A})$. Several authors (Chukhrov et al., 1974; Gang and Langmuir, 1974; Schwertmann and Fischer, 1973; and Taylor and Schwertmann, 1978) report that amorphous ferric oxyhydroxide readily precipitates under natural and laboratory conditions. The solid phase designated as ferric oxyhydroxide by these investigators ranges from amorphous to poorly crystalline, reflecting, in part, the rapidity of its formation and the age of the material. The crystalline phase has been named ferrihydrite (Fleischer et al., 1975) and, based on the data of Chukhrov et al. (1973), has the composition $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$. The presence of amorphous ferric hydroxide and/or ferrihydrite as a component of the alteration products of the basalt may explain the appreciable amount of extractable Fe for the "clays" analyzed by Benson and Teague (1979).

Four of the published ground-water analyses include concentrations of dissolved Mn and PO_4 . The disequilibrium indices for crystalline MnHPO_4 compute to be within its equilibrium error band for these four waters. These results suggest that MnHPO_4 could be limiting the concentration of the trace constituents Mn and PO_4 in the ground water. The log K for MnHPO_4 in the WATEQ2 model was computed from a Gibbs free energy taken from Wagman et al. (1969), and MnHPO_4 frequently computes to be a solubility-limiting phase in a variety of environments (E. A. Jenne, unpublished data). Although Lindsay (1979) discusses the potential importance of MnHPO_4 as a solubility-limiting phase in the soil environment (based on the same source of free energy data), our cursory review of X-ray and mineralogical references shows no evidence for a geologic occurrence of this solid phase.

SUMMARY

Calcite disequilibrium indices indicated equilibrium with most water samples, which is in agreement with mineralogical data. The ground waters are in equilibrium or slightly undersaturated with respect to the zeolites, as represented by the minerals wairakite and analcime. Amorphous ferric hydroxide computes to be an equilibrium phase or oversaturated in the few instances for which E^H measurements are available. All of the solid phases calculated to be at equilibrium with the basalt ground water are listed in Table 1. A comparison of the solid phases identified in the published characterization studies (Table 1) versus those computed to be in equilibrium with these waters leads to a number of useful observations. Many of the solid phases calculated to be in equilibrium with the basalt ground waters have been identified in the basalt fractures and vesicles. These solids include calcite, wairakite, analcime, and amorphous ferric hydroxide [possibly the "easily dissolvable" iron compound noted by Benson and Teague (1979) and the "hydrated iron oxides" of Ames (1980)]. However, certain of the calculated equilibrium phases (allophane, dolomite, sepiolite, $MnHPO_4$, and fluorite) have not been identified in mineral characterization studies, and some of the identified minerals (primarily the clays and crystalline SiO_2 phases) do not compute to be at equilibrium with the majority of the ground-water samples. The lack of correspondence between some of the modeling results and actual mineral occurrences may be due to a variety of reasons discussed below.

Some of the solid phases that compute to be solubility controls may occur in the reaction zone associated with the basalt surface in contact with the ground water. Results summarized by Aagaard (1979) indicate that the alteration products "do not form a coherent and continuous surface coating" on the hydrolyzed silicate surfaces. Recent studies with electron microscopy (Berner and Holdren, 1979; Eggleton and Buseck, 1980; and Holdren and Berner, 1979) show that feldspar weathering is controlled by reactions at the interface between the mineral grains and the aqueous solution, and not by diffusion through a surface coating. Therefore, detailed phase characterization of the

hydrolyzed basalt surfaces, which have not been examined in studies carried out to date, may be critical to the identification of the solubility-limiting phases.

The failure to identify allophane in the core samples is not surprising, because special techniques are required to determine the presence of noncrystalline solids. The lack of identification of crystalline solid phases, such as dolomite and sepiolite, among the secondary minerals in the altered basalt may be due to: 1) their absence, which suggests that the calculated equilibrium with the water is coincidental, 2) their absence at the locations where aquifer material was sampled; and/or 3) their presence in such small quantities that the other minerals mask their identification. It is not surprising that MnHPO_4 and fluorite were not identified in previous characterization studies. The solid MnHPO_4 would undoubtedly exist as a minor constituent in the assemblage of secondary minerals, and fluorite computes to be at equilibrium only in ground waters with elevated F concentrations.

A question arises concerning the occurrence of secondary minerals which have been identified in samples of altered basalt, but which did not compute to be at equilibrium with the samples of present-day ground water. The majority of the secondary minerals that have been identified are layer silicates, zeolites, and various polymorphs of crystalline SiO_2 (Table 1). With the exception of the zeolites which are in equilibrium with the ground waters, the disequilibrium indices show that these water samples are all generally supersaturated with these minerals. If these minerals are forming under the present chemical conditions in the basalt aquifers, there are two possible modes for their formation. These secondary minerals might be the result of either dissolution and precipitation or solid state transformation of the initially precipitated amorphous compounds (SiO_2 , allophane, and ferric hydroxide) into more stable crystalline minerals. Alternatively, these phases may be precipitating directly from the ground water, but at such a slow rate that they do not limit the concentration of their constituent elements in the aqueous phase. In either case, these minerals would not be expected to be at equilibrium with the present-day ground water although they may be forming. A further possibility exists that, as later basalt flows were emplaced, one or more of these

minerals formed during the cooling or reheating of the basalt as meteoric water entered the cooling fractures. Lloyd Ames (1980) considers this as a possible mode of origination for much of the calcite observed in the altered basalts, based on the crystal morphology and the trace element content of the precipitated calcite. However, there presently are no stable isotopic or fluid inclusion data to test this hypothesis.

A complex assemblage of secondary products resulting from basalt alteration are present in these aquifers. These solid phases represent all stages of stability between amorphous compounds and crystalline minerals, but the amorphous phases will play the major role in limiting the dissolved concentrations in the ground water of their constituent elements. By the same token, these less stable phases will be more sensitive to chemical and physical alterations in the basalt aquifers. The presence of alteration products, both amorphous and crystalline, affects the entire composition of the ground water because of: 1) the solids' ability to exchange solute species with the solution via adsorption processes, 2) coprecipitation of elements in the structure of the alteration products (Koons et al., 1980; Yariv and Cross, 1979, p. 254), and 3) the coating effect of precipitates on stable mineral surfaces which changes the surface properties of the substrate (Sholkovitz, 1973). These factors must be considered in assessing the geochemical aspects of the performance of a nuclear waste repository in the basalt environment. The geochemical model of the system must be able to accurately simulate the important ongoing processes, including equilibration of the water/rock system.

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APPENDIX

SELECTED DISEQUILIBRIUM INDICES FOR
COLUMBIA PLATEAU BASALT GROUND WATERS

APPENDIX

SELECTED DISEQUILIBRIUM INDICES FOR COLUMBIA PLATEAU BASALT GROUND WATERS

To provide a link between the analyses used in the modeling study and their publication source, Tables A.1 to A.4 of this appendix equate the modeling number for each analysis used in this study with the water sample number assigned in the original reference. The measured pH values, calculated cation/anion balances, and the calculated disequilibrium indices ($\log AP/K$) for selected minerals and amorphous compounds are also included.

TABLE A.1. Calculated Disequilibrium Indices Using Ground-Water Chemistry Data from La Sala et al. '(1973, Table 1)

Modeling Number	Sample Number	pH	Cation/Anion Balance %	Log AP/K				
				Calcite	Dolomite	Sepiolite	SiO ₂ (A,gl)	Allophane
5050	6/23-11P1	8.1	+0.0	-0.27	-0.69	-1.22	0.00	
5051	6/23-15J1	7.9	+0.3	-0.43	-1.02	-1.82	+0.04	
5053	8/31-34H1	9.0	-1.0	-0.01	-0.77	+0.91	+0.10	-0.03
5054	9/30-18H1	8.6	+0.5	-0.19	-0.71	-0.68	0.00	+0.21
5055	11/26-34R1	8.8	+0.3	-0.46			+0.09	+0.76
5057	13/24-25E1	8.0	+0.6	+0.08	+0.21	-0.02	-0.01	+0.76
5058	13/25-30G1	8.1	+1.2	+0.16	+0.34	-0.37	-0.04	+0.43
5059	13/26-35H1	8.6	+0.2	-0.24	-1.09	-1.29	-0.07	+0.69
5060	13/28-13N1	8.6	-0.7	-0.66	-1.33	-0.15	+0.01	-0.30
5061	14/31-36J1	8.8	-0.9	+0.01	-0.73	+0.26	+0.05	
5063	15/29-3J1	8.2	+0.4	-0.16	-0.29	-0.22	+0.03	

TABLE A.2. Calculated Disequilibrium Indices Using Ground-Water Chemistry Data from La Sala and Doty (1971, Table 7)

Modeling Number	Sample Number	pH	Cation/Anion Balance %	Log AP/K				
				Calcite	Dolomite	Sepiolite	SiO ₂ (A,gl)	Allophane
5265	ARHDC1 362-712	8.5	+2.0	-0.28	-1.15	-1.29	-0.04	+1.25
5266	ARHDC1 362-890	9.6	-0.5	+0.41	+0.40	+3.17	-0.07	+0.19
5267	ARHDC1 362-1190	9.6	+0.5	+0.39	-0.32	+1.45	+0.02	
5268	ARHDC1 362-2242	9.6	-0.4	+0.50	-0.08	+2.16	-0.07	-1.17
5269	ARHDC1 450-530	8.9	-0.2	+0.01	-0.58	-0.32	-0.21	+0.26
5270	ARHDC1 540-620	8.6	-0.1	-0.20	-0.98	-1.09	-0.11	+0.40
5271	ARHDC1 636-726	8.9	+0.1	-0.03	-0.41	+0.49	-0.05	+0.16
5272	ARHDC1 720-810	9.3	-0.5	-0.04	-0.15	+3.10	+0.04	+0.28
5273	ARHDC1 980-1120	9.7	+0.8	+0.04	+0.02	+3.70	-0.05	
5274	ARHDC1 1090-1280	10.5	+8.8	+0.83	+0.18	+4.06	-0.59	-0.65
5275	ARHDC1 3146-3236	10.1	-1.8	+0.08			-0.62	-2.00
5276	ARHDC1 3166-3196	9.8	-0.2	+0.04	-0.39	+3.38	-0.32	-1.60
5277	ARHDC1 3206-3246	9.7	-1.2	-0.02	-0.44	+1.35	-0.36	-1.63

TABLE A.3. Calculated Disequilibrium Indices Using Ground-Water Chemistry Data from Van Denburgh and Santos (1965, pp. 40-91)

Modeling Number	Sample Number	pH	Cation/Anion Balance %	log AP/K			SiO ₂ (A, g/l)
				Calcite	Dolomite	Sepiolite	
5185	20	7.7	-2.7	-0.28	-0.99	-2.16	+0.08
5186	21	7.5	-1.0	-0.46	-1.18	-3.17	+0.03
5187	22	7.8	-1.0	-0.24	-0.70	-2.10	+0.01
5188	24	7.7	+5.7	-0.03	-0.12	-1.25	+0.02
5189	25	9.2	+6.0	+0.53	+0.89	+1.83	-0.48
5190	30	7.9	-2.0	+0.12	-0.12	-1.22	-0.02
5191	39	7.8	+0.0	-0.08	-0.09	-0.56	+0.06
5192	49	7.8	-1.3	-0.10	-0.21	-0.93	+0.07
5193	41	7.7	-0.1	-0.22	-0.41	-1.12	+0.07
5194	42	7.6	+0.7	-0.46	-0.93	-2.37	-0.12
5195	44	7.8	+0.4	-0.08	-0.14	-0.58	-0.00
5199	92	8.1	+2.2	+0.08	+0.11	-0.22	+0.01
5201	93	7.7	+1.1	+0.17	+0.04	-2.05	-0.08
5202	94	8.2	+0.4	-0.13	-0.34	-0.58	+0.03
5204	96	8.0	-5.4	-0.31	-0.70	-0.54	+0.14
5205	97	7.8	+2.4	-0.26	-0.68	-2.03	+0.02
5207	99	8.0	-2.7	-0.15	-2.82	-5.46	+0.23
5208	100	8.0	-2.7	-0.14	-0.28	-0.65	+0.11
5217	101	7.9	+0.2	+0.68	+1.39	+0.01	-0.03
5218	102	7.7	+4.1	+0.05	-0.14	-2.34	-0.21
5219	103	8.0	+3.6	+0.07	+0.09	-0.54	-0.00
5221	104	7.9	+1.0	-0.07	-0.27	-0.95	-0.01
5279	4	8.2	-2.2	-1.26	-0.83	-1.06	+0.17
5280	5	8.1	-0.5	-0.41	-0.87	-1.85	-0.12
5281	6	8.6	-1.2	-0.16	-0.64	+0.06	+0.04
5282	7	7.9	-1.8	-0.34	-0.40	-0.60	+0.06
5283	8	8.2	+1.1	-0.21	-0.17	-0.10	-0.05
5284	9	8	+0.1	-0.23	-0.70	-1.84	-0.08

TABLE A.3. (continued)

Modeling Number	Sample Number	pH	Cation/Anion Balance %	log AP/K			SiO ₂ (A, g/l)
				Calcite	Dolomite	Sepiolite	
5285	10	8.0	-1.2	-0.18	-0.33	-1.37	-0.12
5286	11	8.1	-2.3	-0.10	-0.29	-1.39	-0.19
5287	12	7.8	-0.6	-0.05	-0.73	-2.76	-0.07
5288	13	8.0	-1.4	-0.04	-0.27	-1.32	-0.01
5289	14	8.2	+1.9	+0.85	+1.73	+1.37	-0.14
5290	15	7.9	-0.7	-0.17	-0.39	-2.00	-0.12
5291	16	7.8	+3.0	+0.04	-0.15	-1.34	-0.04
5292	17	8.0	-2.9	-0.15	-0.51	-1.01	+0.06
5293	80	7.7	+2.3	+0.20	+0.37	-0.95	-0.13
5294	109	8.0	-0.6	-0.20	-1.33	-2.43	-0.02
5295	111	7.9	+3.2	-0.15	-0.50	-1.15	+0.06
5296	112	7.6	-2.9	-0.54	-1.20	-1.93	+0.13
5297	114	7.9	+0.8	+0.38	+0.78	-0.07	-0.03
5298	115	7.7	-0.2	+0.16	+0.37	-0.71	+0.02
5299	117	7.9	+1.0	+0.13	+0.36	-0.39	+0.04
5301	120	8.4	-1.9	+0.06	-0.23	+0.40	+0.15
5302	121	8.4	-1.7	+0.10	-0.20	+0.39	+0.15
5303	122	7.8	+3.4	+0.06	+0.07	-0.74	+0.08
5304	126	7.9	+3.0	+0.23	+0.43	-0.14	+0.11
5305	128	8.1	+2.0	+0.25	+0.58	+0.28	+0.02
5306	129	7.9	-0.4	+0.23	+0.27	-0.83	+0.05
5307	130	7.9	+1.0	+0.17	+0.43	+0.06	-0.02
5308	133	7.8	+0.6	+0.10	-0.02	-1.06	+0.08
5309	139	8.7	-0.6	-0.18	-1.30	-0.95	+0.13
5310	141	8.3	-2.3	-0.16	-0.74	-0.82	+0.13
5312	142	8.1	-1.6	-0.37	-0.97	-1.59	-0.11
5313	144	7.8	+1.0	+0.02	+0.06	-0.74	+0.02
5314	145	8.0	+0.1	-0.01	+0.08	-0.26	+0.04
5319	152	7.6	+1.0	+0.03	-0.23	-2.73	-0.09
5320	154	7.5	-0.3	-0.60	-1.45	-2.76	+0.13
5321	156	8.1	+1.6	+0.18	+0.30	+0.00	+0.09

TABLE A.3. (continued)

Modeling Number	Sample Number	pH	Cation/Anion Balance %	log AP/K			SiO ₂ (A, g/l)
				Calcite	Dolomite	Sepiolite	
5322	157	8.1	-1.0	-0.08	-0.34	-0.95	-0.01
5323	158	8.2	-0.2	+0.05	-0.12	-0.57	-0.04
5324	159	8	+1.2	+0.07	-0.11	-0.90	-0.01
5325	161	7.5	-0.2	-0.36	-1.16	-2.95	+0.04
5326	162	7.4	+0.0	-0.45	-1.05	-2.81	+0.13
5327	163	7.5	+0.3	-0.51	-1.23	-2.73	+0.09
5328	164	7.8	+1.4	+0.37	+0.51	-1.26	-0.03
5329	165	7.5	+2.7	-0.75	-1.76	-3.33	+0.00
5330	166	7.4	+0.5	-1.08	-2.35	-3.76	+0.08
5331	167	8.1	-1.1	-0.03	-0.19	-0.70	+0.04
5332	301	7.8	-1.0	-0.04	-0.17	-1.50	-0.02
5333	423	7.3	-0.9	-0.81	-2.14	-4.18	+0.14
5334	425	8.0	+0.8	+0.03	-0.24	-1.21	+0.02
5335	426	7.8	-1.3	-0.08	-0.59	-2.93	-0.41
5336	427	7.9	-0.5	-0.79	-1.98	-2.74	-0.05
5337	429	7.7	+0.6	-0.26	-0.89	-2.38	+0.07
5338	430	8.0	-2.7	-0.16	-0.48	-1.22	+0.04
5339	431	7.8	-2.4	-0.14	-0.40	-1.56	+0.03
5340	432	7.8	-1.5	-0.25	-0.82	-2.03	+0.01
5341	487	8.2	-0.1	-0.03	+0.65	-0.50	+0.10
5345	494	8.2	+0.4	+0.15	-0.03	+0.11	+0.10
5346	495	7.7	-0.5	-0.69	-1.67	-2.66	+0.10
5347	496	8.1	-3.0	-0.01	-0.44	-0.83	+0.15
5348	497	8.2	-1.2	+0.14	+0.04	+0.21	+0.05
5349	498	8.2	+0.4	+0.11	-0.11	-0.49	-0.01
5352	503	8.0	+1.2	-0.30	-0.89	-1.18	+0.12
5353	546	7.7	-1.7	-0.42	-0.79	-1.27	-0.03
5354	548	7.9	-1.7	-0.47	-1.19	-1.76	+0.09
5355	549	7.9	+0.2	-0.58	-1.23	-1.78	-0.09
5356	559	7.9	+0.0	-0.23	-0.37	-0.77	+0.01
5357	561	7.7	-1.3	-0.40	-0.88	-1.00	+0.02

TABLE A.4. Calculated Disequilibrium Indices Using Ground-Water Chemistry
Data from Apps et al. (1979, Table III-2)

Modeling Number	Well Designation	pH	Cation/Anion Balance %	Log AP/K					
				E_{pt}^H (V)	Calcite	Dolomite	Sepiolite	SiO ₂ (A,gl)	Fe(OH) ₃ (A)
5468	DC-2	9.9	-0.1	-0.05	-0.39			-0.16	+0.24
5555	DC-6	10.1	+4.7	-0.03	+0.07	+0.63	+6.27	-0.74	-0.02
5556	Ford Well	8.0	-11.7	+0.15	+0.07	+0.11	-0.35	-0.02	+1.99
5557	McGee Well	8.0	-7.9	+0.09	+0.09	+0.08	-0.23	-0.04	+1.22

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