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APPENDIX D

SUPPORT INFORMATION

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Conversion Table

To convert from	Multiply by	To convert to metric*
Inches	25.4	Millimeters
Inches	2.54	Centimeters
Feet	0.305	Meters
Miles	1.61	Kilometers
Acres	0.40	Hectares
Gallons	0.00379	Milliliters
Gallons	3.79	Liters
Ounces	0.028	grams
Pounds	.454	Kilograms
Atmospheres	0.1013	Megapascals

* To convert <u>from</u> metric, divide by factor in center column.

To convert from degrees Fahrenheit	Subtract 32 and multiply by 0.56	To convert to degrees Centrigrade

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EXPLANATION OF CHEMICAL SYMBOLS AND UNIT ABBREVIATIONS

Chemical Symbols

Al aluminum
As arsenic
Ba barium
Ca calcium
Cd cadmium
Cl chlorine or chloride
Cr chromium or chrome
Cu copper
F fluorine or fluoride
Fe iron
H hydrogen
^{2}H deuterium
^{3}H tritium
K potassium
Mg magnesium
Mn manganese
Mo molybdenum
N nitrogen
Na sodium
O oxygen
P phosphorous
Pb lead
S sulfur
Si silicon or silica
Sr strontium
U uranium
V vanadium
Zn zinc

Unit Abbreviations

mm millimeter
cm centimeter
km kilometer
mg milligram
g gram
kg kilogram
ml milliliter
l liter
hc hectare
MPa megapascal
°C degrees Centigrade

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1.0 GROUNDWATER AGE CALCULATIONS

The age or residence time, T, of groundwater was calculated from tritium and/or carbon-14 contents using the following equation:

$$T = -8{,}270 \ln(A_m/A_o) \quad (1)$$

where initial activity (A_o) is taken as 75 pmc (pmc = percent modern carbon) (Mazor 1986) for the spring water samples.

This assignment is supported by the analysis of tritium and carbon-14 in 30 spring water samples (at 9 sites) collected from the study area (Chapter 4.0, Figure 4-1) during the same period as the well water samples were collected. A linear regression of tritium and percent modern carbon for the spring samples yields 74 percent modern carbon for the 0.5 turbidity unit intercept and 78 percent modern carbon for the 1 turbidity unit intercept. This correction allows for bomb-produced carbon-14 as well as for equilibration with dead carbon in the soil profile. (Bomb produced carbon-14 explains the greater than 100 pmc for surface water and springs shown in Chapter 5.0, Table 5-2). The delta carbon-13 for the spring samples ranged from -16 o/oo to -11 o/oo while the four wells ranged from -14 o/oo to -10 o/oo. Thus, a stable carbon isotope correction is not considered significant in this case (Mazor 1986).

The appropriate A_o for the groundwater samples is more difficult to assign for two reasons: (1) recharge water to the unconfined aquifer probably consists of spring water that might have reemerged and or reequilibrated with the atmospheric carbon dioxide and (2) percolation through the vadose zone along the margin of the sample site might have come in contact with soil carbonate (caliche, etc.).

In those cases where it is clear that pre-industrial age groundwater carbon-14 concentrations are involved, an alternative is to assume that all of the CO_2-^{14}C in infiltrating water reacts with soil carbonate. Under these conditions, one mole of CO_2-^{14}C is consumed per mole of calcium carbonate. Assuming no carbon-14 in the soil carbonate, the A_o is 50 percent of the initial value in atmospheric/recharge water. If this were the case, however, it is difficult to explain how one of the wells (24-95) is significantly above 50 percent modern carbon (i.e., 71 percent modern carbon). Thus, age estimates for the unconfined aquifer are calculated using an A_o of 75 percent modern carbon. A value of about 85 +/- 5 percent modern carbon has been suggested to be appropriate for shallow groundwater systems in temperate climates. However, because of this uncertainty, an absolute age cannot be calculated using the carbon-14 method. However, the calculated ages might provide some indication of relative or approximate residence times for groundwater and thus, time available for rock-water reaction or equilibration.

It also should be noted that Bard et al. (1990) recently recommended carbon-14 time scale corrections because of the oscillations in the atmospheric production rate of carbon-14 over the last 20 to 30,000 years.

Thus, there might be some shift in calculated ages shown above by +/- 10 to 15 percent (Bard et al. 1990). However, in view of these uncertainties, this refinement was not considered significant for purposes of this document.

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2.0 REDUCTION-OXIDATION COUPLES AND BACTERIAL MEDIATION

The existence of reducing conditions in the unconfined suprabasalt aquifer is, at least in part, due to a combination of inorganic oxidation-reduction (redox) reactions (oxygen exclusion) and/or bacterial respiration. It is indicated from the relatively low carbon-14 contents in samples from these wells (Chapter 4.0, Table 4.12B) (with modern carbon values approaching 5 percent) that the sampled portions of the aquifer were effectively 'shielded' from the diffusion of atmospheric gases into the aquifer. This could be due in part to the extended perforated intervals [about 50 feet (915 meters)] and sample pump depth.

Under these conditions, microbial degradation of dissolved and/or sediment-bound organic matter would deplete the dissolved oxygen originally present in aquifer recharge water. Additionally, methanogenesis could contribute to the reducing conditions. For example, methanogens reduce bicarbonate to methane, which might also result in negative oxidation reduction potential value. Although methane was not analyzed in samples evaluated for this study, there is good isotopic evidence for biogenic methane production by this mechanism within the upper Ellensburg Formation beneath the Hanford Site, including some sedimentary interbeds (Johnson et al. 1991; McKinley 1990). Because the Ringold Formation and sedimentary interbeds of the uppermost Ellensburg Formation are thought to have similar properties, and given the apparent exclusion of atmospheric gases for at least the wells with negative oxidation reduction potential values, methanogenesis might occur in the Rattlesnake Ridge interbed and portions of the Ringold Formation.

A diverse microbial community exists in most subsurface environments, with one or more bacterial metabolic groups dominating in numbers and impact in response to environmental factors. In oxygenated systems, for example, the dominate bacteria uses oxygen to oxidize organic matter. In anaerobic systems, dominant bacteria will be those using ferric iron ($Fe^{3+} \rightarrow Fe^{2+}$), sulfate ($SO_4^{-2} \rightarrow H_2S$) or other redox couples will dominate. The bacteria (methanogens) producing methane from dissimilation of acetate ($C_2H_4O_2 \rightarrow CO_2 + CH_4$), for example, are easily dominated by sulfate reducing bacteria in systems where sulfate is abundant. Although methanogens might be present in such systems, methanogens will only exert a dominant effect in systems where more energetically favored transitions are not possible. Direct culturing of artesian water from confined aquifers has produced coexistent iron reducing, sulfate reducing, and methanogenic bacteria from the Ellensburg Formation (Stevens et al. 1992). Cultured samples from the unsaturated zone in the Hanford and Ringold Formations at the Yakima Barricade also produced a diverse microbial community (Ghiorse and Wilson 1988). The nature and extent of microbial activity in the saturated zone of the Ringold Formation is undetermined.

The presence of elevated iron and manganese, and some very low nitrate concentrations (0.5 parts per million) in some of the wells, provides circumstantial evidence for bacteria/redox controls. Specific measurements for redox couples would be needed for confirmation of such conditions in the target aquifers. However, it has long been known that certain bacteria are in

general capable of reducing the higher oxidation states of several elements of interest (Bowen 1966). Furthermore, in view of the large number of species of bacteria and their well known occurrence in a wide range of aquatic environments (from hot springs to deep sea sediments), the presence of bacterial populations in Hanford Site unconfined groundwater should come as no surprise.

In addition to the obvious or direct regulatory implications for manganese and iron noted previously (Chapter 4.0, Figure 4.1.3), the existence of reducing conditions in the suprabasalt and upper confined aquifer might have an important influence on the mobility of certain radioactive waste constituents in Hanford Site groundwater (e.g., radioisotopes of uranium, plutonium, technetium, neptunium, americium, and selenium).

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3.0 SUMMARY OF RECHARGE STUDIES AT THE HANFORD SITE

Potential recharge at the Hanford Site is not homogeneous with respect to location, and is in part defined by soil type and extent of plant cover. An area with coarse soil and little vegetation affords rapid migration of water to depth. In areas of fine, organic-rich soils with abundant plant cover, infiltration might be inhibited entirely by evapotranspiration. A model study of recharge (Bauer and Vaccaro 1990) indicated that mean annual recharge due to rainfall was in the range of 0.25 to 1.27 cm/yr. As indicated in Figure 3-1, taken from Bauer and Vaccaro (1990), the areas of highest potential infiltration are on or adjacent to Rattlesnake Mountain and along the Columbia River north of the city of Richland.

Groundwater flow across the Hanford Site is generally from west to east. Recharge resulting directly from rainfall infiltration within the Hanford Site is very limited. Ongoing studies on infiltration suggest that there might be essentially no annual recharge from this source.

A number of estimates of recharge rates have been made or attempted for the Hanford Site. Murphy et al. (1991) found recharge at a location near the Yakima barricade to be negligible based on the soil chloride profile showing that no modern-day recharge has occurred at that location. Given the low estimates of recharge across the Hanford Site (Table 3-1), infiltration of rainfall accompanied by evaporation as an effective modifier of groundwater compositions is considered to be unlikely.

Other estimates of recharge near the Hanford Site have been based on modeling studies as well as measurements of environmental variables using lysimeters and ^{3}H soil profiles. As discussed in Murphy et al. (1991), modeling studies provide Hanford Site-wide recharge estimates, while field studies provide recharge estimates at particular study sites within the Hanford Site.

Modeling studies rely on the estimation of the magnitude of known environmental effects to estimate the fraction of incoming precipitation that reaches the water table. Several models have been applied at the Hanford Site, as summarized in Table 3-2. The Morton Model (Morton 1975) uses a simple water balance approach to determine recharge, given mean atmospheric pressure, precipitation, air and dew-point temperature, and the ratio of observed to maximum possible sunshine. The USGS model was applied to Hanford Site grid elements of variable size for which simulations of snow accumulation and snowmelt, precipitation, run-off, evaporation from plant cover, evaporation from bare soil, and plant transpiration were simulated. Mean recharge was estimated to be 0.25-1.27 cm/yr, but recharge was estimated at 2.54-5.08 cm/yr in the vicinity of Rattlesnake mountain. The model UNSAT-H (Morton 1975) uses climate, soil, and plant data to generate values for infiltration, evaporation, redistribution, and drainage. In this approach, soil texture has a marked impact on recharge.

Results of each model, as summarized in Table 3-2, give a maximum Hanford-wide recharge of 1.1-1.3 cm/yr. Modeled recharge in both the USGS and

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UNSAT-H models is soil-texture dependent, with coarse-grained sedimentary cover producing a higher level of recharge than a sedimentary cover with a fine-grained component.

Lysimeter studies at the Hanford Site, summarized in Table 3-2, indicate that recharge varies from less than measurable amounts in areas covered by fine soil with deep-rooted plants to more than 50 percent of annual precipitation in unvegetated areas with coarse soil. Gee and Hillel (1988) estimated that extreme events (e.g., rapid snowmelt) could result in local recharge in excess of annual precipitation. As indicated by the results for two soil types included in Table 3-2, vegetation, as well as soil texture, is important in determining recharge; vegetated Warden silt-loam cover resulted in zero local recharge, while bare Quincy sand cover resulted in recharge of 5-10 cm yr-1 at the sites tested. Quincy sand is the most widely distributed soil type on the Hanford Site.

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4.0 GEOCHEMICAL MODELING

Geochemical modeling and other theoretical considerations can be useful in constraining groundwater conceptual models and interpretations of chemical and isotopic data within the limitations of the techniques. However, the use of such models is limited by the availability and quality of thermodynamic data necessary for equilibrium calculations and also by reaction kinetics, which might be more important than equilibrium in determining chemical compositions in low-temperature, dynamic systems.

Geochemical modeling of Hanford Site groundwater was done as part of the BWIP repository characterization effort (Early et al. 1984). The primary interest for repository studies was the deep basalt aquifers; however, shallow groundwater and springs also were included in these studies. In addition, groundwater in the confined Grande Ronde aquifer in the surrounding Columbia Plateau, which in part has a range of chemical compositions similar to that of shallow Hanford Site groundwater, was modeled using several geochemical codes (Warner 1986).

The major findings of these studies that are relevant to the natural background study are summarized in the following sections.

4.1 HANFORD SITE SPRINGS AND VICINITY GROUNDWATER

Several dozen spring water samples and over 100 groundwater samples were evaluated using the computer code WATEQ2 (Deutsch et al. 1982) and MINTEQ (Krupka and Jenne 1982; Early et al. 1984). Solubility calculations were performed at ambient environmental temperatures and pH for the Hanford Site and at contiguous locations.

Results of these modeling efforts suggest springs and shallow groundwater are at or near saturation with respect to amorphous silica and perhaps allophane, while deeper groundwater appear to be undersaturated with respect to these phases. The apparent undersaturation is probably a result of much higher solubility limits in the deeper groundwater. These higher solubility limits might be, at least in part, a result of higher temperatures in the deeper aquifers; however, the principal effect is almost certainly a result of the higher pH (greater than 9) in the deeper groundwater (DOE 1988).

Springs and shallow groundwaters are undersaturated with respect to calcite and fluorite; however, these phases tend to reach saturation at depth. The saturation with respect to calcite will be affected by increasing depth because calcite solubility decreases with increasing temperature and pH. In addition, contribution of bicarbonate from ongoing leaching of basalt materials or microbial activity might play a role. In general, bicarbonate concentrations decrease with depth in the confined aquifer as does calcium (DOE 1988). Saturation with respect to calcite (and fluorite, by inference), apparently is maintained by calcite precipitation at elevated temperature and pH, with cation exchange also acting to remove calcium from solution.

Nearly all the clay minerals and zeolites in the MINTEQ database are oversaturated in groundwaters from all stratigraphic zones, including the unconfined aquifer. The latter observation suggests that if these mineral phases are forming within the aquifers, the related solute concentrations in the groundwaters are controlled by kinetic rather than equilibrium effects.

Ion exchange reactions involving clays and zeolites could modify groundwater chemical composition (e.g., exchange of calcium and magnesium and other divalent ions for sodium and potassium in mineral phases).

The extent of equilibrium with respect to calcite is important because of the influence of calcite dissolution or precipitation on groundwater composition. The concentration of bicarbonate affects pH, which is a major determinant of solubility and reaction rate controlling precipitation of secondary minerals and dissolution of solid phases. In addition, bicarbonate strongly complexes some metal ions including uranyl (UO_2^{2+}), enhancing their mobility. Dissolution and or precipitation of minerals, including calcite, might affect permeability within the aquifer. Surface waters and shallow groundwaters are undersaturated with respect to calcite. The depth at which calcite becomes a solubility-limited phase and the geographic variation in this depth are not known for the unconfined Hanford aquifer. Sampling over the entire depth of the aquifer has been accomplished in only a restricted number of locations; none of these locations have been characterized in detail.

In addition to implications for controls on chemical composition, undersaturation with respect to calcite suggests that loss of bicarbonate along the flow path by precipitation of calcium carbonate is unlikely in the area of interest for the background study. Dissolution of sedimentary carbonate in the unconfined aquifer does not appear to be likely because the stable carbon isotopic composition does not vary systematically from the recharge area (springs) to downgradient locations in the unconfined aquifer (Chapter 5.0, Table 5-2). If sedimentary carbonate in the aquifer were either dissolving or undergoing isotopic exchange, the del carbon-13 values would become heavier (more positive; i.e, shift from negative to positive values).

4.2 COLUMBIA PLATEAU BASALT AQUIFERS

Approximately 100 samples from the Columbia Plateau acquired by the USGS (Hearn et al. 1985) were modeled using MINTEQ, mass balance, and EQ3/6 reaction path models (Warner 1986). The aquifer examined was in the Grande Ronde basalts in a large area upgradient and much shallower than the same aquifer at the Hanford Site (i.e., to the north and east of the Hanford Site, in the Spokane vicinity). This aquifer might represent an immature analog of the Hanford Site groundwaters. In contrast to the results of modeling Hanford Site groundwaters, the aqueous speciation/solubility calculations for the Grande Ronde aquifer samples suggest that these waters are undersaturated with respect to amorphous silica, but are oversaturated with respect to silicate minerals. This apparent difference for silica saturation could be due to differences in physical conditions between the two systems, or differences in the thermochemical data in the databases used for the calculations. The

ambiguity inherent in geochemical modeling of solubility controls on dissolved silica is compounded by the interpretational ambiguity introduced by the contradictions between the two studies. The conceptual model of Hearn et al. (1985) presented the basalt-water system as a dynamic interaction of ongoing dissolution of primary (unstable) basaltic glass and minerals, with concurrent precipitation of secondary (stable or metastable) phases including smectite, silica polymorphs, and other minerals. Warner (1986) concluded that undersaturation for amorphous silica in the Grande Ronde aquifer suggests that conditions are favorable for regional dissolution of basaltic glass. Warner (1986) also found this aquifer was undersaturated with respect to calcite near the assumed recharge areas, but reached equilibrium at greater downgradient distances.

4.3 RELATIONSHIP TO BACKGROUND STUDY AREA

Chemical characteristics of the Grande Ronde aquifer near areas of recharge represent chemically immature precursors to deep groundwater at Hanford. This shallow confined groundwater inherits its composition from interaction with basalt glass and mineral phases. To the extent of similarity between this groundwater and unconfined groundwaters, the same process may be considered to be responsible for compositions of both: shallow interaction of meteoric water with basalt determines in part unconfined aquifer compositions. This hypothesis is also consistent with similarities in sample depths and solid phase compositions. With respect to interactive effects on groundwater, the Grande Ronde, Wanapum, and Saddle Mountain Basalts are compositionally similar (Hoover and Murphy 1989; Lambert et al. 1989). Recharge distances to sampled compositions for the Grande Ronde Aquifer are within 20 kilometers and sampled depths are less than 250 feet, similar to expected distances and depths for the unconfined aquifer at Hanford.

The above considerations suggest that springs (and/or surface run-off initially in contact with basaltic rock) represent major input source type to the unconfined aquifer which undergoes relatively little additional modification after a relatively long residence time in the unconfined aquifer. This scenario is reasonable if the initial reaction of recharge water for the unconfined aquifer is the basalt that forms the ridges on the western border of the Hanford Site. Dilute acid, formed from carbon dioxide in the meteoric water, would be neutralized by reaction with basalt, giving the groundwater its initial chemical imprint. Subsequent modification of groundwater along flowpaths by processes such as mixing with other waters, dissolution of evaporites, and mineral activity must be evaluated.

4.4 REACTION PATH MODELING

Simple equilibrium reaction path calculations (EQ3/6) and nonthermodynamic mass balance calculations suggest the basalt aquifer hydrochemistry on the plateau can evolve by glass hydrolysis and formation of calcium-zeolites, iron-calcium-magnesium smectites, and pyrite (Warner 1986). Chemical modeling also indicates that the deep Hanford sodium-chloride facies

may not result from dissolution of basalt alone and may have a deeper source as proposed by Early and Solomon (1985).

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5.0 ROCK-WATER REACTION LABORATORY STUDIES

Laboratory testing and experiments on rock-water reactions are important sources of data and information that provides a basis for understanding the natural composition of groundwater. Data obtained from laboratory tests have been used to develop and refine the scientific basis for understanding the principles of chemical reaction between water and geologic materials, and to also obtain site- or case specific information on rock-water reactions for comparison to natural systems.

The relevance of on rock-water reaction tests to groundwater background studies at the Hanford Site is that they are capable of providing fundamental information on:

- The extent to which compositional variability in groundwater composition due to rock-water reaction can be expected to occur naturally within the aquifer

- Spatial relationships and scale of compositional variation due to rock-water reactions

- The upper concentrations that can be expected to occur in the aquifer and the processes that control these concentrations.

Rock-water reaction is the most fundamental process in the evolution of groundwater composition because the primary source of most total dissolved solids in groundwater is from the dissolution of geologic materials in the aquifer. Rock-water tests in the laboratory provide a basis for evaluating the extent to which these processes and/or other processes adequately explain the composition of groundwater by isolating the effects of rock-water reaction from those of other processes, provided the tests are well designed and can be correctly interpreted. An understanding of the nature of the reactions that occur also provides valuable information on the extent of natural variability and constituent concentration levels that can be expected to exist naturally in the groundwater.

Experiments on silicate mineral dissolution in aqueous systems reported in the literature generally fall into two categories: (1) experiments involving dissolution systems where water and minerals are reacted in containers in which there is no flow-through (e.g., Garrels and Howard 1957; Wollast 1967; Houston 1972); and (2) experiments in which water is passed through mineral materials packed as porous media in cylindrical containers (e.g., Bricker 1967; Bricker et al. 1968; Deju 1971). It is indicated from the results of experiments in both categories that the dissolution of minerals such as feldspars and micas proceeds in two main stages. The first stage involves the exchange of cations on the mineral surfaces for hydrogen ions in the water, and occurs in a matter of minutes. This exchange is followed by a much slower and gradually decreasing rate of dissolution. This dissolution stage contributes an appreciable amount of dissolved products to the water over a period of hours or days before the net transfer of cations and anions from the solid to the liquid becomes extremely small. Dissolution during the

first stage of dissolution is normally congruent. During the second stage, dissolution gradually becomes incongruent (Freeze and Cherry 1979).

Although the general nature of reactions in simple systems such as feldspar and water are well known and documented in the literature (e.g., Aagaard and Helgeson 1982; Helgeson et al. 1984), laboratory tests involving more complex systems are largely restricted to site-specific studies. To date, most laboratory tests on rock-water reactions pertaining to the natural composition of groundwater at the Hanford Site have been limited to basalt-water systems.

The extent to which the results of laboratory tests may be useful for the characterization of natural groundwater compositions depends on the nature of the tests and the extent to which the data represent natural groundwaters or natural processes that influence groundwater composition. The results of previous rock-water reaction studies and the results of new tests involving basalt and Ringold sediment are summarized in the following sections.

5.1 PREVIOUS STUDIES

Several laboratory test programs were initiated in conjunction with the BWIP to evaluate reactions between Columbia River basalt and water (e.g., Lane et al. 1984; Moore et al. 1985). The results of these tests are useful in that they provide a source of information on the nature of rock-water reactions specific to the confined aquifer and to basaltic systems. The applicability of these data for the purpose of this report are limited, however, because these tests were designed and carried out primarily to evaluate hydrothermal reaction with fractured basalt in a simulated high level radioactive waste repository environment. Much of this data is not relevant to evaluations of the chemistry of the natural aquifer environment because the phase relationships, reaction paths, and solubilities at temperatures of 100 °C to 300 °C and pressures up to 30 MPa differ significantly from those of groundwater. Factors such as the use of synthetic confined aquifer groundwater as starting material and high water:rock ratios limit the use of these data for purposes other than those for which the tests were designed. The results of much of this work have not been published, or is of limited value because of the lack of specific information regarding test conditions and raw data on tests results.

Example of laboratory test results that potentially provide useful information include unpublished results of column recirculation tests using crushed Grande Ronde Basalt and natural groundwater at 85 °C, and the experimental results of McKinley (1990). The results of two recirculation tests, approximately 3 months in duration, provide information on chloride to fluoride release ratios, which were found to be approximately 2.6:1 for these tests.

Laboratory studies of basalt-water reactions designed to evaluate the evolution of groundwater in the confined aquifer in the Pasco Basin have been reported by McKinley (1990). These studies was performed using crushed Grande Ronde Basalt and deionized water reacted up to three months in a

internally-stirred direct-sampling autoclave at 85 °C. Although these tests were designed for the evaluation of basalt-water reaction in the fractured basalt in the confined aquifer (initial water rock ratio of 10:1 by mass) these results provide a baseline for basalt-water reactions. These results together with information on natural groundwater compositions in the confined aquifer provides a baseline for comparison to groundwater compositions in the unconfined aquifer, particularly those consisting of basaltic sediment. These data are also applicable to evaluations of the unconfined aquifer because basaltic material is common in the clastic matrix material in the Ringold aquifer, and also because this basaltic material is the principal source of many of the constituents of concern in the groundwater (e.g., F, Cl, Ba, Pb, As, Zn, Cd, V).

McKinley concluded that the composition of groundwater in the Columbia River Basalt confined aquifer beneath the Hanford Site reflected four main processes, each having distinct compositional characteristics. These processes are: (1) prograde rock-water interaction with basalt in the shallower parts of the aquifer, (2) mixing with brine resulting from the dissolution of evaporites (NaCl) from interbeds deeper in the aquifer, (3) sulfanogenisis/microbial processes, and (4) a systematic pattern of lower Mg and Ca concentrations with reaction in progressively deeper parts of the aquifer due to the stabilization of secondary clay minerals and ion-exchange.

Experimentally produced water compositions were seen to have temporal reaction progress trends in solute concentrations similar to trends seen in groundwater composition in the confined aquifer. The following were interpreted as the key steps in basalt-water alteration reactions:

- Initial congruent dissolution reactions involving stoichiometric contributions of most major constituents (Si, Na, K, Ca, Mg, Fe, and Al) to solution and attendant saturation or near saturation of silica

- Increase in pH from near-neutral to a maximum of 8.9

- Initial increase in essentially all solute components except for Al, and Fe, ±Si to maximum values before the onset of carbonate/clay precipitation

- Precipitation of saponite, clinoptolite, silica, and calcite cause Ca and Mg to decline, removing Fe and Al from solution, and stabilizing concentrations of constituents with solubility limit controls (e.g., Si)

- Residual Si, Na, and K remain in solution

- Secondary trend of progressively decreasing concentrations of Mg and Ca resulting from the subsequent stabilization of secondary clay minerals (smectite) and a shift of concentration controls from dissolution to lower solubility limit controls for Mg; decreasing Ca due to the stability of carbonate ±zeolite stability, and ion exchange for Na with Ca in double-layer clays

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- Attenuated increase in Na (±K) concentrations with reaction progress associated with the release of Na and K from the hydration of basaltic glass to palagonitic montmorillonite.

McKinley (1990) also concluded that the alteration of basalt by metoric water can explain the variation of groundwater chemistry (except for Cl in the deeper groundwaters), and that water-rock interaction operates continuously along groundwater flowpaths. These flowpaths were interpreted to be approximated by sampling depth. In general, the compositional characteristics of groundwater in the upper parts of the confined aquifer were concluded to be similar to those in the unconfined aquifer, in that both appear to be the result of the earlier stages/parts of reaction paths with basalt plus or minus other silicate material, primarily dominated by dissolution. Evidence for prograde rock-water interaction was suggested to be the dissolution of pyroxene (augite), plagioclase, and the hydration of glass in the basalt as the primary source for most constituents in the groundwater as well as in the water compositions from the laboratory tests. The dissolution process results in attendant initial trends of increasing concentrations of Ca, Mg, Si, and most minor elements.

5.2 NEW STUDIES

Some new analyses and scoping studies were initiated in conjunction with the Site-wide soil and groundwater background data compilation and characterization efforts. These efforts were initiated to provide fundamental information on the compositional characteristics of soil and aquifer materials and to also provide baseline information regarding the nature of rock-water interaction controls on the composition of groundwater in the unconfined aquifer. The design of the scoping studies used the data quality objectives process for the Site-wide background activities and represent some of the first studies to provide results that pertain directly on the compositional evolution of groundwater in the unconfined aquifer beneath the Hanford Site.

The objectives of these tests, starting materials, test conditions and parameters for these tests are described in Sections 5.3.1 and 5.3.2. The results of these tests are summarized in Tables 5-1 through 5-3 where the compositions of water reacted with basalt and with Ringold sediment as a function of time and test conditions are tabulated. A synopsis of the these test results is described in the following Section.

5.2.1 General Test Objectives

The objectives of these tests were to evaluate the compositional characteristics associated with rock-water reactions specific to the aquifer materials at the Hanford Site and to provide a basis for evaluating the extent to which these reactions influence the composition of groundwater in this region. A small number of tests were designed to provide baseline information on water composition, constituent ratios, and the manner in which water chemistry varies with reaction time and flow conditions by bracketing the range of physical conditions that occur in the aquifer. Data from these tests

are also intended to aid in determining the extent to which natural groundwater compositions reflect predictable site-specific reaction path compositions, and the extent to which such reaction paths lead to steady state or equilibrium compositions.

The test design involved the systematic variation of key parameters while controlling other conditions of the tests to understand the respective roles of these parameters in the system. The key parameters varied in these tests include: solid starting materials, reaction time, reaction kinetics (open versus closed system reaction), and initial atmosphere composition. Parameters controlled in these tests include rock:water ratios, temperature, particle size, and rate of water flow.

Basalt and Middle Ringold sediment were selected as starting materials to bracket the expected range of solid reactants present in the unconfined aquifer, and those expected to participate in rock-water reactions (Section 5.3.2.1). Basalt also was chosen because it is a major component in upper parts of the aquifer where the Hanford formation is within the saturated zone, and also because sand to silt sized basaltic material appears to be a subordinate, but ubiquitous component in the matrix and interbed material of the Middle Ringold sediments.

5.2.2 Test Conditions

Two main types of tests were performed: (1) tests in which water and solid starting materials were allowed to react continuously for various amounts of time in sealed containers (Figure 5-1), and (2) tests in which successive volumes of water were passed through porous solid starting material, with samples of the 'leachate' water collected for analysis (Figure 5-2). The first type of test is intended to simulate rock-water reactions that occur under conditions of stagnant or restricted flow, and are referred to here as 'closed-system' tests. The second category of tests, performed in permeameter vessels, are intended to simulate conditions of dynamic flow through porous solid media such as an aquifer, and are referred to here as 'open-system' tests. All of these tests were performed at room temperature (23 °C).

Two other types of tests were also performed: a hydrothermal test using basalt, and closed system reaction tests with basalt and Ringold sediment previously reacted (flushed) in the open system flow-through test.

The hybrid open-closed system tests were conducted to determine the extent to which aquifer materials previously flushed of their more readily soluble components could further react under conditions of restricted flow static reaction, and to compare the water composition from these tests to those of groundwater in the springs and unconfined aquifer. These tests were primarily motivated by the observation that the compositions of the waters resulting from the open and closed tests bracket most of the natural groundwaters. However, few of these experimentally produced waters actually resemble natural groundwater compositions. These tests are, therefore, designed to evaluate the extent to which the relatively uniform compositions

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obtained in the open-system tests represented dynamic equilibrium or steady state concentrations corresponding to reaction progress leading to equilibrium compositions. The results of these tests are summarized in Table 5-4.

The primary objective of the hydrothermal test was to determine if solute concentrations resulting from reaction with basalt become significantly larger at elevated temperatures than those reacted at room temperature, because reaction progress is known to increase with temperature (e.g., Aagaard and Helgeson 1982; Rimstidt and Barnes 1980). This test potentially provides information on the upper limit of constituent solubilities compared to those produced by reaction in tests of up to 128 days. This information may be useful in determining the extent to which the composition of highly evolved groundwater in the unconfined aquifer might be expected to approach groundwater compositions in the confined aquifer, recognizing potential differences in phase relationships and the temperature and compositional dependence on solubility controls.

5.2.2.1 Starting Materials. Two types of solid starting materials were reacted with water in both the open and closed system tests: (1) crushed basalt, and (2) Ringold Formation matrix material. These materials were selected as starting materials in order to bracket the expected range of solid reactants present in the unconfined aquifer, and those expected to participate in rock-water reactions.

5.2.2.1.1 Water. Deionized water (DIW) was used as starting material in all tests to ensure uniformity and comparability of results between open and closed systems tests, and also as the most effective choice of a reference composition for measuring the evolution of water chemistry with reaction path progress.

5.2.2.1.2 Basalt. Basaltic material was chosen as a starting material because (1) it is a common and nearly ubiquitous component throughout much of the matrix of the Hanford and Ringold Formation sediments within the saturated zone, (2) basalt is the aquifer material for springs that serve as a primary recharge source to both the confined and unconfined and aquifers, and (3) it is the aquifer material in the underlying confined aquifer. Basaltic material is also the primary natural source of many of the constituents of concern for environmental activities involving groundwater (e.g., heavy metals, transition metals, halogens, sulfur).

Columbia River Basalt from the Umtanum flow of the Grande Ronde Basalt flows was chosen primarily because it has been extremely well characterized in terms of its bulk and leachate compositions for major and trace constituents, and also because the mineralogy, mineral and glass composition, and petrology of Grande Ronde Basalt (Table 5-5) has also been well characterized (e.g., Nelson 1989; Hoover and Murphy 1989). It is indicated from the results of previous work that this basalt is remarkably uniform in composition throughout its thickness. More recent work also has indicated that this basalt is chemically homogenous (Table 5-6).

The Umtanum basalt was prepared initially for testing and analysis by crushing, sorting, and seiving into six size fractions and a pan fraction at

Washington State University, Department of Geological Sciences. After crushing, all material with weathered surfaces or bearing crusher marks was removed. Approximately 10 kg was processed to yield material for these size fractions. A uniform size fraction (0.25 mm diameter; phi size = 2; fine to medium grained sand-size) was used as starting material for the water leach tests. The bulk composition and EPA digestate composition were determined for this and all other size fractions. Results of these analyses are listed in Table 5-7.

5.2.2.1.3 Ringold Sediment. Clastic sediment and matrix material from the Ringold Formation was chosen as the second type of solid starting material because the unconfined aquifer beneath the Hanford Site consists primarily of Ringold Formation sediments. This starting material was collected from Middle Ringold sediments on the east side of the Columbia River. Approximately equal proportions of sand to silty clay-sized material were collected from three localities at this outcrop, and composited for use as the starting material. This part of the Ringold sequence was chosen because the Middle Ringold sediments comprise much of the upper part of the unconfined aquifer beneath much of the Hanford Site (DOE 1988, v.2; Jensen et al. 1986; Landon and Bjornstead 1986). Also, the samples collected at these three localities would represent the most porous and permeable materials in an aquifer environment. This consideration is important because groundwater would be expected to flow through and react most extensively with the most porous and permeable parts of the aquifer, and especially those in the upper parts of the aquifer where hydraulic conductivity is generally regarded as relatively large (Lindsay and Gaylord 1989; Lindsay 1991).

The three localities chosen for the composited Middle Ringold starting material include: (1) sand-sized matrix material within the predominately pebble- to cobble-sized matrix supported conglomerate, (2) light-yellow to white sandy silt lens within the conglomerate, and (3) a light grey-tan fine silt to clay-sized lens within the conglomerate. Care was taken at each locality to appropriately clean and prepare the sampling site by excavating about 0.3 meter into the exposed outcrop to obtain a sample with minimal potential for surficial influences. About 1 kg of each type of material was collected for the composite sample. About 2 kg of the composite sample was submitted for water leach testing, and 50-gram splits were submitted for chemical analysis according to EPA soil analysis protocols (EPA 1986; EPA 1989c), and for bulk chemical analysis by X-ray fluorescence spectroscopy methods at Washington State University, Department of Geological Sciences. Results of these analyses are listed in Table 5-8.

5.2.2.2 Analysis of Run Products. The aqueous fluids were removed from each of these tests by placing the run products in a 0.45 micron filter and separating the fluid by vacuum extraction methods. About 30 to 50 ml of water leachate was recoverable for tests with basaltic material. However, only about 20 ml of water leachate was recoverable from the tests with Ringold sediment. These volumes of water leachate were sufficient for chemical analyses of the samples.

The filtered water run products were analyzed for the cations identified in EPA protocols (e.g., EPA 1990), and for nitrate, sulfate, alkalinity,

chloride, and fluoride at Pacific Northwest Laboratory's Chemical Measurements Laboratory using Pacific Northwest Laboratory procedures. Analyses were performed using inductively coupled argon plasma emission spectroscopy methods for cation analyses, and ion chromatography and specific ion electrode methods for anions. Selected samples also were analyzed for Cr, Mn, Cu, Zn, As, Sr, Mo, Cd, Ba, and Pb using inductively-coupled plasma mass spectrometry (ICP-MS) methods. Chemical analyses of the run products for these tests are summarized in Table 5-8.

All water leach tests were performed using DIW as the initial starting material. The DIW also was handled and processed as a blank, in the same manner as test samples, but without the addition of sediment. These samples serve as test blanks and checks on the composition of the initial starting fluid.

5.2.2.3 Closed System Rock-Water Reaction Test Design. A total of at least 18 reaction tests for each type of solid starting material were performed; eight with both basalt and Ringold sediment in a nitrogen atmosphere, and 10 with both types of solid starting materials in air for a total of 36 closed system reaction tests (Figure 5-1). The two additional tests with a 1-hour and a 6-hour duration were run using both types of solids with an air headspace. Eighteen separate aliquots of crushed basalt 0.25 mm to 0.50 mm in diameter (2 phi) and Ringold sediment were reacted with DIW for periods ranging from 1 hour to 128 days (Table 5-1). These tests were performed in 120 ml glass bottles washed with DIW and oven dried before use. The bottles were loaded with 120 grams of solid starting material and 60 ml of DIW, and tightly sealed with Teflon*-lined caps. Both the basalt and Ringold sediment starting material were mechanically split into 22 equal aliquots for these tests. Eight bottles containing basalt and eight bottles containing Ringold sediment were prepared, loaded, and sealed under a dry nitrogen atmosphere in a glovebox. Ten bottles containing both types of starting material also were prepared, loaded, and sealed in air.

These tests were carried out by placing the bottles and blanks in a shaker that agitated the rock-water mixture in the bottles over the duration of the tests. Tests performed under dry nitrogen also were opened in a nitrogen atmosphere, where fluid samples were extracted and placed into clean vials, sealed, and sent to the analytical laboratory for chemical analysis. Tests performed in air also were opened and processed in an air atmosphere.

The ratio of water volume to effective surface area of the solid is a fundamental parameter in controlling the species concentration and phase relationships in aqueous systems (e.g., Helgeson and Murphy 1983). This is most commonly expressed in terms of rock-water ratio in laboratory tests, either by volume or mass. The use of a uniform sand-sized fraction for tests with basalt was intended to minimize the number of variables in these tests and to also simulate the size/surface area of basaltic material in the aquifer materials (Hanford formation and/or Ringold Formation). Mechanical splitting of the Ringold starting material ensured uniformity of size of this starting

*Teflon is a trademark of E.I. DuPont de Nemours & Company.

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material and ensured that the effective size/surface area also was comparable to that in the aquifer. The rock-water ratio used in these tests was designed to optimize the amount of fluid that could be recovered from each test for analysis, while also approximating the saturated conditions in the aquifer.

It was estimated that a rock to water ratio of approximately 5:1 by mass is required for saturated conditions in media with 50 percent porosity and a density from 2.5 to 3.0. However, a rock:water ratio of 2:1 (120 gm solid and 60 ml DIW) was used to approximate saturated conditions and to provide a sufficient volume of water leachate for chemical analysis (estimated at 20 to 50 ml).

5.2.2.4 Hydrothermal Basalt-Water Test. One closed system test was performed with crushed basaltic material and DIW at a temperature of 105 °C. This test was performed by placing crushed basalt and DIW in a high temperature permeameter vessel at 105 °C for 8 days. The vessel was cleaned and reacted with pure DIW at 105 °C for 8 days before the actual test to ensure the integrity of the test. The vessel was loaded with 150 grams of crushed basalt and 75 ml of DIW in air into a high temperature permeameter vessel to preserve the same rock:water ratio used in closed system tests at 23 °C. The vessel was closed and sealed to prevent vapor fractionation over the duration of the test. The temperature was controlled by placing the sealed vessel in a temperature controlled oven and allowed to react for 8 days. The aqueous fluid resulting from reaction was removed at the termination of the test by placing the run products in a 0.45 micron filter and separating the fluid by vacuum extraction methods.

5.2.2.5 Open System Leach Tests. Flow-through leach tests, referred to as open-system tests, were performed in Teflon permeameter vessels in which DIW was reacted separately with about 380 grams of crushed basalt and Ringold sediment packed into permeameter reaction vessels approximately 5 cm in diameter (Figure 5-2). These tests were performed to evaluate the effect of dynamic flow and rock-water reaction through porous media comparable to that of coupled flow-reaction in the aquifer environment. These tests were designed to simulate dynamic aquifer flow conditions corresponding to reaction/residence times of approximately 2 days and 8 days. These conditions correspond approximately to flow rates of 0.5 pore volume per day (PVPD) and 0.25 PVPD respectively. Fourteen successive samples were collected at 2-day intervals for the 0.5 PVPD tests, and at 8-day intervals for the 0.25 PVPD tests (Tables 5-2 and 5-3). The tests were performed by packing approximately 380 grams of oven dried solid starting material into Teflon permeameter vessels approximately 5 cm in diameter and 12.6 cm long, resulting in a bulk density of approximately 1.6 g/ml. Four columns were prepared, two containing crushed basalt, and two containing Ringold sediment. Initial saturation of each column was performed under vacuum conditions with deionized water. The volume of water required for saturation (1 pore volume) was measured and recorded for each column. Flow rates were established by adjusting the height of the constant head source to correspond to the desired flowrate (0.5 or 0.25 PVPD).

5.2.2.6 Open-Closed Reaction Test. The basalt and Ringold sediment materials present after continuous leaching for 56 days in the 0.25 PVPD leach tests

were removed and subsequently reacted with DIW for 5 days in the same manner as the closed system tests described in Section 5.3.2.3.

5.2.3 Laboratory Test Results

The compositions of water resulting from rock-water reactions with basalt and Ringold sediment are listed in Tables 5-1 through 5-4. Some of the main findings resulting from these tests and the relevance of these results to the objectives of this report are summarized in this section.

Most of the information routinely obtained from these tests is on the composition of water resulting from reaction for the conditions of the test design. These data typically are major and minor anionic and cationic concentrations that are the fundamental indicators of the chemical evolution of groundwater. The implications of these data to the behavior of other unanalyzed constituents (e.g., trace elements) are based on the extent to which the system and the processes are understood.

The relationship between these test results and groundwater background composition at the Hanford Site is that these results can be used to provide fundamental data for understanding the nature of groundwater chemistry and the processes that control its composition. The most direct use of these data are comparisons to natural compositions. However, proper interpretation of the results provide a basis for understanding the extent and scale of natural variability in groundwater composition that can be expected to occur naturally due to rock-water reaction, spatial trends in groundwater composition, and the upper concentration limits associated with rock-water reaction.

5.2.3.1 Chemical Characteristics of Test Results and Compositional Trends. A summary of the test results, and the interpretations and models based on these test results, are summarized in the following sections.

5.2.3.2 Closed System Tests. The chemical compositions of the water reacted with crushed basalt and with Middle Ringold sediment for periods of up to 128 days are summarized in Table 5-1. The general results common to tests with both basalt and Ringold materials include the following:

- A majority of the reaction that occurred within 128 days occurred within first 1 to 6 hours
- Comparable magnitude of concentrations for major and minor constituents
- Chloride concentrations up to 9 mg/L to 14 mg/L, and Cl:F ratios of up to 12
- pH increases with time from 6.8 (DIW) up to 8.5 for both types of starting materials

- Minor differences in test results involving air and nitrogen headspace

- Concentrations of Al and Fe are very low (at or near detection).

The main compositional patterns and trends observed in the closed system tests include the following:

- Rapid increase in the concentration of all constituents within the first 24 hours

- Attenuation in the rate of increase in constituent concentrations after the first day of reaction

- Patterns of largely constant concentrations with increasing reaction time for some constituents (e.g., Si, Cl)

- Slightly increasing concentrations with time for most constituents after the first 24 hours (e.g., Ca, Mg, Na)

- Reversal in concentration time trends with time for K, organic carbon, and to some extent, nitrate

- Basalt-water reaction produces larger solute concentrations than Ringold-water reactions for all major and minor constituents except chloride

- Strongly correlation of Ca and Mg, and Ca and Na in both test groups, and also similar molar ratios of Ca:Mg and Ca:Na (1.5-2.5 and 0.4-1.8 respectively)

- Relatively constant concentrations of Cl and F (molar ratios of Cl:F from about 1.2 to over 5) are produced from both basalt-water and Ringold-water tests.

5.2.3.3 Open System Leach Tests. Compositional data from the results of open system leach tests are tabulated in Table 5-2 and 5-3; compositional trends with time for selected analytes are shown in Figures 5-3 to 5-6. The most notable results of tests involving successive batches of flowing water reacted with both crushed basalt and Ringold sediment for 1 day (0.5 PVPD) and 4-day periods (0.25 PVPD) include the following:

- Open system reaction between water and both basalt and Ringold sediment occur rapidly

- Leachate concentrations are initially very large (10-100 times larger than those of subsequent leachate), and systematically decrease with subsequent flushing

- The same trends in leachate composition with time (flushing) occur in the 0.5 and 0.25 PVPD leach tests, and also yield largely similar leachate concentrations with time for most analytes with the exception of Ca in the tests with Ringold sediment.

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- Larger range of water concentrations in open system reactions than those obtained in closed-system reactions

- pH range from less than 7 (DIW) to 8.3, converging on to 7.9 for 0.25 PVPD tests, and pH 7.7 for 0.5 PVPD tests

- Noticeably lower concentration levels are produced in open system tests compared to those in closed-system tests

- Significantly greater amounts of initially leachable material in Ringold sediment than in basalt

- Leachate concentration for nearly all constituents converge to similar levels with time for both Ringold and basalt starting materials.

- Large amounts of initially leachable chloride are present in the basalt and Ringold starting materials (9 mg/L and up to 790 mg/L respectively)

- Chloride:fluoride mass ratios range from about 1 to 2 in leachate after initial flushing

- Molar ratios for nearly all open system tests converge to values of about 2.5-2.7 for Ca:Mg, 0.3-0.5 for Ca:Na, and about 1.0 for Cl:F, with the exception of the 0.25 PVPD runs with Ringold sediment that were about 1.7 times larger for Ca:Mg and Ca:Na.

5.2.3.4 Open-Closed System Reaction Test. Water reacted with previously leached crushed basalt and Middle Ringold sediment have major and minor constituent concentrations generally intermediate between those produced from the flushed open system tests, and those resulting from the closed system reaction tests (Table 5-4). These results are interesting because the results indicate that the aquifer materials flushed of their readily soluble components undergo a substantial amount of subsequent reaction under lower flow or restricted flow conditions. It is also notable that these reactions produce as much as 10 mg/L of chloride and 3 mg/L of fluoride.

5.2.3.5 Hydrothermal Test Results. Basalt reacted with DIW a closed container at 105 °C for 8 days yielded slightly acidic water (pH 6.05) with dissolved solids levels significantly larger than those obtained in closed system tests at 23 °C (Table 5-4). The concentrations of most major and minor constituents are greater than those produced in closed system tests with a comparable reaction time (8 days) by factor of 2-4, and F is 20 times greater. The main exceptions are Ca and Mg, which are about the same, and bicarbonate which is 10 times smaller. The concentration of most trace elements in water produced in these tests are 2 to 40 times greater than the maximum concentrations obtained in closed system tests with basalt. However, the concentrations of Sr and Ba resulting from these tests are lower than the largest concentrations produced in the closed system tests.

5.2.3.6 Trace Element Concentrations. Trace element analyses for Cr, Mn, Cu, Zn, As, Sr, Mo, Cd, Ba, and Pb using more sensitive ICP-MS methods also were

performed to evaluate the extent to which trace constituents such as these might exist naturally in groundwater due to rock-water reaction. These constituents were selected because most are of interest in environmental restoration activities as hazardous waste constituents. However, Sr and Mn also were included for comparison to the inductively coupled plasma analytical results.

Selected samples from both open and closed rock-water tests were analyzed. These included samples from closed system basalt-water and Ringold-water tests reacted for 16 days that were analyzed along with the first and second pore volumes of water produced from the open system tests with both basalt and Ringold sediment. The results of these analyses are reported in Table 5-4. The result of the hydrothermal test with basalt also was run for comparison.

It is seen from these analyses that the largest concentrations of most measured constituents were produced in the first pore volume of water passed through Ringold sediment. However, the largest concentrations in other tests were from closed system reactions. Closed system tests with basalt contained the largest contents of Mn, Cu, Zn, Mo, and Pb; closed system Ringold-water tests produced the largest contents of Cr, As, Sr, Cd, and Ba. The copper concentrations with basalt, however, may have been influenced by the use of brass sieves in sample preparation. The water samples produced from hydrothermal reaction of basalt generally have concentrations of Cr, Mn, Cu, Zn, and Pb as much as 20 to 40 times larger than those in the closed system tests.

5.2.4 Interpretations and Discussion

The results of the these tests have many implications for the nature of rock-water reactions in the aquifer environment at the Hanford Site, and to the evolution of groundwater composition in the unconfined aquifer. The most important results relating to the understanding of groundwater evolution in the unconfined aquifer at the Hanford Site are summarized in this section.

Although the results of these laboratory tests provide a basis for understanding the nature of rock-water reactions in the aquifer, the interpretation of these results and comparisons between the results of laboratory tests and natural groundwater compositions can be misleading without a clear understanding of what the test and the test result represents. Thus, a brief description of what these tests are interpreted to represent is presented to provide a basis for the evaluation and interpretation of these test results, and their relationship to groundwater composition.

5.2.4.1 Reaction Paths in Open and Closed Systems. Open and/or closed system rock-water interaction tests have applications that include the simulation of coupled transport-reaction in dynamic aquifer systems (e.g., Lichtner 1988). Differences commonly are observed in the results of tests in open and closed systems involving identical starting materials because the processes and phenomena associated with the reactions can vary with changes in the type and rate of the mass transport in these two types of test conditions. Closed

system reaction paths are manifested primarily by changes in solute concentration with time. Reaction paths in open systems are a function of average linear flow velocity (advection) and are manifested by differing solute concentrations in succession of reaction zones along the course of the flow path (i.e., along the length of the column) as the system is flushed. These reaction zones are established along the length of the column or along flow paths as regions of steady state conditions for conditions of constant flow velocity. Regions of dynamic equilibrium might exist in the column depending on the reactant types, dimensions of the column, and flow conditions (Hoover and Thornton 1989). However, this dynamic equilibrium region generally is not present in rock-water test columns because the residence time requirements for equilibrium (e.g., long column and/or low flow velocity) might be impractical or unachievable with available apparatus.

Closed system reaction paths can be used to provide conservative approximations of dynamic equilibrium reactions because reaction paths in open and closed systems are often similar or identical during the time that most significant reactions occur (Wolery 1979; Helgeson and Murphy 1983; Helgeson et al. 1984). Also, reaction paths can be used because the attainment of equilibrium in closed system tests is often less problematic.

The results obtained from open system flow-through tests, however, can be difficult to interpret if the tests systems are not designed for the attainment of dynamic equilibrium. Thus, fluid compositions obtained from unscaled open system flow-through tests are likely to represent the chemical evolution of fluids along a portion of the reaction path (i.e., a reaction zone) rather than equilibrium compositions (Hoover and Thornton 1989).

5.2.4.1.1 Open System Tests. The composition of water produced in the most evolved open system reaction tests are interpreted to represent conservatively low estimates of the concentration levels expected under dynamic flow conditions. The low concentrations observed in these tests are interpreted to reflect the steady state composition of a relatively primitive part (reaction zone) of the open system reaction path. This interpretation is based on the model of flow-through systems described previously, and the relatively short residence time for reaction in these tests (one day for the 0.5 PVPD tests and four days for the 0.25 PVPD tests). This interpretation is supported by the observation that open-closed closed system tests (Section 5.3.3.1) produced constituent concentrations significantly larger than the steady state levels produced in the open system tests. The general convergence of water compositions produced by open system reaction with both basalt and with Ringold sediment for both 0.5 PVPD tests and the 0.25 PVPD tests also indicates that the reaction paths for reaction with both types of materials are very similar.

The largest solute concentrations produced in any of the tests occurred in the first pore volume of water leachate of the open system tests with Ringold sediment. These large concentrations appear to be attributable to a small amount of soluble salt in the starting material based on the greatly elevated concentrations of many constituents present only in the first 1-2 pore volumes of water collected in the open system tests.

5.2.4.1.2 Closed System Tests. The results of the closed system tests appear to represent near-equilibrium or steady state conditions based on the compositional trends with time for the major and minor constituents. It is likely that these test results represent steady state conditions resulting from the stoichiometric dissolution of solids rather than thermodynamic equilibrium based on geochemical models for time required for the attainment of equilibrium in feldspar-water systems (e.g., Helgeson and Murphy 1983). However, these tests might reflect the maximum extent to which stoichiometric dissolution occurs in these aquifer materials. This steady state condition might be more relevant to the compositions groundwater than dynamic equilibrium compositions if most groundwater in the unconfined aquifer has not reacted to that extent. Reactions involving feldspar and water, for example, require over 20 years to reach equilibrium at 20 °C. It is possible that the composition of most groundwater in the unconfined aquifer and upper confined aquifer might be dominated by dissolution reactions associated with the precipitation of Si- and Al-bearing minerals. This possibility is based on the similarity in compositions between groundwater from the upper confined and unconfined aquifers and of composition of rock-water test results interpreted to be controlled by these processes (McKinley 1990).

Based on these interpretations, the compositions of the open and closed system tests might be expected to bracket the mean composition of natural groundwaters and perhaps the entire range, provided that the results of these tests represent the same type of open and closed system behavior expected in the aquifer. The concentrations of some analytes in these test results, however, might be somewhat larger than those otherwise expected owing to the nature of the starting materials.

The closed system tests with crushed basalt used a single size fraction (0.25 mm to 0.5 mm diameter) to more closely represent the particle size and effective surface area of basaltic components in the aquifer size fraction (effective surface area). Although the effect of increased surface area from fine particles resulting from crushing (Schott et al. 1981; Holdren and Berner 1979) and/or broken bonds can enhanced solubility, these test were not pre-washed because the evaluation of upper extent of solubilities was one of the objective of these tests. The somewhat larger concentrations of Ca, K, Na, and Si in the closed system tests with basalt compared to those in the open-closed test (Section 5.3.4.1.3) might be attributable to this effect.

Water compositions produced in closed system tests with Ringold sediment appear to include a small amount of soluble salt components based on the composition of the first pore volume of water in the open system tests. Soluble salts generally would be expected to have been flushed from the system in most parts of the aquifer. Thus, the concentrations of these salt constituents in the test results (e.g., 20 to 28 mg/L Na; 13.6 mg/L chloride) might be slightly larger than aquifer materials reacted to the same extent in the absence of salts. Based on the result of the open-closed test, however, (e.g., 21 mg/L Na; 9.8 mg/L chloride), the amount of salt present in the starting material might be relatively small.

5.2.4.1.3 Open-Closed Tests. The concentrations of the major and minor cations and anions produced in the open-closed test with basalt and Ringold

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sediment more closely approximates the natural compositions found in spring waters (for basalt-water reaction) and in the unconfined aquifer. The results of these tests are interpreted to represent water compositions more extensively evolved along the respective reaction paths toward the steady state limits of dissolution-dominated reaction. Because the starting materials for these tests more closely approximate those in the aquifer, i.e., flushed of readily soluble constituents, the water compositions in these tests would be expected to more closely resemble those of the natural waters if the experimental system is analogous to the and natural system.

5.2.4.2 Comparison of Test Results to Natural Waters. The composition of the spring waters that serve as recharge for the aquifer are bracketed for nearly every constituent by the compositions of waters produced in the most evolved open and closed system test basalt-water reaction tests (Figure 5-7). The main exception is the larger concentrations of Si, Cl, and nitrate in the spring waters. The compositions of the spring waters more closely resemble the water produced in the open-closed system test for most constituents than those in other tests. It is indicated from these results that basalt-water reaction is a reasonable explanation for the generation of spring water for essentially all constituents except for the maximum concentrations of chloride and nitrate in the spring waters. The larger average and maximum concentrations of these constituents in the spring water compared to the majority of groundwater in the unconfined aquifer (i.e., low chloride type) indicate that the concentrations of these constituents are effectively lower in the low-chloride groundwater or that more data on groundwater composition are required. If these data are representative, dilution or reactions within the unconfined aquifer would be required to produce averages lower than those in the recharge water.

5.2.4.2 Comparison to Groundwater. The compositions of essentially all groundwater samples in the unconfined aquifer are bracketed for nearly every constituent by the compositions of waters produced in the most evolved open and closed system test with basalt and/or Ringold sediment (Table 5-9). The main exception is the somewhat larger concentrations of Na, Cl, and SO_4 in the high-chloride groundwaters. In nearly all cases, the composition of water produced from the hybrid open-closed test is intermediate between the concentrations of the open and closed system test results for the major and minor constituents, and more closely resemble the composition of groundwater than do waters from either the open or the closed tests. The composition of high-chloride groundwater also is bracketed by the open and closed system tests with Ringold sediment for nearly all constituents except for only Na and Cl (Figures 5-8 and 5-9).

These results reflect the adequacy of rock-water reaction to account for essentially all of the dissolved solid constituent concentrations in the groundwater from the unconfined aquifer because these relationships are seen for all major and minor constituents. The validity and representativeness of these test results as analogs for groundwater also is supported by the similarity in pH to those of the groundwaters.

5.2.4.3 Trace Element Concentrations. The concentrations of As, Mn, Cu, and Ba measured in the closed system tests are about as large, or exceeded, the

provisional threshold levels determined for the groundwater background data set (Section 6.2). The trace element contents in the closed system test results generally are smaller than those in groundwater from the unconfined aquifer, with the exception of Mn, Sr, and Ba which are comparable.

The trace element contents produced in the hydrothermal tests indicate that significantly larger concentrations of most of these elements can be produced by thermally enhanced reactions alone. The elevated concentrations of major, minor, and trace constituents produced in the hydrothermal test presumably reflect enhanced dissolution, particularly of glass (Lane et al. 1984; Ulmer et al. 1986), and reaction with some of the more refractory minerals entrained in and enclosing the mesostasis (Hoover and Murphy 1989). However, even these concentrations do not approach the concentrations of Cr, Mo, Cd, and Pb in groundwater. Thus, the results of these tests alone do not constrain the trace element contents in groundwater. Although the effect of reaction time greater than 16 days in these tests is not known, the concentrations for these trace elements might be expected to increase with residence time (i.e., reaction path progress) in a similar manner to most major and minor constituents based on trace element data for groundwater from the upper confined aquifer.

5.2.5 Discussion

It is apparent from these results that basalt-water reactions are capable of explaining most aspects of the compositional range of the recharge spring water, and that basalt-water and/or Ringold-water reactions are capable of explaining most aspects of the compositional range of groundwater in the unconfined aquifer.

It also is implied from the interpretations of the open system tests that compositional variability can be expected to exist along the length of the flow path (i.e., reaction path). Although many factors also can affect groundwater compositions (e.g., mixing, microbial process, redox), the largest solute concentrations often are associated with the most chemically evolved groundwaters. In general, the concentrations of many dissolved constituents increase toward some solubility-controlled steady state or equilibrium level with reaction progress. Thus, the most evolved groundwater is associated with rock-water reaction under conditions of low-flow and/or greater local residence times, and can be expected to have larger solute concentrations than those that evolve along flow paths of higher-flow and/or lower local residence times.

The scale of compositional heterogeneity within the unconfined aquifer therefore is likely to exist on the same scale as the three-dimensional lithologic heterogeneities within the aquifer referred to as hydrofacies by Poeter and Gaylord (1990). Preliminary findings on groundwater background composition from the Yakima Barricade indicate that significant compositional heterogeneity in the unconfined aquifer exists on the scale of meters vertically with respect to groundwater and microbial composition. Lateral variation in groundwater composition therefore might be manifested as a function of distance from recharge and also in directions normal to flow paths

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where adjacent regimes of high and low downgradient flow exist. The extent of compositional variability expected is uncertain, however, because these variations might primarily reflect adjustments in reaction path from those established by reaction with basalt (spring water) to those associated with the aquifer materials in the unconfined aquifer. Based on the results of the laboratory tests with basalt and Ringold sediment, these differences might be small except for the concentrations of certain trace elements.

One of the most notable results observed in all tests is the rapidity of reaction at room temperatures. The initial rate of reaction is best reflected in the results of the closed-system tests. In these tests with both the basaltic and Ringold starting materials, the solute concentrations observed in the first hour of reaction account for over 60 to 83 percent of the total dissolved solids observed after 128 days, 81 to 87 percent of the dissolved solids after the first 24 hours, and 80 to 100 percent after the first week of reaction.

The general similarity between water compositions produced from closed system tests performed with air and nitrogen is most likely associated with the rapidity of reaction and the relatively small gas volume in the closed system tests. It is likely that most of these tests involved reactions that were moderately reducing due to dissolution reactions. The reducing capacity of basaltic material has been shown to be very large under hydrothermal conditions (Ulmer et al. 1986), because of the large amounts of ferrous iron (Hoover and Murphy 1989). The general consistency in results performed with air and nitrogen headspace, and also with results of the open system tests, therefore is interpreted to be attributable to the locally effective reducing capacity of both the basalt, and to a lesser degree, Ringold sediment by reaction with water at relatively low temperature (23 °C).

The general nature of the rock-water reaction path for both basalt and Ringold sediment appears to be similar to the initial stages of groundwater evolution in the confined aquifer, based on the similarities in compositional trends and patterns to those observed in groundwater from the upper confined aquifer (McKinley 1990). This reaction path appears to be characterized by initial reactions dominated initially by rapid dissolution of rock/sediment materials (i.e., less than 24 hours). For water reacted with basalt, and sediments containing basaltic material, the composition appears to be dominated by congruent dissolution of plagioclase and pyroxene, and dissolution/hydration of interstitial glass. Although relatively large amounts of Al and Fe are present in the starting materials, their low concentrations in the test results and in groundwater are attributed to the stability and low solubility of Al in phases such as kaolinite, and the stability and low solubility of Fe in precipitated phases such as Fe-smectite or ferrihydrite.

The composition of reacted waters also can be influenced by the dissolution of more soluble materials, such as salts, if they are present, and not flushed from the system. The dissolution of micaceous minerals (biotite and/or muscovite) also may be important in influencing the chemistry of water reacting with sediments containing these materials (e.g., Ringold and some Hanford formation sediments). The dissolution of basaltic glass is one of the

most important aspects of the rock-water reaction path, because the glass and crystallites contained in the glassy mesostasis are one of the primary sources of constituents of interest for environmental concerns (e.g., Ba, F, Cl, Pb). Sulfide grains, apatite, and other silicate minerals such as pyroxene, feldspar, and Fe-Ti oxides associated with the mesostasis material also may be an important source of sulfur, halogens, and other trace elements.

It is also indicated that the concentrations of F and Cl are much larger than those expected from release by glass dissolution in the proportions present in the glass, or by the effective release associated with the hydration of glass to palagonite (montmorillonite). It is indicated that the release of F and Cl from interstitial glass in basalt might be controlled by a different mechanism than that of Na and K (which are important constituents in the glass) by a factor of greater than 100 times, even when the effects of palagonitization are considered. The most likely process is reaction with apatite.

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6.0 EVAPOTRANSPIRATION

Evapotranspiration is a natural process that also can influence the composition of groundwater through its effect on recharge water. Evapotranspiration, herein referred to as evaporation, occurs in all climates, and can have a major control on water composition in arid climates (Drever 1982, p. 200). The fractionation of water by evaporation affects water chemistry by increasing the concentration of dissolved components and the heavier isotopes of hydrogen and oxygen as pure water is distilled (i.e., removed) by evaporation. Evaluation of the extent to which evaporative fractionation influences the composition of groundwater in the unconfined aquifer is important for the purpose of this study for the following reasons:

- Evaporation influences on recharge resulting directly or indirectly from meteoric water
- Evaporation is a process that influences the natural chemical composition of groundwater and is a component of the groundwater background conceptual model
- Evaporation potentially influences the extent of natural compositional variability in groundwater composition and the spatial distribution associated with the natural variability in composition
- The extent of evaporation on groundwater composition can influence decisions regarding the collection of new data on groundwater background (e.g., well location).

6.1 EVALUATION METHODS

The extent to which the evaporation of recharge water influences the composition of groundwater in the unconfined aquifer can be evaluated by considering mass balance and stable isotope systematics. Mass balance considerations involve comparisons between the concentration of key indicator solute concentrations, such as fluoride and chloride, in recharge waters and groundwater. Evaluation of the isotoptic composition of hydrogen and oxygen are regarded as the most sensitive indicators of evaporation because the stable isotopic ratios of both elements vary systematically with evaporation (e.g., Faure 1977; Drever 1982).

Studies of groundwater and formation water evolution have been made throughout the world for many years using stable isotope ratios and solute concentrations separately and together. These studies have been most effective in the evaluation of systems that have undergone marked evaporation (e.g., Eugster and Jones 1979), where evaporation is known to have been the dominant mechanism of geochemical evolution (e.g., in evaporite deposits, Knauth and Beunas 1986), or where mixing between evaporated brines and relatively dilute ground or surface water has occurred (e.g., Gat and Issar 1974; Schwartz et al. 1981). Gat and Issar (1974), for example, found differences in data groupings based on water origin and location, which showed

that relatively dilute water at high elevations in mountainous regions of the Sinai desert had a more negative isotopic signature than waters occurring downgradient that were enriched in both solute and heavy isotopes by evaporation. Salinity in these waters varied from 31 to 267 mg Cl/L, with and accompanying del-D increased from -26 to -12.

6.1.1 Solute Mass Balance

The general solute mass balance approach for evaluating the extent of fractionation processes such as evaporation is to compare the relative concentrations in the material fractionated (i.e., initial parent concentration) to that resulting from the fractionation process (i.e., daughter compositions) as a function of the extent of fractionation. The relationship between these parameters is described by the Rayleigh equation (equation 2) where C_o is the initial concentration of constituent i in the fluid (i.e., liquid water), C_n is the concentration of constituent i in a daughter fluid resulting from an amount of fractionation given by 1-F, where F is the mass fraction of fluid remaining. In this equation, D is the bulk distribution coefficient between the fractionated phase(s) (e.g., mineral) and the coexisting fluid for constituent i:

$$C_n^i / C_o^i = F^{(D_b-1)}. \qquad (2)$$

The general equation for the bulk distribution coefficient D_b in is given in equation (3), where $f_{1...n}$ is the mass fraction of phase $\phi_{1...n}$ fractionated (i.e., removed) from the system, and $D\phi_{1...n}$ is the distribution coefficient for constituent i between fractionated phases of constituent i between phases $\phi_{1...n}$ and coexisting liquid L:

$$D_b = \Sigma\ (f_1 * D\phi_1^{C1/CL} + f_2 * D\phi_2^{C2/CL} + \ldots\ldots\ f_n * D\phi_n^{Cn/CL}). \qquad (3)$$

The distribution coefficient for phase $f_{1...n}$ is defined as the ratio of the concentration of constituent i in phase f and coexisting liquid L:

$$D\phi_n = C_n/C_L. \qquad (4)$$

For the purpose of evaluating evaporation here, it is assumed that the only fractionated phase is water (w) containing no dissolved constituents, so that $D_b = Dw = 0$.

Thus, the equation (2) becomes:

$$C_n^i / C_o^i = 1 / F \qquad (5)$$

$$\text{and, } (1-F) = C_o^i / C_n^i. \qquad (6)$$

The extent of the fractionation process (1-F) can then be evaluated by comparing the concentration of a constituent (i) in the parent fluid (C_o^i) to that in a daughter fluid (C_n^i), provided that constituent (i) is detectable in both fluids, and that constituent (i) behaves as an incompatible constituent (i.e., remains totally in solution and is not fractionated by a secondary process such as the precipitation of a solid,under normal conditions). In general, the composition of groundwater to be evaluated is regarded as the daughter fluid (C_n^i). The initial parental composition generally is assumed to be that of recharge water to the aquifer.

6.1.2 Stable Isotope Constraints

One of the most sensitive indicators of evaporative fractionation in water is its stable isotope composition by stable isotope ratio analysis (SIRA) of the component atoms of oxygen and hydrogen in the water (Drever 1982). During evaporation, the isotopic ratios of these elements will be altered by fractionation because removal of water vapor by evaporation causes the remaining water to be enriched in the heavy isotopes of hydrogen (deuterium, ^2H) and oxygen (^{18}O). If the isotopic compositions of recharge waters prior to evaporation are known, the effects of evaporation on groundwater can be estimated by calculation and compared with observed groundwater compositions. Variations in isotopic ratios along a groundwater flowpath or differences between recharge and groundwater isotopic composition can then be compared to variation in solute concentrations to evaluate the extent to which these variations result from evaporation. Thus, the relationship between the extent of evaporation can be constrained separately from the evaluation of and solute concentrations through the reduction of solute mass, and can be compared for internal consistency.

The effects of evaporative fractionation of aqueous hydrogen and oxygen on water can be evaluated using the equations of Craig and Gordon (1965), Craig et al. (1963), and Sofer and Gat (1975), along with available data on groundwater compositions, meteoric conditions, empirical relationships between geochemical constants, and published values for pertinent constants. The equations used in these calculations are described below.

The equation describing the change in isotopic ratio for a given element is:

$$dLog\ R_L/d\ log\ f = ((Ei/E)/R_L)-1 \qquad (7)$$

Where R_L is defined as the abundance ratio of isotopes of interest in the bulk liquid of interest, f is the volumetric fraction of original water remaining, Ei is the evaporation rate of the heavier isotope of interest, and E is the overall evaporation rate. Isotopic signatures are expressed in delta notation; the defining relationship for this notation expresses the required conversion for using:

$$del\ (i) = ((R_{SPL}-R_{STD})/R_{STD})\ X\ 1{,}000 \qquad (8)$$

where R_{SPL} and R_{STD} are the isotopic numerical abundance ratios of a sample of interest and arbitrary standard. Examination of this expression shows that standard notation is an expression of the deviation of the abundance ratio from that of the standard in parts per thousand. The abundance ratios for the standard used for water (standard mean ocean water or SMOW) are: D/H = 0.0001558, and 18O/16O = 0.0020052. The overall evaporation rate, E, is defined as:

$$E = (a-h)/p \tag{9}$$

where a is the activity of water (unity in dilute systems such as Hanford Site groundwater with an ionic strength of approximately 5 mM), h is fractional humidity with reference to ambient temperature, and p is a factor describing transport resistance through atmospheric layers for light molecules. The isotopic evaporation rate is defined as:

$$Ei = a(Ta'R_S - hR_A)/pi \tag{10}$$

where T is a function of activity ratios between isotopes of the same element (unity in dilute solutions), a' is the temperature-dependent fractionation factor for partitioning of isotopes between two phases (e.g., liquid water and vapor), the subscripts S and A denote numerical abundance ratios in the aqueous surface layer and atmosphere, respectively, and pi is the transport resistance for heavy molecules. The ratio p/pi has a numerical value of approximately 0.982 for both H and O. The temperature dependence of a' for hydrogen fractionation between condensate and vapor is:

$$1{,}000 \ln Da'_{c-v} = (24{,}844{,}000/T^2) - 76248/T + 52.612 \tag{11}$$

and for oxygen:

$$1{,}000 \ln {}^{18}Oa'_{c-v} = (1{,}137{,}000/T^2) - 415.6/T - 2.0667 \tag{12}$$

In applying each of the above empirical relationships to evaporation, their inverse must be applied to yield fractionation between vapor and condensate (e.g., for hydrogen obtaining by inversion Da'_{v-c}).

Given the above equations, measured or approximate values for temperature, humidity, R_A, R_L, and R_S must be used to determine the magnitude of evaporative fractionation.

6.2 PARENTAL AND DAUGHTER COMPOSITION

Meteoric water (rainfall), spring water, and river water serve as recharge to the unconfined aquifer at the Hanford Site. However, spring water is the primary source of upgradient recharge to most of the unconfined aquifer, and is influenced by evaporation when it flows as surface water. Thus, spring water is the most appropriate parental source composition for use in mass balance and the isotopic evaluatons on the role of evaporation on the composition of groundwater that recharges the aquifer. For the purpose of this evaluation, the composition of groundwater is regarded as the daughter

The main indicators of chemical evolution of groundwater in the unconfined aquifer in this model are the chloride and fluoride concentrations in the various water types. In this model, it is assumed that chloride concentrations serve as an indicator of the extent of evaporation, and that fluoride concentrations serve as an indicator of the extent of reaction of the water with the host basalt. The framework for this model is, therefore, based on the assumption that chloride concentrations of groundwater in the unconfined aquifer originate (are derived) principally from the chloride in meteoric waters originating from entrained sea salt, and that very little chloride is gained or lost through rock-water reaction or lost through the subsequent precipitation of chloride-bearing solid phases. It also is assumed that any contribution of chloride from reaction with basalt is small and will not significantly change this analysis and is, therefore, ignored in the following discussion and analysis.

6.4.1.1 Model Parameters. The primary compositional data used in this model are the concentrations of chloride and fluoride in meteoric water, spring water, and groundwater in the unconfined aquifer. These data are tabulated in Table 6-1 and include the chloride and fluoride concentrations for the population of high-chloride and low-chloride groundwater.

These data are used in this model to evaluate the extent to which the compositions of spring water and groundwater in the unconfined aquifer potentially have been influenced by evaporation or snow sublimation. In this model, the chloride concentrations for parent and daughter waters to be evaluated are compared (e.g., meteoric water to spring water, or spring water to groundwater) by substituting the appropriate concentrations for C_o^i and C_n^i in equation (2)

It is indicated from these calculations that relative enrichment factors associated with fractionation processes (such as evaporation in Table 6-2), that 48 to 94 percent evaporation is required to produce the range of chloride concentration observed in the spring water from the evaporation of meteoric water alone. It also is indicated that about 73 percent of the additional fractionation/evaporation would be required to produce the mean chloride concentration in the high-Cl groundwater. Thus, the potential influence of evaporation on the evolution of groundwater in the unconfined aquifer might range as high as 98 percent (i.e, enrichment of up to 50 times) for a meteoric water chloride source.

6.4.1.2 Model Summary. The chemistry of groundwater in the background study area indicates that infiltration of precipitation, mostly snow melt, on the ridges bounding the Hanford Site is the major recharge source for both the confined and unconfined aquifers.

The observed variations in groundwater chemistry involve several stages of infiltration, evaporation, and rock-water reaction. The process starts with the infiltration of carbon dioxide-charged precipitation on the ridges surrounding the Pasco Basin. The ridges to the south and west of the Pasco Basin receive roughly twice as much precipitation as the basin floor, mostly as snow, and snow melt is the principal source of recharge. The infiltrating water enters a complex groundwater plumbing system within the folded, faulted

that the primary source of chloride in the hydrologic system is derived primarily from meteoric water. In the other position, it is believed/suggested that rock-water reaction might also be the dominant source of chlorine in this hydrologic system. This issue is important because it has consequences for the conceptual model of chemical evolution in the aquifer in term of the natural processes responsible for the compositional and spatial range of background compositions. The most important implication of this issue is that the conceptual model serves as the basis for recommendations on the acquisition of new data (e.g., well locations, depths, etc.).

6.4 EVAPORATION MODELS

Two models used for the evaluation of evaporative processes are described in the following sections. These models use the same data for groundwater, spring water, and surface (meteoric) water. The main differences in these models is the nature of the conceptual model regarding the source of chloride that occurs in spring waters that serve as recharge to the unconfined aquifer, and consequently, the relative influence of evaporation on the evolution of groundwater in the unconfined aquifer at the Hanford Site. The main elements of the two positions regarding the source of chlorine in the aquifer system and justification for assumptions made in the models are provided in the following sections.

6.4.1 Model A

Evaporation models are based primarily on the observed distribution patterns of fluoride and chloride in springs, groundwater, and basaltic materials. It is indicated from the statistical analysis (Chapter 4.0, Section 4.1.4) of solute concentration groupings from the 16 existing wells chosen for this preliminary background study that a more complex conceptual model might be required where evapotranspiration and reaction with basaltic materials, before recharge of the unconfined aquifer, play a major role in determining groundwater compositions (Hodges and Johnson 1991). A multistage process model for the development of groundwater compositions in the unconfined aquifer has been proposed (e.g., Hodges and Johnson 1991). The following stages and associated processes are the integral elements of this model:

(1) Evaporation of meteoric water during infiltration on the basaltic ridges bounding the Pasco Basin

(2) Reaction between water and basalt in the perched aquifers that serve as the source of the springs

(3) Evaporation of spring waters discharged onto the surface (e.g., Dry Creek) with preceding infiltration as recharge into the aquifer

(4) Subsequent rock-water interaction within the aquifer.

6.4.1.3.1 Springs and Unconfined Groundwater. Comparison of the average compositions of spring waters with the average compositions of groundwater in the unconfined aquifer indicates a relatively good match between the spring waters and the low chloride groundwater (Table 6-3), particularly for chloride and fluoride. The average presented in Table 6-3 does not include wells 699-66-103 and 699-S24-19 in which the groundwater has apparently been diluted through the mixing with the waters of the Columbia and Yakima Rivers, respectively.

The fluoride/chloride ratios (wt.) versus chloride concentrations in groundwater of the unconfined aquifer plotted in Figure 6-2 indicates the difference between the high chloride and low chloride groundwater and illustrates the impossibility of deriving the observed fluoride/chloride ratios through evaporation of meteoric water. The fluoride/chloride of meteoric waters is near 0.00007 and will not be effectively increased by evaporation. Evaporative processes result in identical proportional increases in the two components.

The fluoride/chloride ratios (wt.) versus chloride concentrations in the spring waters plotted in Figure 6-3. The dashed line area outlines the compositional field of the low chloride groundwater plotted on Figure 6-2. The close correspondence between the spring waters and the low chloride groundwater is indicative of a similar origin for the two waters. The relation between the fluoride/chloride ratios and chloride for the spring water and the low chloride groundwater illustrates the dilution of material leached from the basalt by the increase in evaporation concentrated meteoric chloride.

The concentrations of fluoride and chloride in the spring waters are plotted in Figure 6-4. The concentrations of fluoride and chloride in the groundwater of the unconfined aquifer are plotted in Figure 6-5, where the dashed line encloses the field of spring water compositions on Figure 6-4. The filled circle marked "S" indicates the average spring composition from Table 6-3 and the filled circle marked "U" indicates the average composition of low chloride groundwater from Table 6-3. The similarity of the compositional fields and of the average concentrations of fluoride and chloride in the springs and low chloride unconfined groundwater indicates similar degrees of evaporation and basalt-water interaction, a strong argument for a similar origin for the two populations.

The average compositions presented in Table 6-3 indicate that several of the components are higher in the low chloride groundwater than in the springs. This difference might be a result of interaction between groundwater and aquifer materials in the unconfined aquifer or a result of longer flow paths through basalt for waters discharged directly into the unconfined aquifer.

The apparent source of the spring waters is infiltration of meteoric water on the basalt ridges bounding the Pasco Basin. The similarities between the spring waters and the low chloride unconfined groundwater indicate that infiltration of meteoric water on the ridges is also a major recharge source for the unconfined aquifer. The folded, basalt ridges must contain a multitude of groundwater pathways, allowing for large variations in degrees of

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ridges; some emerging as springs, some recharging the unconfined aquifer beneath the surface of the basin fill sediments, and some remaining within the basalt to recharge the confined aquifer system beneath the basin.

Before (sublimation of snow) and during infiltration, precipitation undergoes a large degree of evaporation. On an average, approximately 80 to 90 percent of the infiltrating water is lost to evaporation if the chloride concentrations in the spring waters are indicative of the degree of evaporation that takes place on the ridges. After infiltration, the mildly acidic carbon dioxide (carbonic acid)) charged waters react with the basalt, presumably the highly reactive glassy mesostasis, and the fluorine and various other rock components, including various incompatible elements that do not readily enter the crystal lattices of the major rock forming minerals, and are leached into the water. This initial evaporation and basalt/water interaction determines the essential chemical compositions of the springs, the low chloride waters of the unconfined aquifer, and the groundwater of the shallow confined aquifer (Chapter 4.0, Section 4.1.1).

Locally, spring waters form streams (i.e., Dry Creek and Cold Creek) that flow some distance across the Pasco Basin before losing their water to evaporation and infiltration. Spring water that has undergone secondary evaporation in these streams is the most likely source for high chloride groundwater in the unconfined aquifer. The average chloride concentrations in the high chloride groundwater is 23 parts per million, indicating a concentration over the average spring water of 3.75, or approximately 70 percent evaporation of the spring water. However, the water infiltrating along the course of the streams will be diluted by low chloride groundwater in the aquifer and the actual percentage evaporation in the streams must be considerably greater than 70 percent. The observed chloride concentrations in the high chloride groundwater correspond to approximately 95 percent evaporative loss relative to original meteoric precipitation, having a chloride concentration of 1 part per million.

6.4.1.3 Discussion and Assumption Criteria. Chloride in meteoric waters is regarded in this model as an excellent conservative indicator of evaporative water loss because very little is gained or lost through rock-water reaction or lost through precipitation under normal conditions. A contour map showing the magnitude of meteoric chloride Figure 6-1) indicates a chloride deposition rate from 2 to 4 Kg/hc/yr. Annual precipitation on the Hanford Site ranges from 6.5 inches (16.5 centimeters) at the Hanford Meteorological Station in the 200 Areas to approximately 15 inches (38.1 centimeters) at the Rattlesnake Mountain Observatory. Combining these numbers indicates potential meteoric chloride concentrations between 0.5 and 2 parts per million. The only available analysis of Hanford Site precipitation, collected at the Rattlesnake Mountain observatory as part of the BWIP Project (Early et al. 1986), indicates meteoric chloride less than 1 part per million. Sodium concentration in precipitation is approximately 0.2 part per million, and on the assumption that NaCl is the principal source of both sodium and chloride in the precipitation, indicates a chloride concentration of 0.3 part per million. It will be assumed that the A meteoric chloride concentration of 1 part per million is assumed in this model, and might be lower with attendant higher percentages of evaporation.

undergone a greater degree of evaporation than indicated by their present chloride concentrations. The groundwater in well 699-19-88, which is located near the source of Dry Creek, is a typical low chloride groundwater. Highly evaporated waters from Dry Creek would mix with the low chloride groundwater on their travel down the Dry Creek Valley, diluting the full effects of evaporation in the stream.

The most likely source of the high chloride groundwater observed in the background study area is secondary evaporation of spring water and subsequent recharge along the course of Dry Creek. However, most of the evidence for this source is circumstantial. Groundwater chemistry data from the 5 mile gap separating the end of Dry Creek and the high chloride wells, as well as chemical data for the waters of Dry Creek, would greatly help in either proving or disproving this hypothesis. If this hypothesis is correct, second stage evaporation in the upper Cold Creek Valley might result in high-chloride background values. This is important because the upper Cold Creek valley is upgradient to the Hanford Site 200 Areas.

6.4.1.3.3 Leaching of Chloride From Basalt. It is assumed in this model that chlorine in basalt occurs principally within the glass phase, and that fluorine is concentrated in the fine-grained apatite that occurs within the mesostasis. However, the extent to which fluorine is tied up in apatite depends on the availability of phosphate in the rock. For example, BCR-1 contains 0.36 weight percent P2O5 (Flanagan 1973). If all of this phosphorus is assumed to form pure fluorine saturated apatite (fluorapatite), approximately 160 parts per million of the initial whole rock fluorine (470 parts per million) would remain concentrated in the glass phase. Unfortunately, because of the general lack of fluorine analyses for Columbia River Basalts, it is uncertain to what extent this is a general condition.

Chlorine occurs, along with fluorine, as a relatively minor component in basalts. Both do not enter the major crystalline phases in basalts and will be concentrated in the fine-grained glassy mesostasis within the basalts. Thus, there is a possibility that chloride observed in springs and groundwater is derived from rock-water reaction along with the fluoride.

Sluggish kinetics in low-temperature, near-surface geochemical processes can result in a great deal of metastability in the near surface region. In considering the potential derivation of groundwater chloride from the basalts, it must be kept in mind that the groundwater is a low temperature, dynamic (flowing) system that contains a large degree of inherent metastability as a result of the presence of glass and fine grained high-temperature phases. As in so many low temperature systems, equilibrium considerations might indicate general directions of system evolution. However, these systems should not be used to predict system behavior.

Krauskopf (1979) reports world-wide average fluorine and chlorine concentrations in basaltic rocks of 400 parts per million and 60 parts per million, respectively. However, very little data on fluorine and chlorine concentrations in Columbia River Basalts are available. The USGS standard rock BCR-1 is a sample of Grande Ronde Basalt from the Columbia Plateau. Analyses of BCR-1 (Flanagan 1973) indicates a fluorine concentration of

evaporation and basalt-water interactions. This variability in groundwater travel paths for the springs is hinted at by the range of observed radiocarbon ages for the spring waters, ranging from 30 years or less to hundreds of years (Chapter 4.0, Section 4.1.1). The intersection of the top of the basin filling sediments with the ridges is an artifact of deposition and erosion and does not affect water flow within the basalt. Thus, it is reasonable to expect the infiltration of spring-like water from the basalt directly into the suprabasalt sediments. Groundwater chemistry indicates this process is a major source of groundwater recharge for the unconfined aquifer.

6.4.1.3.2 High Chloride Groundwater. The high chloride groundwater (Table 6-3) is a chemically distinct groundwater type that occurs in a restricted region of the background study area. If the chloride concentrations in the spring waters represent the range of evaporation that occurs during infiltration on the ridges, the high chloride groundwater represents a source that has undergone a much higher degree of evaporation. Thus, although a ridge infiltration pathway that involves a much higher degree of evaporation cannot be ruled out, it is reasonable to examine the other potential source of highly evaporated recharge waters (i.e., ephemeral streams).

A water table map for the southern portion of the background study area is presented in Figure 6-6. This map also shows the surface course of Dry Creek and the locations of the four high chloride wells. This map also shows the locations of two low chloride wells in the background study set, including well 699-19-88, which is very near the source of Dry Creek. Top-of-water-table contours on this map indicate that the general flow of groundwater in this area is parallel to the trend of Rattlesnake Ridge and that the four high chloride wells generally are downgradient of Dry Creek and any groundwater recharge that occurs as a result of Dry Creek. Thus, the locations of the wells and the general configuration of the water table are consistent with a Dry Creek recharge source for the high chloride groundwater.

As previously indicated, chloride is useful as an indicator of evaporation because it is not added or subtracted by most rock/water reaction. However, the other constituents in the groundwater do not share this virtue. The fourth column in Table 6-3 indicates the concentrations that other constituents would have if the average spring water were concentrated to the degree indicated by the chloride difference between the average spring water and the average high chloride groundwater (multiplied by 3.7492). With the exception of fluoride and sulfate, almost every constituent has a lower concentration than would be predicted on the basis of evaporation alone. The four sulfate concentrations, however, range from 15 to 82 parts per million, indicating that the good match with the average is fortuitous. Sodium, potassium, and magnesium could be lost through formation of or reaction (ion exchange) with clays and potassium could be lost to plants growing along the course of Dry Creek. Calcium could be lost through the formation of calcite. Nitrate could be lost to plants along the course of Dry Creek and to denitrification within the aquifer.

An added complication to understanding the controls on the chemistry of the high chloride groundwater is the possibility that the groundwaters have

Basin, is consistent with the greater distance of the recharge area from the ocean, the higher annual precipitation in the Spokane area, and with a lesser degree of evaporation in the cooler, less arid, Spokane area.

6.4.1.3.5 Laboratory Observations. Column recirculation test, using crushed Grande Ronde Basalt and natural groundwater at 85 °C, were carried out during the BWIP to aid in understanding the evolution of deep Hanford Site groundwaters. Results for two of these tests, approximately 3 months in duration, yielded chloride to fluoride release ratios of approximately 2.6:1. Results for a 3-month autoclave test with crushed Grande Ronde Basalt and DIW, carried out during the BWIP, were reported by McKinley (1990). This test, carried out in a internally-stirred direct-sampling autoclave at 85 °C, indicates a chloride to fluoride release ratio of approximately 1.4:1.

The BWIP test data are not directly applicable to the evolution of shallow waters on the Hanford Site for at least two reasons. First, the temperature maintained during both test was 85 °C, considerably hotter than the conditions under which shallow groundwaters evolve. Higher temperatures will greatly accelerate the breakdown of the glass phase within the basalt and might affect the kinetics of many of the dissolution and crystallization processes involved in basalt-water interactions. Second, the abundance of fresh glass exposed by crushing will lead to higher release rates for glass bound constituents such as chloride. The different results observed in the two tests might result from either the differences in starting solutions or the different dynamics in the two systems. The range of chloride to fluoride release ratios observed in these experiments implies that approximately 8 to 15 percent of the chloride observed in the springs might result from basalt leaching. However, these numbers, particularly the high-end, are considered inappropriately high for the natural system.

6.4.1.3.6 Summary. The value for the chloride to fluoride release ratio of 1.75:1, derived from the USGS data presented in Warner (1986), is much more applicable to the shallow Pasco Basin system and implies that approximately 10 percent of the chloride in the spring waters is a result of basalt leaching. However, this is believed to represent an upper limit to the ratio for the shallow Pasco Basin system. Chloride is concentrated in the residual glass, the most reactive part of the basalt. Therefore, the amount of glass, and thus, the amount of available chloride along a given flow path, will decrease with the passage of successive pore volumes of groundwater. The regional Grande Ronde aquifer considered by Warner (1986) is much tighter than the fractured, relatively shallow basalts on the ridges surrounding the Pasco Basin. Thus, flow times through the Grande Ronde aquifer on the Columbia Plateau are measured in terms of tens of thousands of years rather than the tens to hundreds of years probably required to transit the basalts within Rattlesnake and Yakima Ridges. Because of this difference in flow times, the basalts on the ridges have experienced many more pore volumes than the Grande Ronde aquifer and should be much more chloride depleted. Thus, the 10 percent basaltic chloride indicated by the Grande Ronde Columbia Plateau data should be taken as an upper limit with the realization that the actual basalt contribution to chloride in the springs is probably considerably smaller.

9 3 1 2 8 6 9 1 6 7 3

470 parts per million and a chlorine concentration of 50 parts per million. Analyses of rock from the outcrop where BCR-1 was collected indicate a fluorine concentration of 440 parts per million, in excellent agreement with the fluorine concentration reported by the USGS (Flanagan 1973). There is certainly some variation in fluorine and chlorine concentrations within the Columbia River Basalt sequence; however, the similarity between BCR-1 and the world-wide average for basalts probably indicates that BCR-1 is fairly representative of Columbia River Basalts.

The release of chloride from the basalts is assumed to be controlled principally by the dissolution and/or crystallization of the residual glass phase. However, there are a number of processes that might effect the release of fluoride in low-temperature dynamic systems. These processes include the following:

- Ion exchange between fluorapatite and partially evaporated meteoric recharge waters would contain significant chloride and essentially no fluoride
- Dissolution of the very fine-grained apatite within the mesostasis
- Retardation of apatite recrystallization by ions (e.g. magnesium and carbonate) adsorbed on crystal surfaces
- Scavenging of phosphate from solution by amorphous ferric oxides
- Partial substitution of carbonate for phosphate in apatites recrystallized at low temperatures in carbon dioxide charged groundwaters
- Aging of systems of conduits involved in groundwater transport by preferential leaching of chloride-rich glass during the passage of multiple pore volumes of water through the system
- Effects of groundwater flow rates on dissolution and precipitation during rock-water interaction.

Fluoride release from basalts at low temperature is an extremely complex process and cannot be predicted on the basis of simple models.

6.4.1.3.4 Field Observations. Warner (1986) used USGS water level data to define a groundwater flow path within the Grande Ronde aquifer, from a recharge area near Spokane into the Pasco Basin. Along the first 70 miles of this flow path, changes in groundwater chemistry resulting from rock-water interaction are relatively straight forward and include continuous increases in chloride and fluoride concentration as functions of distance along the flow path. The ratio of chloride to fluoride release from the basalts based on these data is 1.75:1. The best fit line for fluoride intersects the fluoride axis very near zero, consistent with the virtual absence of fluoride from meteoric water. The chloride best fit line intersects the chloride axis near 1.7 parts per million, indicating the chloride concentration in the recharge waters. This lower concentration, relative to that observed in the Pasco

the concentrations of all constituents to increase in the manner described by equation (6), comparisons between the chloride content of meteoric water, spring water, and groundwater by evaporative fractionation alone are likely to be misleading. A more effective indicator of evaluating the evaporative fraction of water is stable isotope composition.

6.4.2.2 Isotopic Evaluations. Application of the SIRA and solute concentration methods to evaluation of the Hanford Site unconfined aquifer requires information concerning aquifer geochemistry and possible sources of recharge water to the unconfined aquifer. Bounding conditions such as compositions and isotopic signatures of potential recharge waters and geochemical processes in which evaporation might be operating (e.g., evaporation during soil infiltration) also must be known or assumed.

The isotopic compositions of spring waters and unconfined groundwaters (Figure 6-7) serve as the basis for the most sensitive evaluation on the extent to which evaporation influences the evolution of groundwater in the unconfined aquifer at the Hanford Site. Unconfined aquifer compositions range from approximately -140 to -120 in del-D values, and spring water compositions range from -130 to -110; both compositional clusters are offset from the meteoric water line in a positive direction. Also plotted on Figure 6-7 are compositions for the Yakima and Columbia Rivers for samples collected at different times. These data have differing signatures within each data type, indicating some temporal (e.g., seasonal) variation in isotopic composition. Isotopic signatures for the two rivers bracket compositions for springs and unconfined aquifer samples. The Columbia River is isotopically lighter than both groundwater and spring water clusters, while the Yakima River is isotopically heavier than both clusters. For comparison to these compositions, the results for Hanford Site meteoric waters (Graham 1983) are presented in Figure 6-8. The range in isotopic signatures for these waters is (in del-D units) -140 to -80. These data also are offset from the meteoric water line toward more positive values and overlie the groundwater and spring water compositions. Small positive departures from the meteoric water line are typical of arid and semiarid regions (Hoefs 1980).

Because rainwater is not a significant contributor to recharge at the Hanford Site, evaporation can only be effective in fractionating spring waters prior to their infiltration to depth. However, the spring waters are predominantly more isotopically positive than groundwaters, i.e., more enriched in deuterium and ^{18}O. In general, evaporation does not appear to be capable of significantly modifying water compositions observed in the unconfined aquifer because fractionation during evaporation produces isotopic relationships opposite to those observed for the springs and unconfined aquifer.

Although the calculated magnitude of fractionation resulting from evaporation is sensitive to such factors as ambient temperature, humidity, and ionic strength, the direction of fractionation with respect the original isotopic signature of the evaporating water is always in a positive direction for both hydrogen and oxygen. Only in concentrated brines at high fractional evaporation is this direction reversed. The ionic strength of groundwater in the unconfined aquifer at the Hanford Site waters is approximately 5 mM

6.4.2 Model B

A second model for evaluating the effects of evaporation involves a reevaluation of evaporative fractionation to reconcile questions regarding the basic assumptions of the fractionation model. The second model also use isotopic data to address the question of solute mass balance.

6.4.2.1 Chloride and Solute Mass Balance. One of the most important aspect of this model concerns the behavior of chloride during rock-water reaction. It is indicated from new data on the composition of rocks and soils at the Hanford Site obtained by regulatory methods that chlorine concentrations in the leachates (up to 60 mg/L) are typically over 10 times larger than fluorine concentrations in the leachate compositions.

It is also indicated from the results of rock-water tests with basaltic material and Ringold sediments that concentrations of chloride and fluoride resulting from rock-water reactions with both these materials are quite similar to those of most groundwaters in the unconfined aquifer, with the exception of the high-chloride groundwaters. These results indicate that significant amounts of chloride are rapidly released to water reacting with basalt or Ringold sediment at low temperatures. Chloride concentrations in water resulting from these tests range from over 13 mg/L Cl in closed system tests to 0.4 mg/L Cl in open system leach tests with both basalt and Ringold sediment. Ratios of chloride to fluoride in the tests consistently exceed 1.0 and range to values greater than 10. Concentrations of chloride of nearly 10 mg/L were produced by reaction with Ringold sediment previously flushed with distilled water for 56 days. It is indicated from the results of these tests that rock-water reaction is an important source of chloride, in groundwater, and that amount of chloride resulting from rock-water reaction exceed those of fluoride.

These results also appear to be consistent with experimental studies on the partitioning of fluorine and chlorine between apatite and fluids, including water by reacting apatite of known composition with distilled water (Brenan 1991). The results of these studies indicated that apatite/water partition coefficients for fluorine (20-30) are about 100 times larger than those for chlorine (0.1-0.3), i.e., chlorine was released from apatite about 100 times more effectively than fluorine. It also is indicated from the results of apatite/melt partition coefficients for fluorine (1 to 2) and chlorine (0.05 to 0.2) (Brenan 1991) that apatite might be expected to contain about 10 times more fluorine than in coexisting glass, and that the glass may be expected to contain about 10 times more chlorine than in the coexisting apatite. It is also suggested from the results of preliminary evaluations of the results of the rock-water tests reported here, that apatite-water reactions occurred in these tests.

The main implication of these empirical results is that chloride concentration might not be a good indicator of the extent of fractionation in processes such as evaporation if chloride does not behave as an incompatible constituent. Mass balance calculations based on chloride concentrations alone therefore could yield misleading results in evaluating the extent of evaporative fractionation. Although evaporative processes would still cause

addition, each isotopic bounding condition was used as input to two humidity/temperature conditions, one for cold months and one for warm months.

Equation (7) was integrated numerically to solve the change in isotopic ratio as a function of the volumetric water fraction remaining after evaporation, f, for both hydrogen and oxygen. Isotopic ratios were converted to standard delta notation and used to construct evaporative fractionation trends. These calculations resulted in four calculated fractionation trends, two each for warm and cold weather evaporation. Results of calculations are shown on Figure 6-7 and Figure 6-10 along with the meteoric water line for reference.

Similar calculations were performed to evaluate the range of possible trends and the magnitude and fractionation paths associated with these trend using a variety of initial compositions, including meteoric water, and the four bracketing sets of conditions described above.

6.4.2.3 Summary of Model Results. Calculations of evaporative isotopic fractionation for unconfined groundwater aquifer compositions indicate the following:

- Hanford Site waters that undergo evaporative fractionation move toward more positive isotopic signatures, but with little deviation from the meteoric water line; i.e., fractionation trends sub-parallel to the meteoric water line.

- The isotopic compositions of the high chloride groundwater cannot be derived from most spring waters

- The maximum amount of evaporation associated with generation of high chloride groundwater with the largest ^{18}O, from spring water with the lowest ^{18}O and ^{2}H is 5 to 15 percent for the range of conditions evaluated

- The generation of this high chloride composition from meteoric water with a composition of del ^{18}O of -18.7 and del ^{2}H of -140, requires only 10 to 20 percent evaporation

- The local meteoric water composition might require less than 15 percent evaporation for most reasonable fractionation paths

- Chloride concentrations in the high chloride groundwaters are not consistent with the amounts of evaporation required for derivation from either spring water or meteoric water (50% to >90%), compared to those corresponding to the maximum extent of evaporation indicated from isotopic constraints.

Based on the isotopic constraints for evaporation controls on the generation of the high chloride groundwaters, it is indicated that an alternative explanation for the composition and evolution of this groundwater might be required. It is seen from comparison between the high chloride

(calculated from mean unconfined aquifer compositions in Chapter 5.0, Table 5-2), and is far too low for this effect to be manifested.

6.4.2.2.1 General Relationships. A comparison of isotopic signatures for spring and groundwaters with solute concentrations also does not support the hypothesis that evaporation has been a significant determinant of groundwater compositions. Hydrogen isotope signatures (del-D) are plotted against chloride concentrations in Figure 6-9. If evaporation were responsible for compositional variation for both isotopic signatures and solute concentrations, a plot of del-D values and the conservative solute chloride should show significant correlation. As shown in Figure 6-9, this is not the case, either for water samples as a whole, or for individual data clusters. Note that the more dilute Columbia River samples are isotopically lighter than the more concentrated Yakima River samples. These samples again approximately bracket spring and groundwater compositions.

The influence of mixing between evaporated brines and nonevaporated groundwaters also might be evaluated by reference to Figure 6-9. If an evaporite brine is mixed with relatively fresh water, a mixing line on a figure such as Figure 6-9 will be apparent. Such a relationship is apparent in comparing compositions for the Hanford Site confined aquifer, where deep-seated evaporated brines have apparently mixed with fresher groundwaters (McKinley 1990). Figure 6-9 shows no such relationship. Increases in chloride are not accompanied by complimentary increases in del-D.

Evaporation does not appear to be a significant contributor to observed groundwater compositions. Deviations from the meteoric water line might be explained by a similar deviation and compositional range observed for meteoric waters and Yakima and Columbia River waters. These waters comprise the potential surface-water recharge for the unconfined aquifer at the Hanford Site.

6.4.2.2.2 Quantitative Relationships. A quantitative evaluation of the possible effect of evaporation also might be made using equations of Sofer and Gat (1975) for fractionation expressed as a function of percent water remaining after incremental evaporation. Because the calculated magnitude of fractionation resulting from evaporation is sensitive to such factors as ambient temperature, humidity, and ionic strength, values for these parameters that reasonably bracket the expected range of conditions were selected to constrain the range of possible solutions.

Because evaporation is assumed to take place during transit of spring waters across the ground surface, RS was assumed to equal RL. Humidity and temperature data were obtained from the Hanford Meteorological Station; warm-month temperature and humidity was taken to equal 30 °C and 35 percent, while cold-month temperature and humidity were taken to equal 6 °C and 75 percenet. Two bounding values, taken from Sofer and Gat, were used for RA. The following constant del values, in pairs for hydrogen and oxygen, were subtracted from initial del values for evaporating waters: 55/7 and 80/12. In other words, RA was set at values corresponding to waters 55 per mil lighter than bulk waters with respect to hydrogen and 7 per mil lighter with respect to oxygen. A similar procedure was followed for the numerical pair 80/12. In

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groundwater and low chloride groundwater compositions that the high chloride groundwater differs primarily in their larger concentrations of Ca, Na, Cl, and SO4. These constituents are also the primary components of the salts NaCl and $CaSO_4$, which are two of the most common minerals in evaporites (Krauskopf 1979). One possible explanation is that the elevated concentrations of these constituents could be attributable to dissolution of small amounts of these salts. This possibility would require parts of the aquifer to be relatively stagnant or not efficiently purged of all soluble salt constituents. This alternative differs from evaporation because the dissolution of residual salt or mixing with brine formed by such dissolution does not impact constituents other than the those in the salts. This explanation is similar to McKinley's (1990) interpretation for the high-chloride groundwaters in the confined aquifer based on isotopic data and compositional characteristics.

6.4.3 Summary

New information provides an improved basis for constraining the extent of evaporative processes associated with the evolution of groundwater in the unconfined aquifer at the Hanford Site. It is indicated that although ubiquitous evaporation in the semiarid region of the Hanford Site clearly influences the composition of waters regionally, it might not have a dominant role in influencing the compositional evolution of spring water or groundwater at the Hanford Site. The evaluation of the role of evaporation in the conceptual model for the range and spatial distribution of natural compositional variability might require further refinement. In addition, the apparently anomalous composition of the high-chloride groundwaters warrants further evaluation.

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fluid (Cn_i). The initial parental composition generally is assumed to be that of recharge water to the aquifer. However, any combination of parent-daughter pairs potentially related by evaporation can be evaluated in this manner.

In considering the role of evaporation on the composition of groundwater in the Pasco Basin, a distinction can be made between the composition of meteoric water in the region, and the potential effects of subsequent evaporation on upgradient recharge water (i.e., spring water).

The regional composition of meteoric water reflects compositional characteristics of the initial source, and also varies systematically with distance from the source. The primary reference for meteoric water is the mean chemical and isotopic composition of sea water (Craig 1961). Airborne meteoric water derived from evaporation of sea water initially has the same hydrogen and oxygen isotopic composition as sea water, and contains traces of dissolved components such as sodium and chloride. As airborne meteoric water is transported away from the source, its composition is modified, i.e., fractionated, by evaporation associated with the transportation process. In general, the concentrations of dissolved solids (e.g., Na and Cl), and ratios of ^{2}H (deuterium) to ^{1}H and ^{18}O to ^{16}O increase systematically with distance from the initial source, reflecting an increasing extent of evaporation. The regional trends in the composition of meteoric water are observed as a consequence of this process. The regional pattern of chloride in rain water is illustrated in Figure 6-1.

6.3 ORIGIN OF CHLORIDE AND FLUORIDE IN GROUNDWATER

The source of chloride and fluoride in surface water, springs, and groundwater in the vicinity of the Hanford Site is a most important aspect of the conceptual model for the evolution of groundwater composition in the region. This aspect of the conceptual model is important because the source of chloride, in particular, is the cornerstone for mass balance considerations for evaluating the extent of evaporation on the composition of groundwater.

Chloride often is used as the indicator constituent of preference for evaluating evaporative water loss in meteoric water because chloride satisfies the provisions identified previously. Fluoride generally is less useful by itself because fluoride often is undetectable in meteoric water, e.g., weight ratio of fluoride to chloride in sea water is approximately 0.00007.

It is clear that fluoride in surface water, springs, and groundwater in the region originates from rock-water interaction because fluoride is virtually absent from meteoric water and because basaltic materials are an expected source of fluorine available for reaction with water. However, there is less agreement regarding the source of chloride in these waters.

Disagreement regarding the source of chloride in the groundwater system has stemmed mainly from the lack of data on the concentrations of this constituent in aquifer materials, and also the lack of data regarding the solubility of this constituent under aquifer conditions. Two positions on this subject have, therefore, emerged. One position is based on the premise

9 3 1 2 8 5 9 1 6 8 3

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9 3 1 2 8 6 9 1 6 9 4

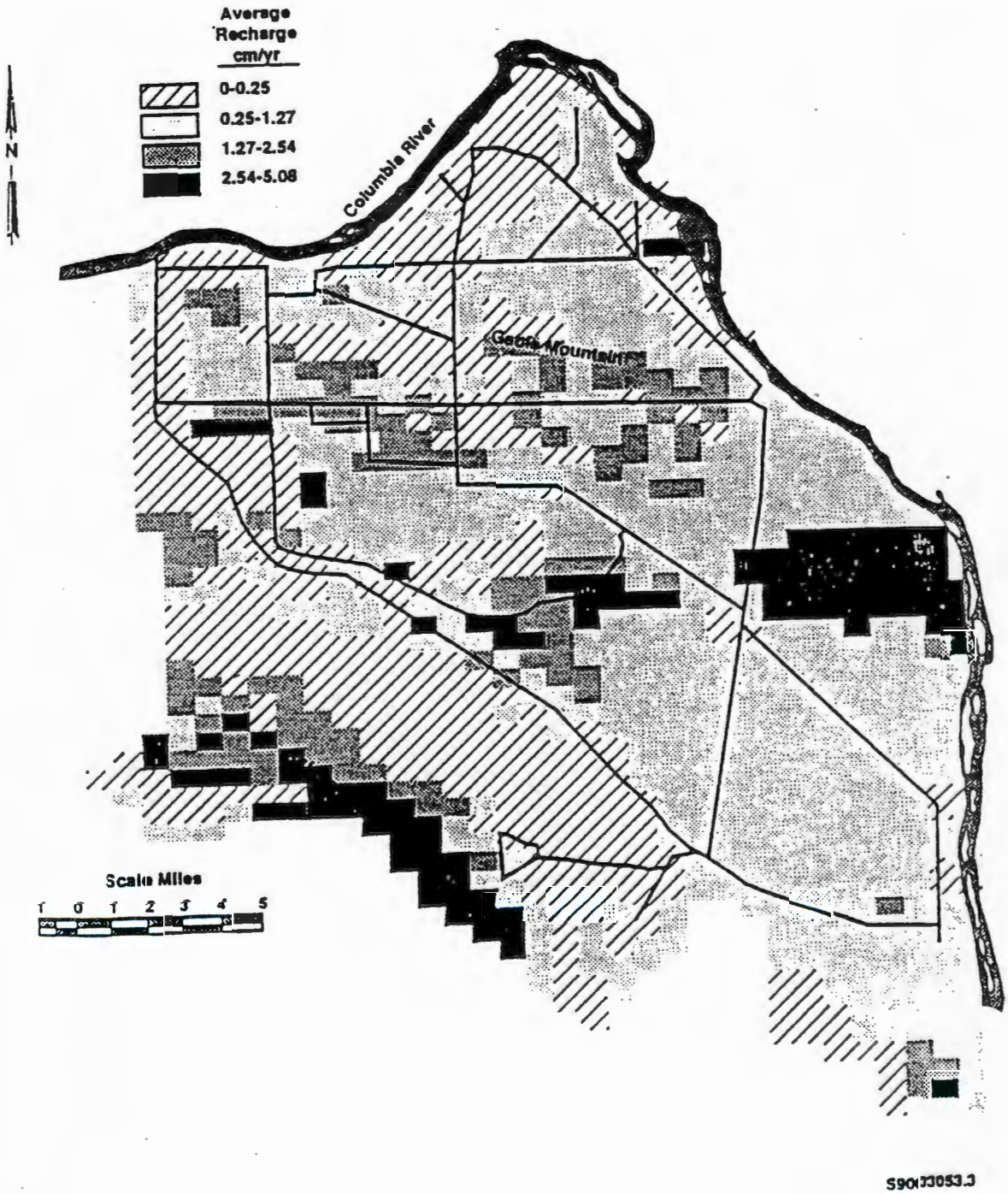


Figure 3-1. U.S. Geological Survey-Modeled Recharge for the Hanford Site (Bauer and Vaccaro 1990).

9 3 1 2 8 6 9 1 6 8 5

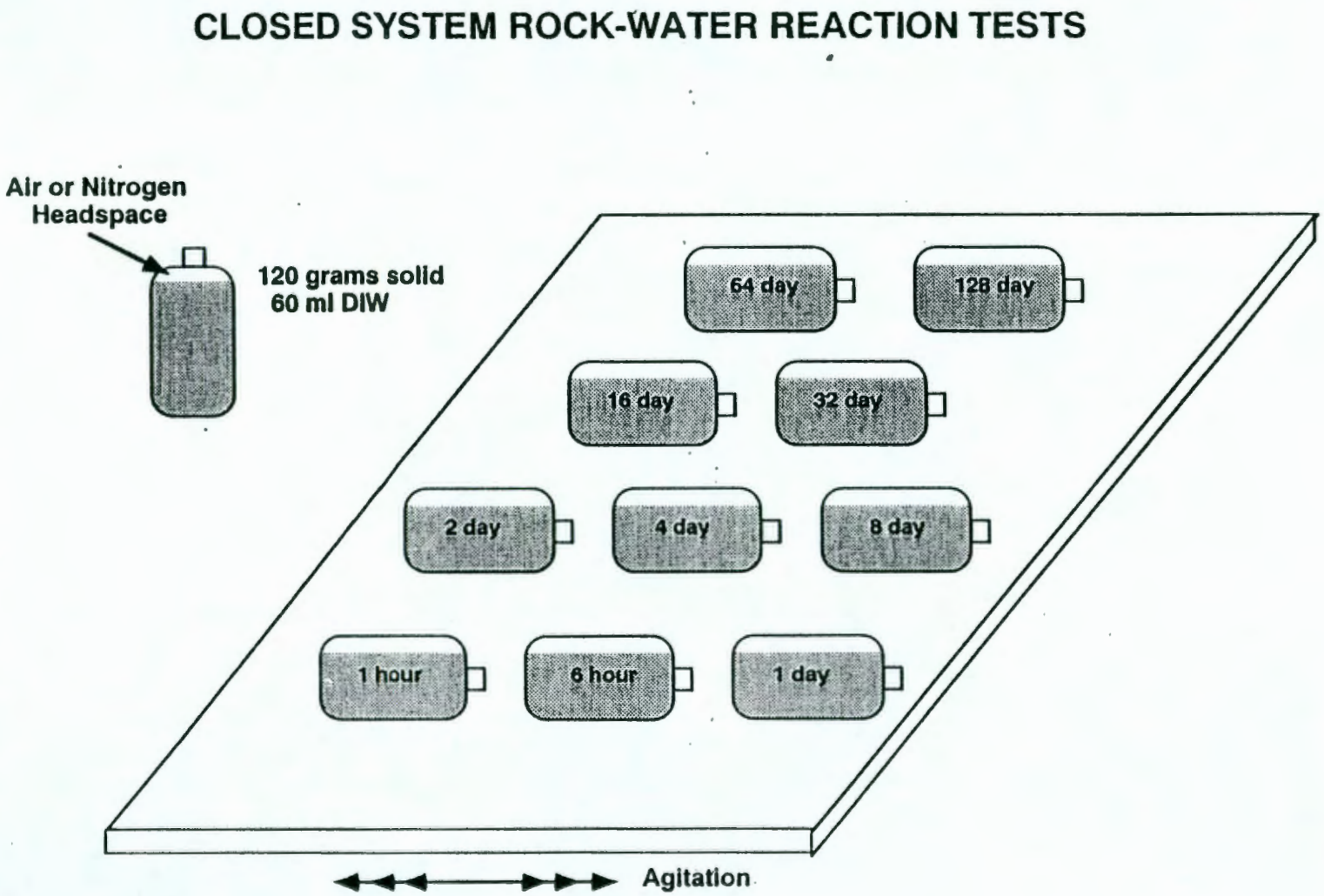
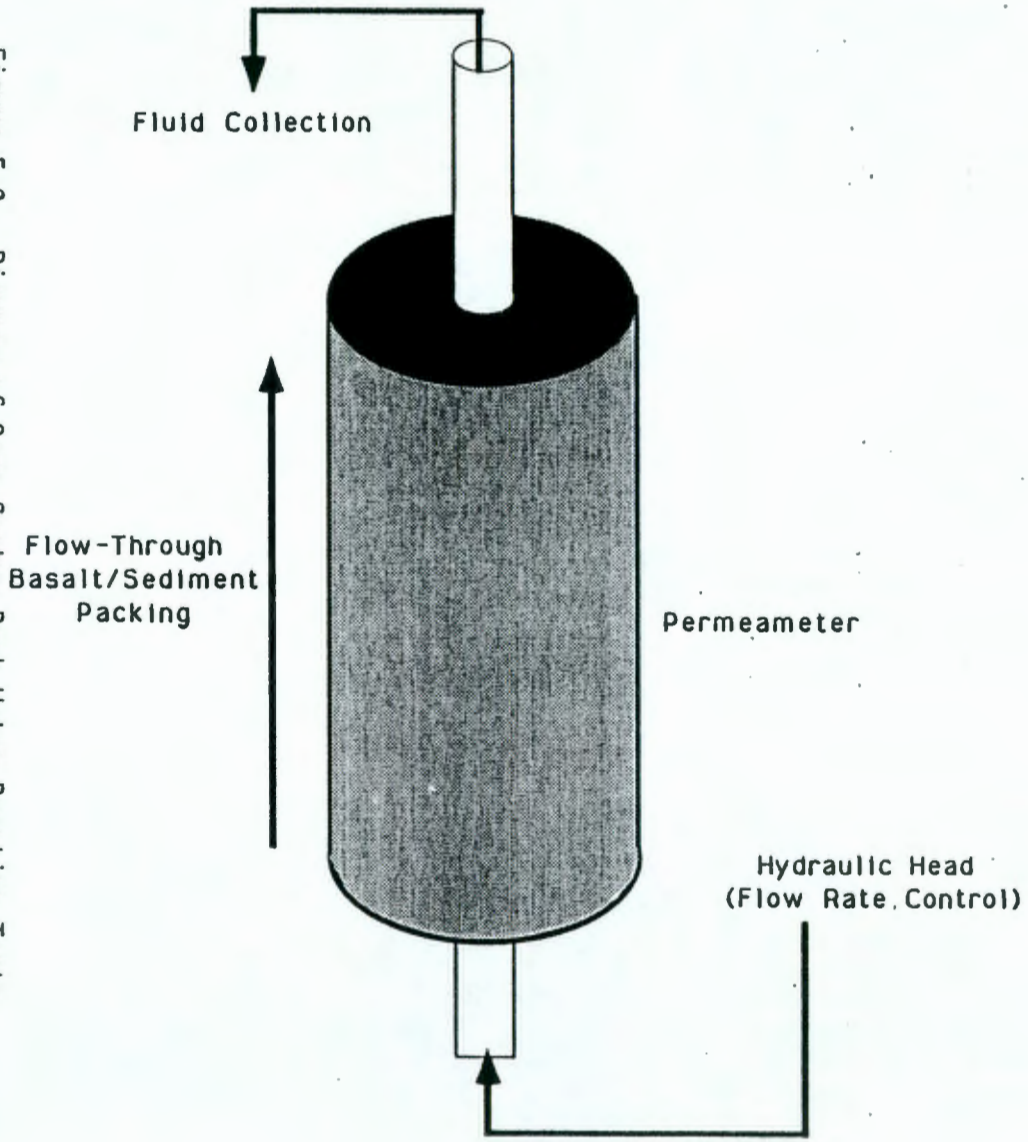


Figure 5-1. Diagram of Closed System Rock-Water Reaction Tests.

OPEN SYSTEM ROCK-WATER REACTION TESTS



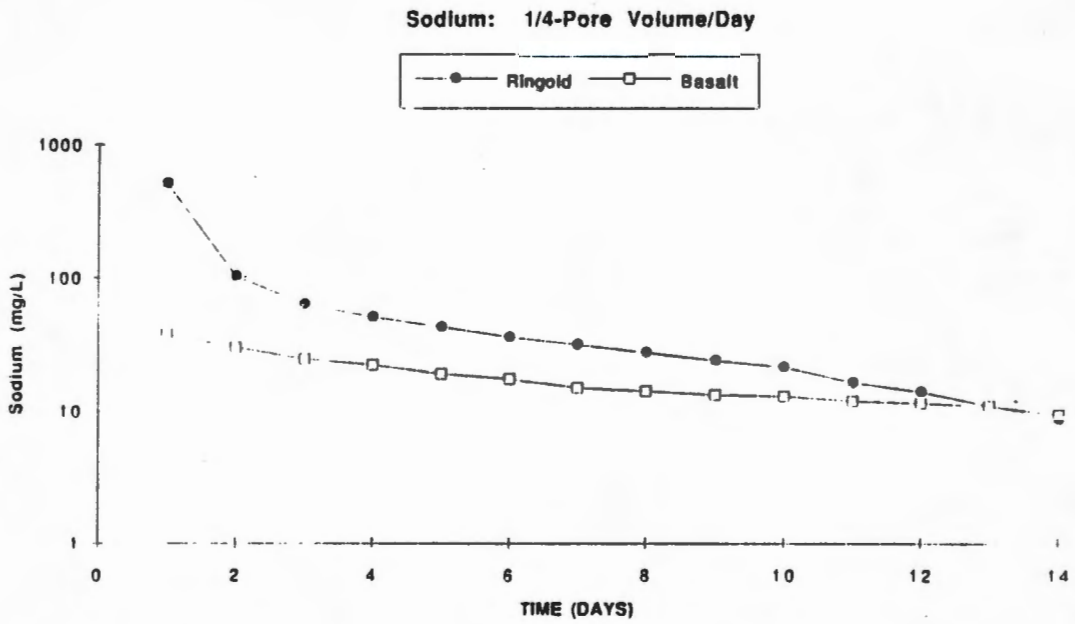
0.50 Pore Volume/Day
(2-Day Residence)

- Crushed Basalt + DIW
- Ringold Sediment + DIW

0.25 Pore Volume/Day
(8-Day Residence)

- Crushed Basalt + DIW
- Ringold Sediment + DIW

Figure 5-2. Diagram of Open System Rock-Water Reaction Tests.



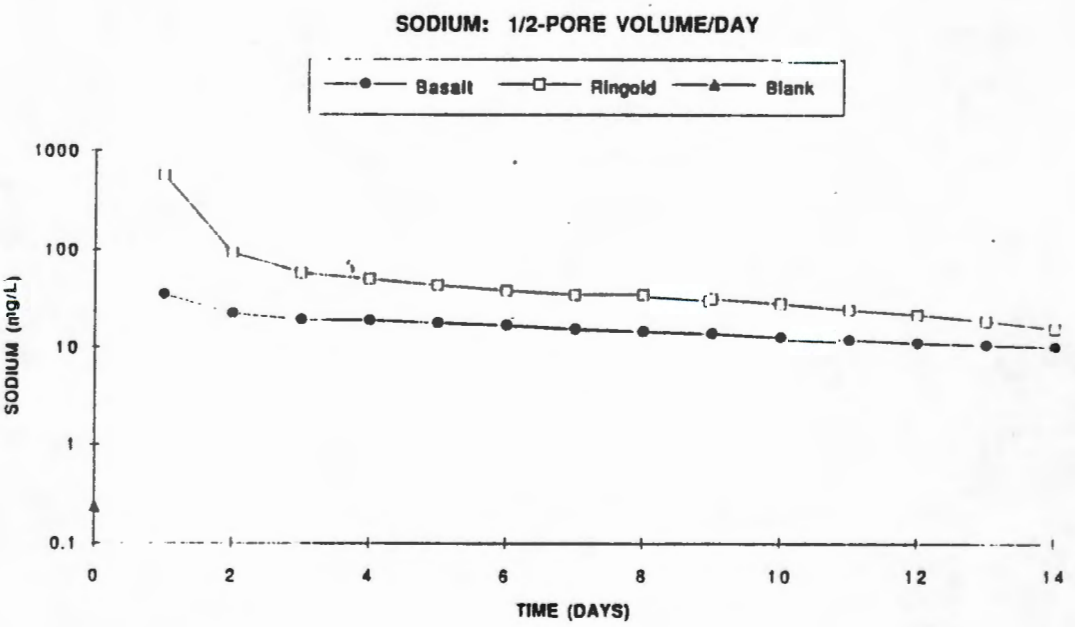
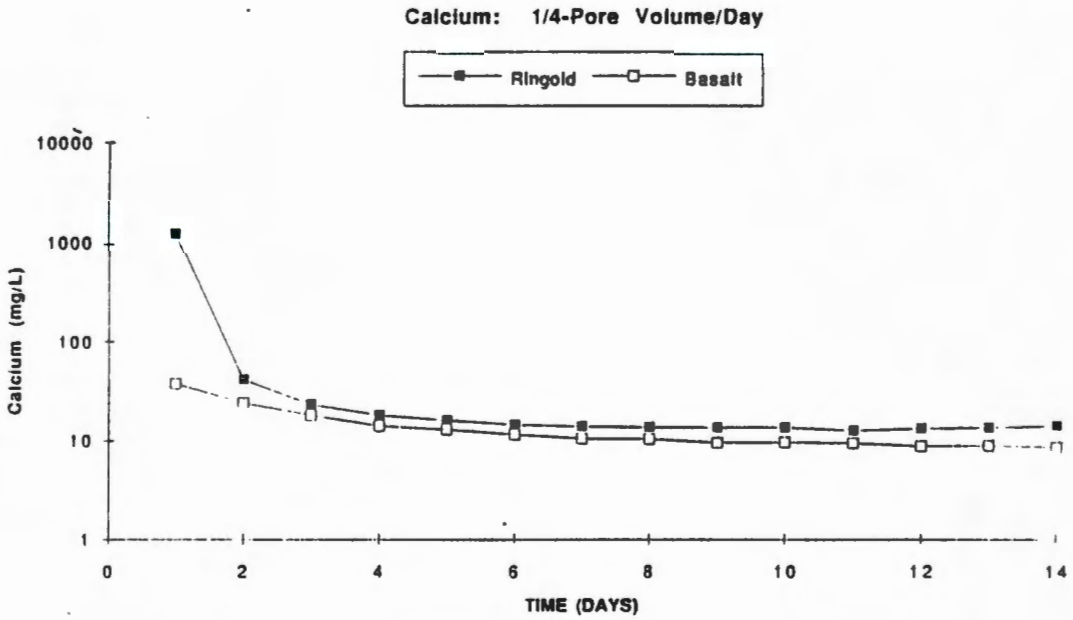


Figure 5-3. Results of Open System Leach Tests, Sodium versus Time.

9 3 1 2 8 6 9 1 6 8 8



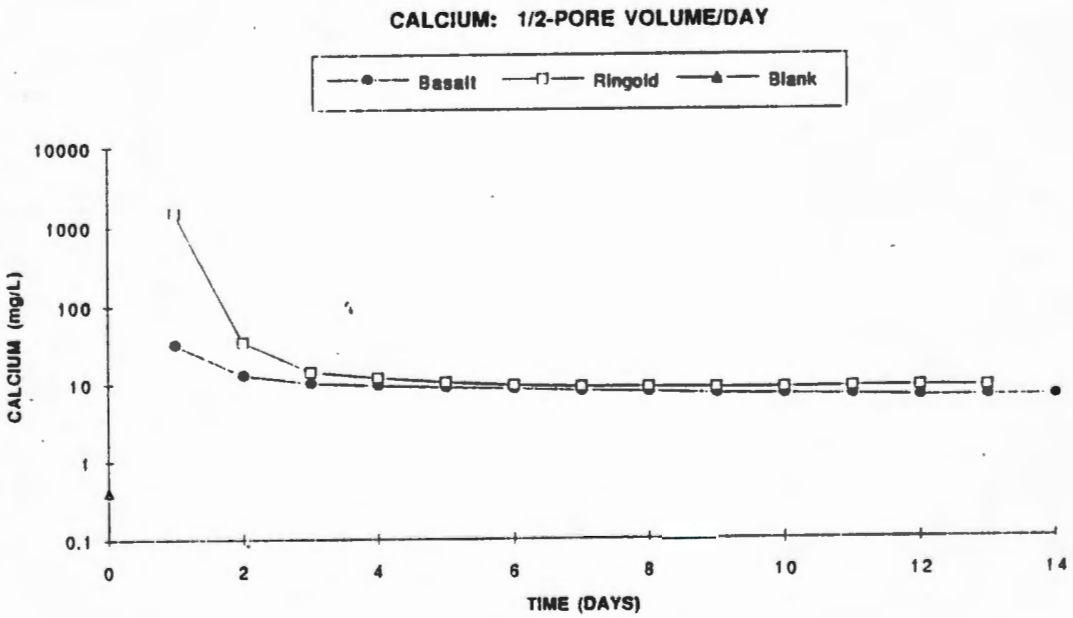
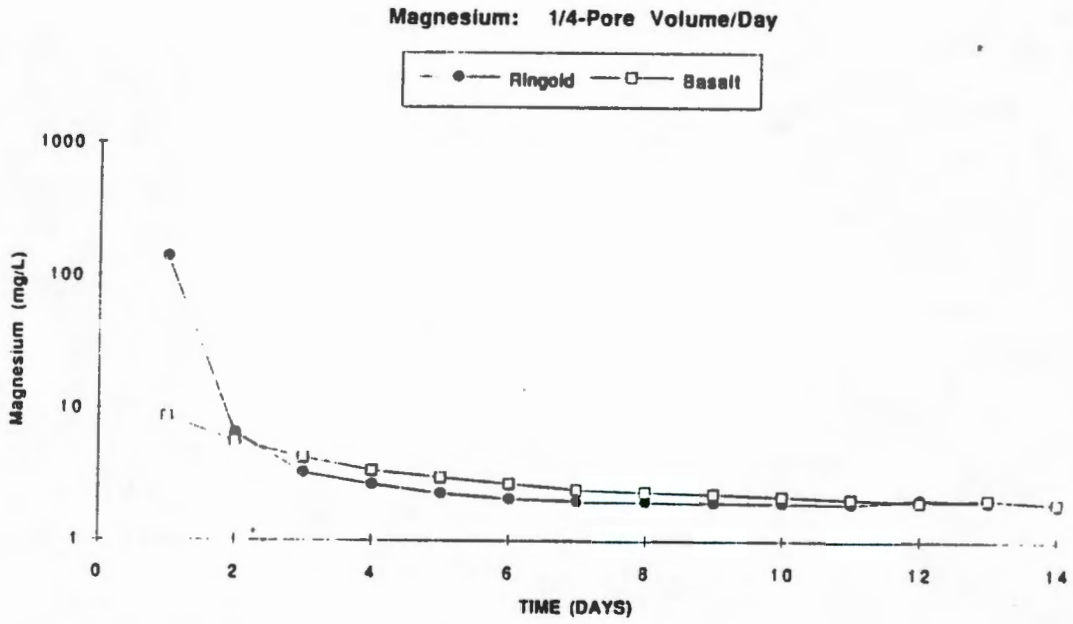


Figure 5-4. Results of Open System Leach Tests, Calcium versus Time.

9 3 1 2 8 5 9 1 6 8 9



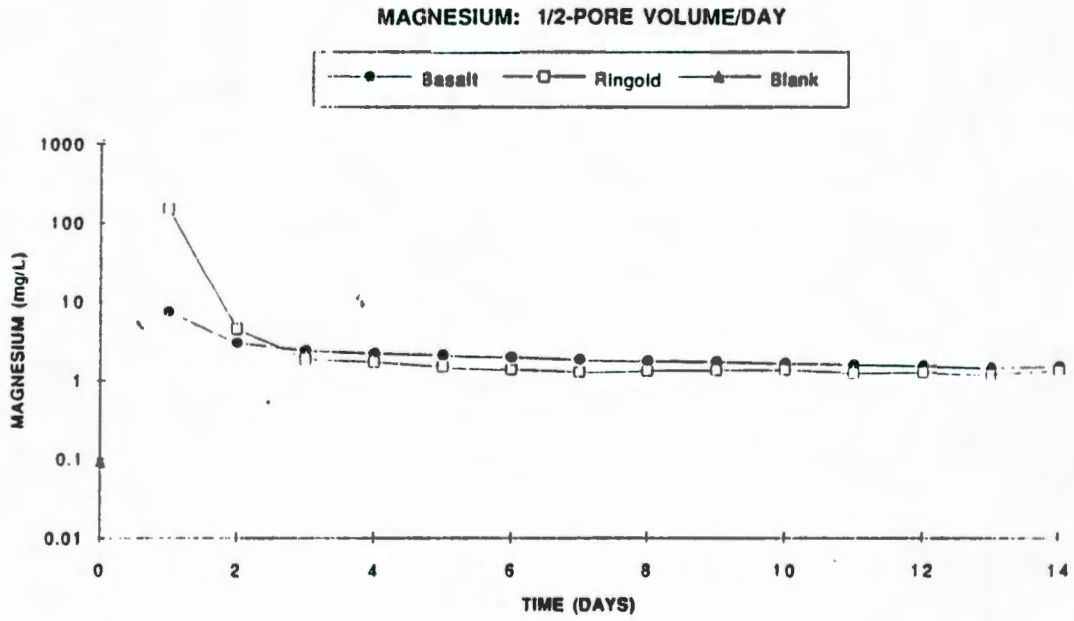


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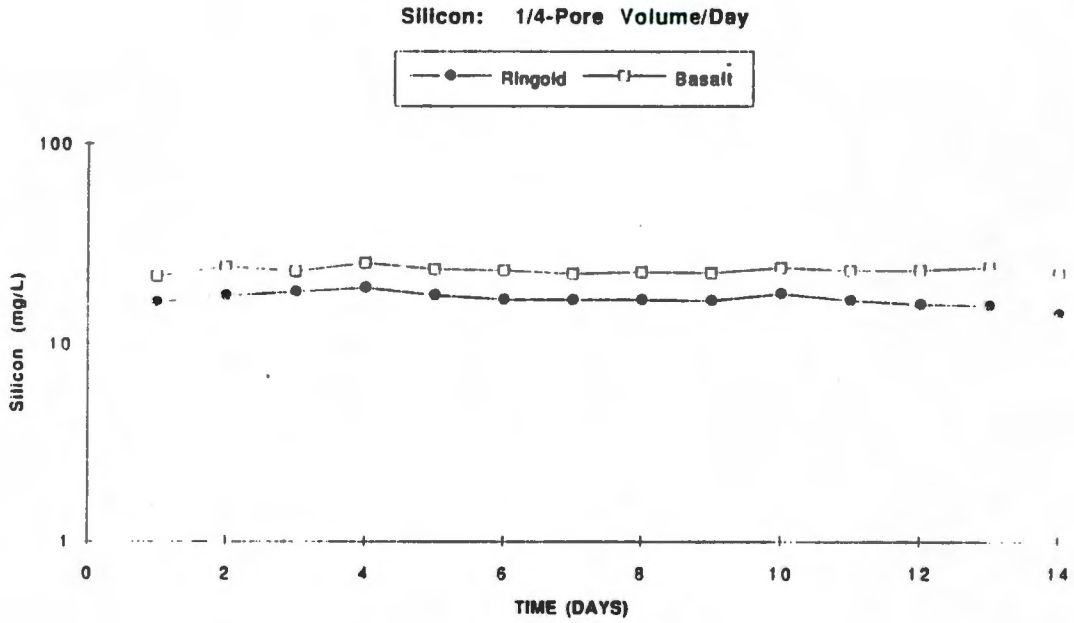
Figure 5-5. Results of Open System Leach Tests, Magnesium versus Time.



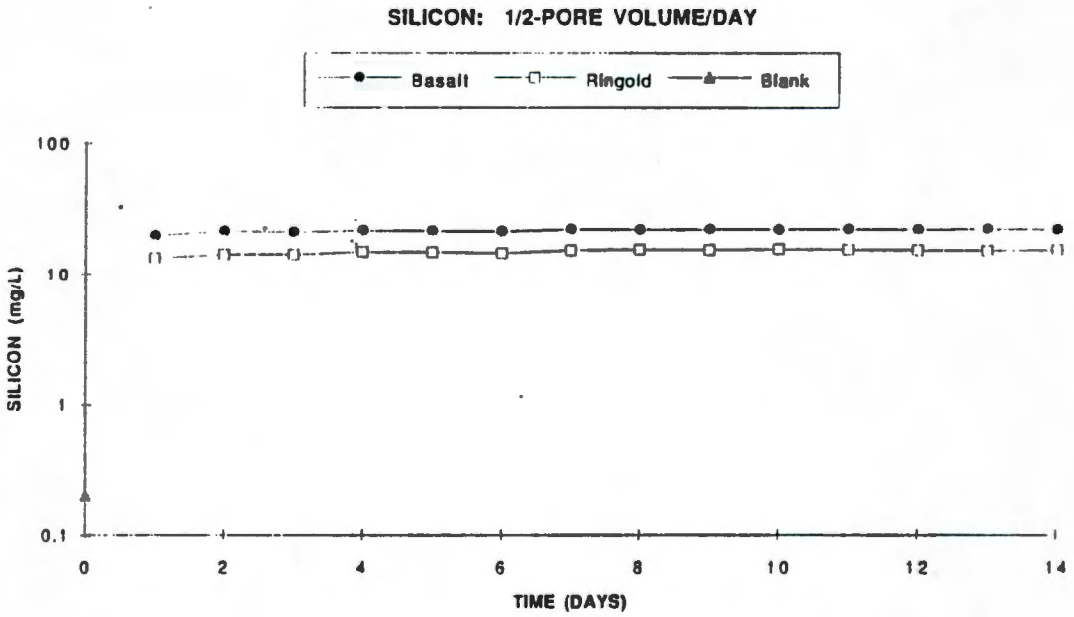


Figure 5-6. Results of Open System Leach Tests, Silicon versus Time.

9 3 1 2 8 6 9 1 6 9 1

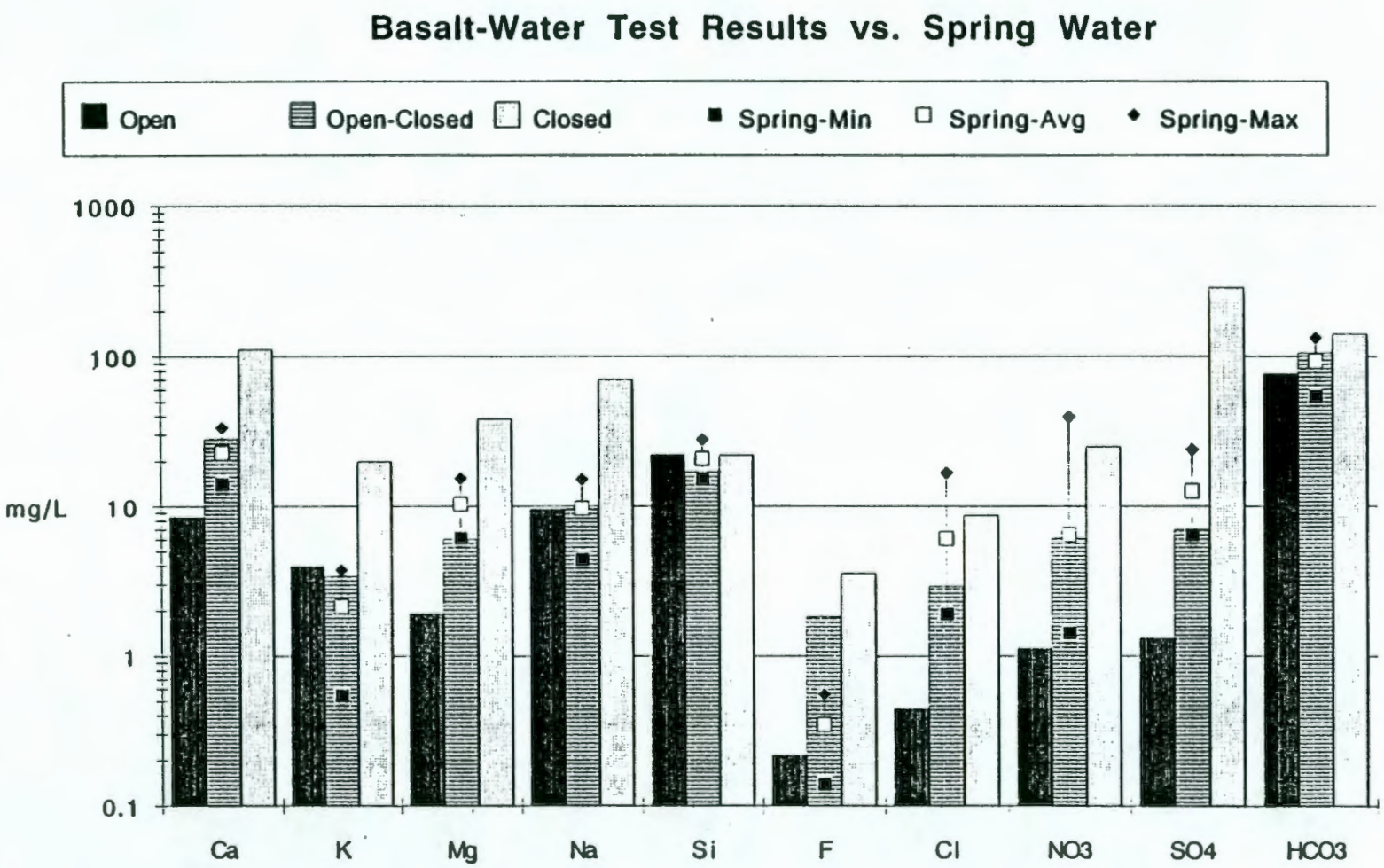


Figure 5-7. Basalt-Water Test Results versus Spring Water.

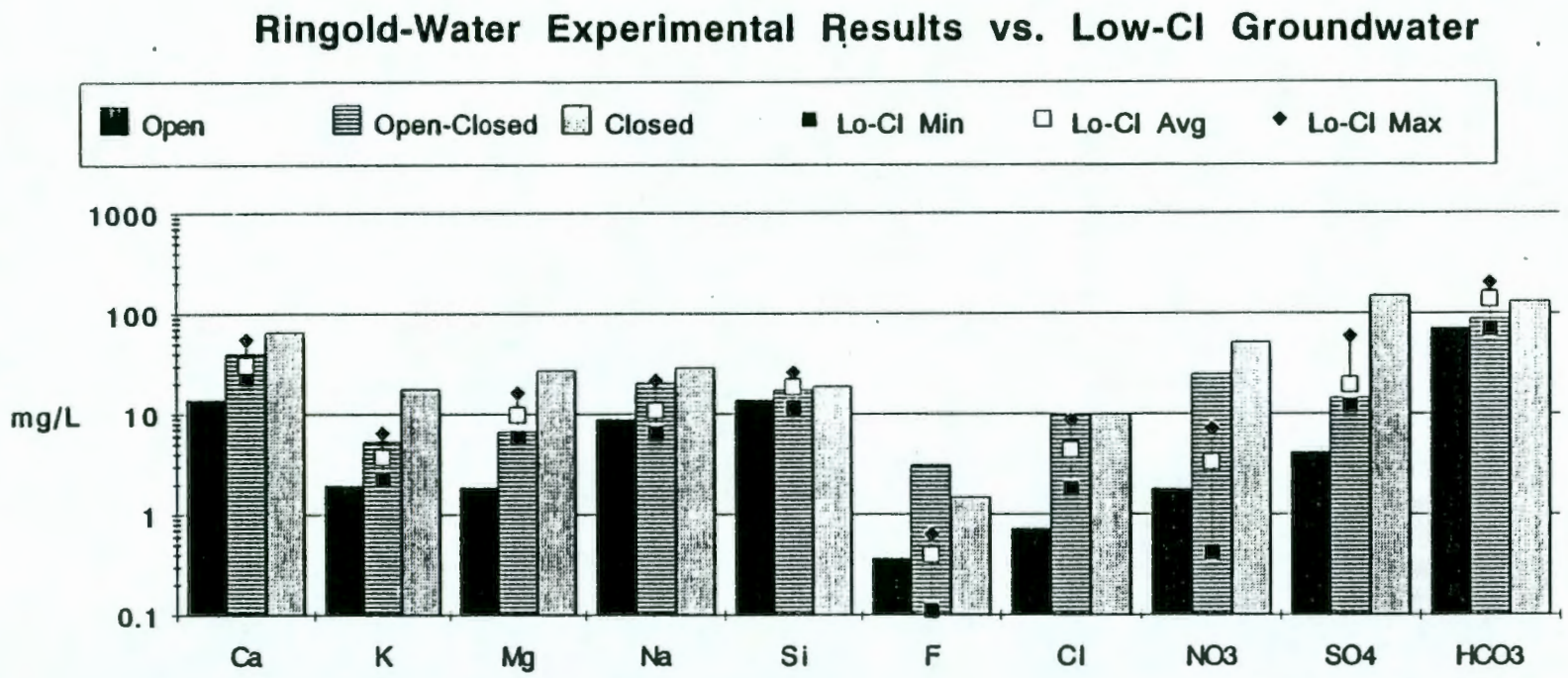


Figure 5-8. Ringold-Water Experimental Results versus Low-CL Groundwater.

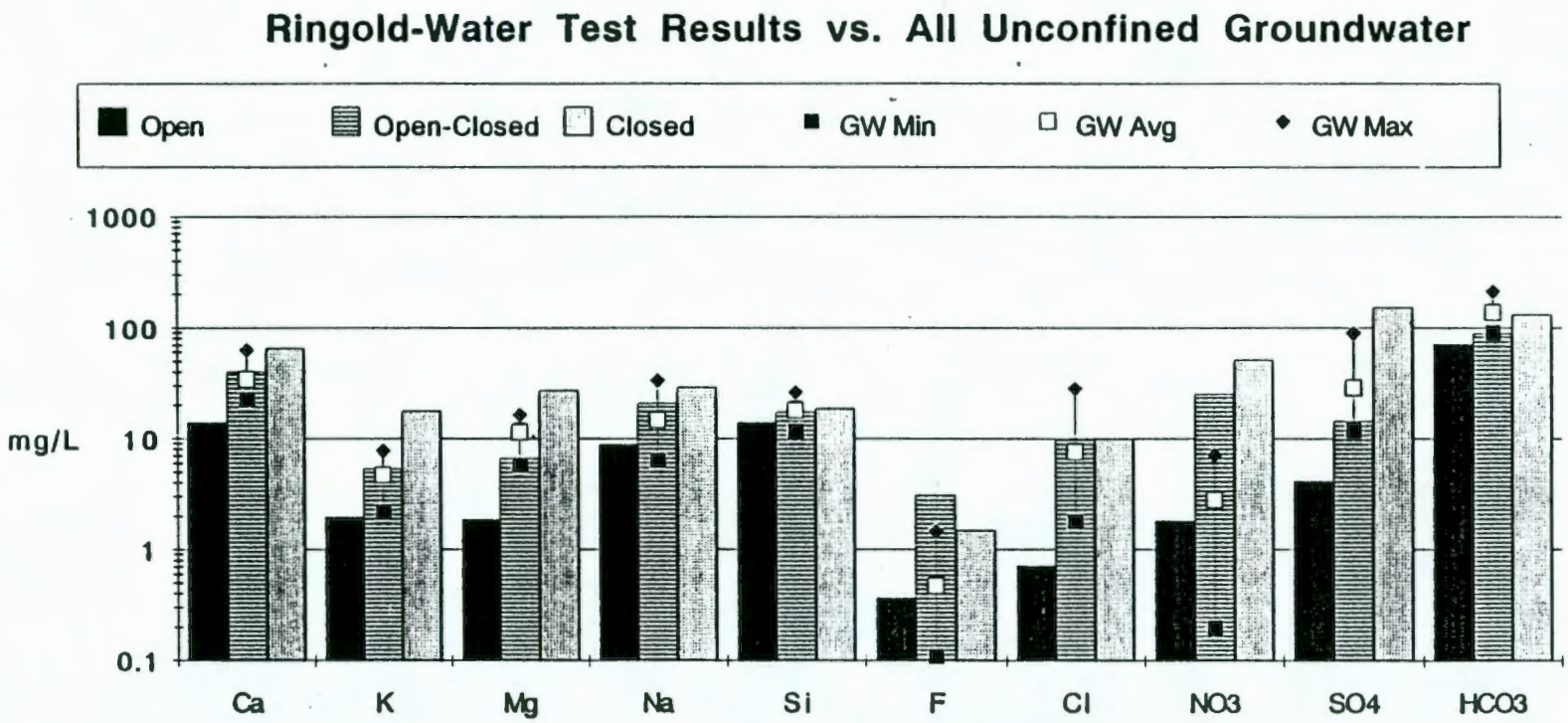
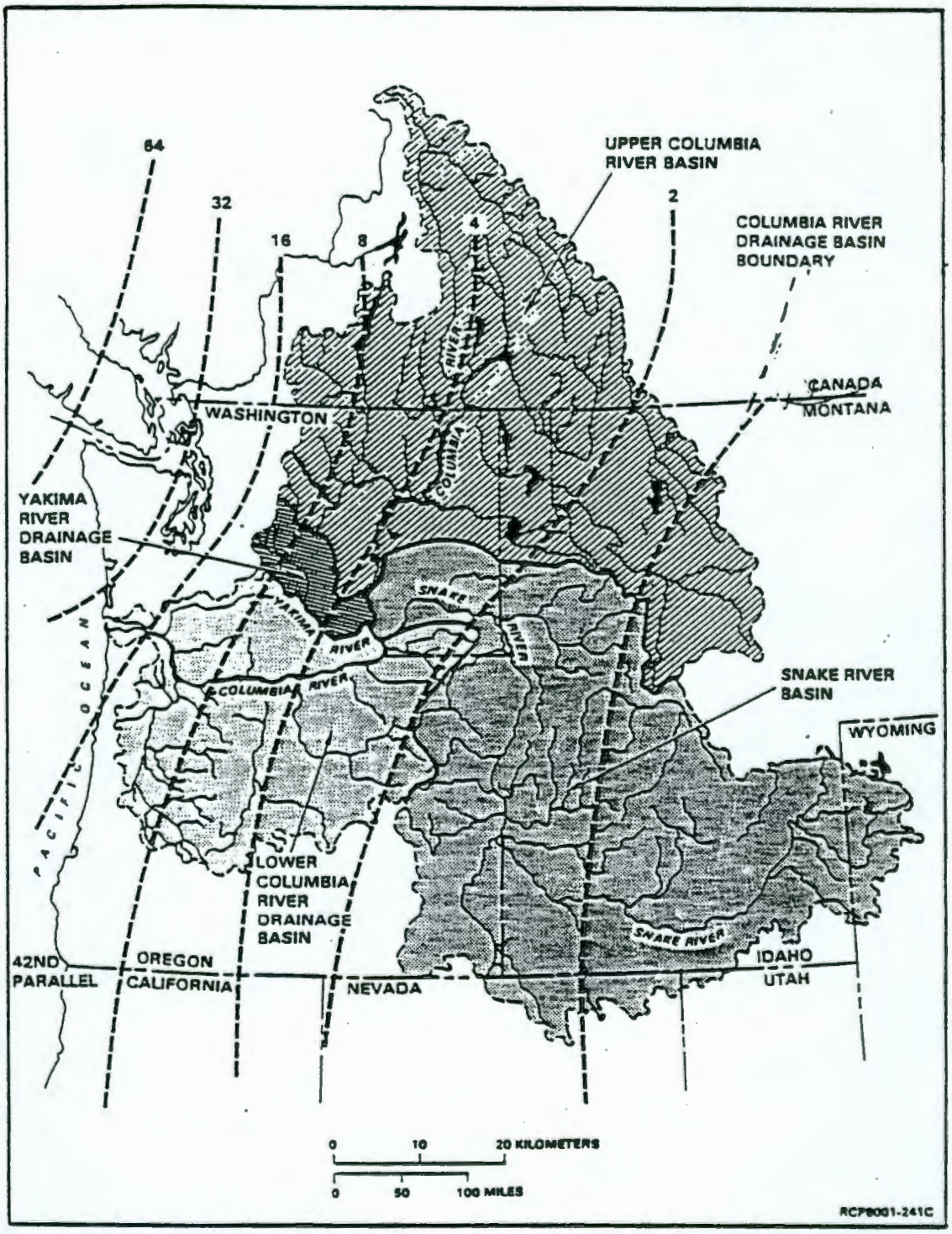


Figure 5-9. Ringold-Water Test Results versus All Unconfined Groundwater.

METEORIC CHLORIDE DEPOSITION RATE (KILOGRAMS/HECTARE/YEAR)



FROM DOE (1988) MODIFIED FROM ERIKSSON (1960)

Figure 6-1. Meteoric Chloride Deposition Rate.

9 3 1 2 8 6 9 1 6 9 5

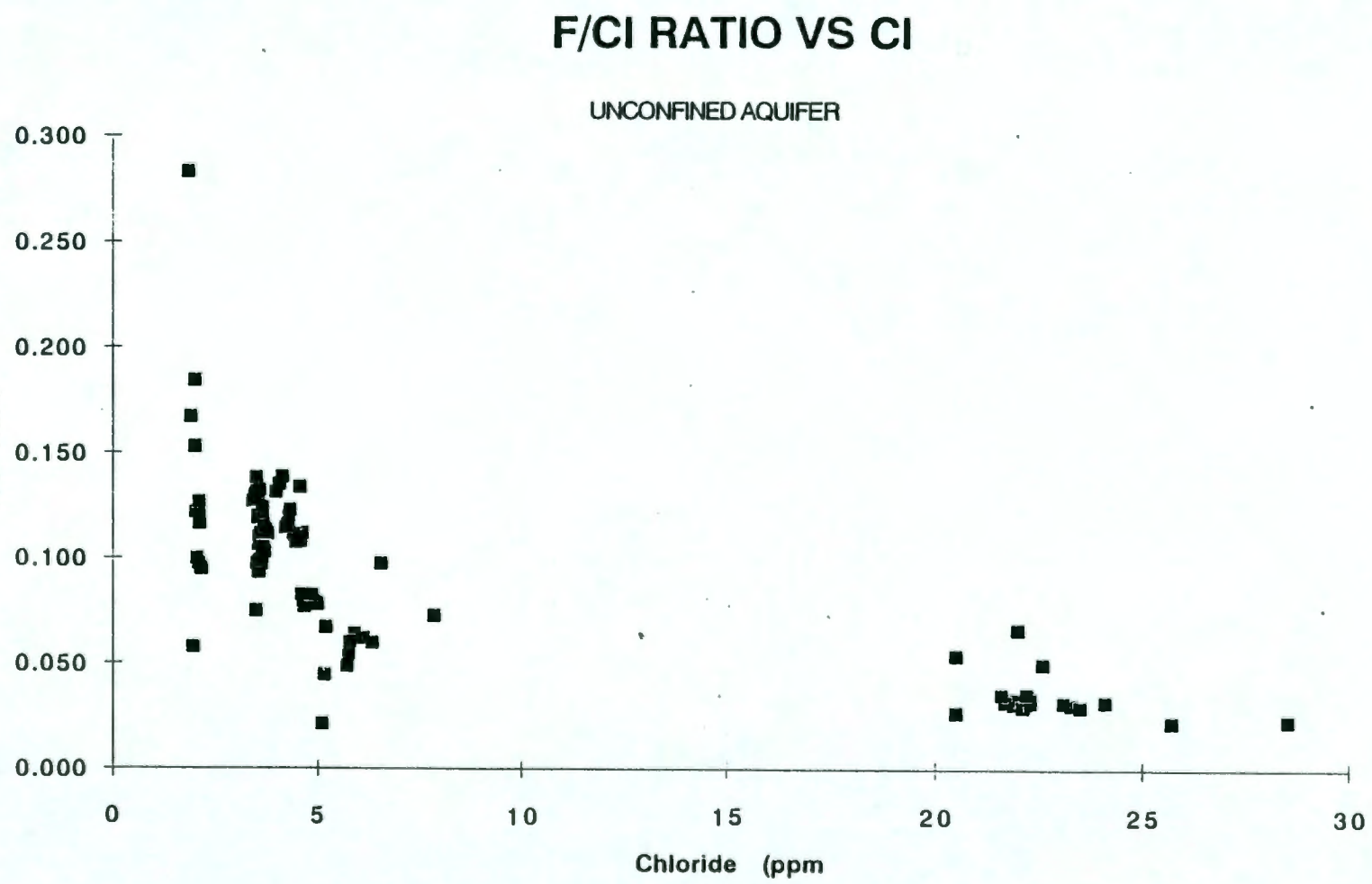


FIGURE D-6.2

Figure 6-2. Plot of Fluoride/Chloride Ratio versus Chloride in the Unconfined Aquifer.

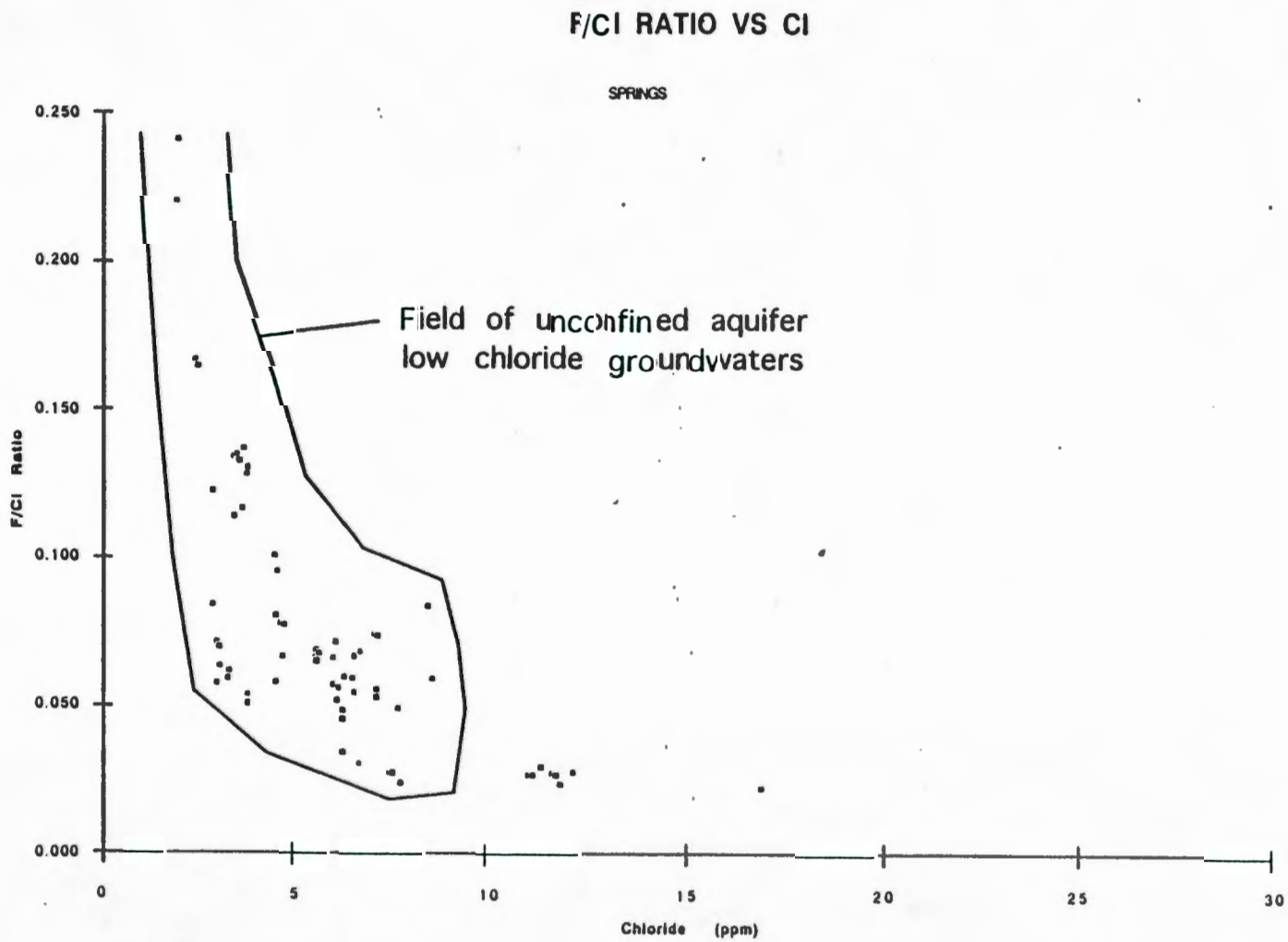


FIGURE D-6.3

Figure 6-3. Plot of Fluoride/Chloride Ratio versus Chloride in Spring Waters.

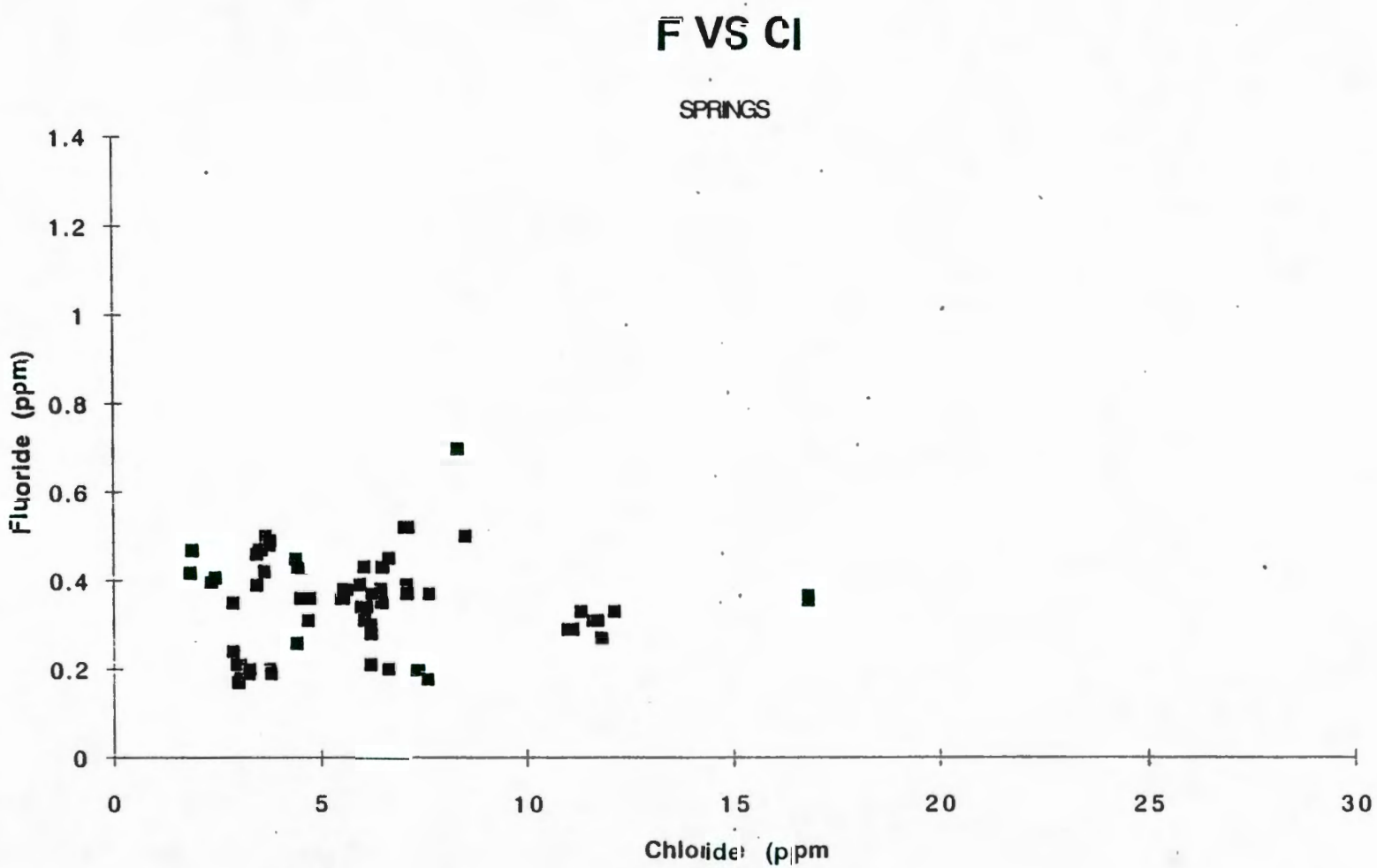


FIGURE D-6.4

Figure 6-4. Plot of Fluoride versus Chloride in Spring Waters.

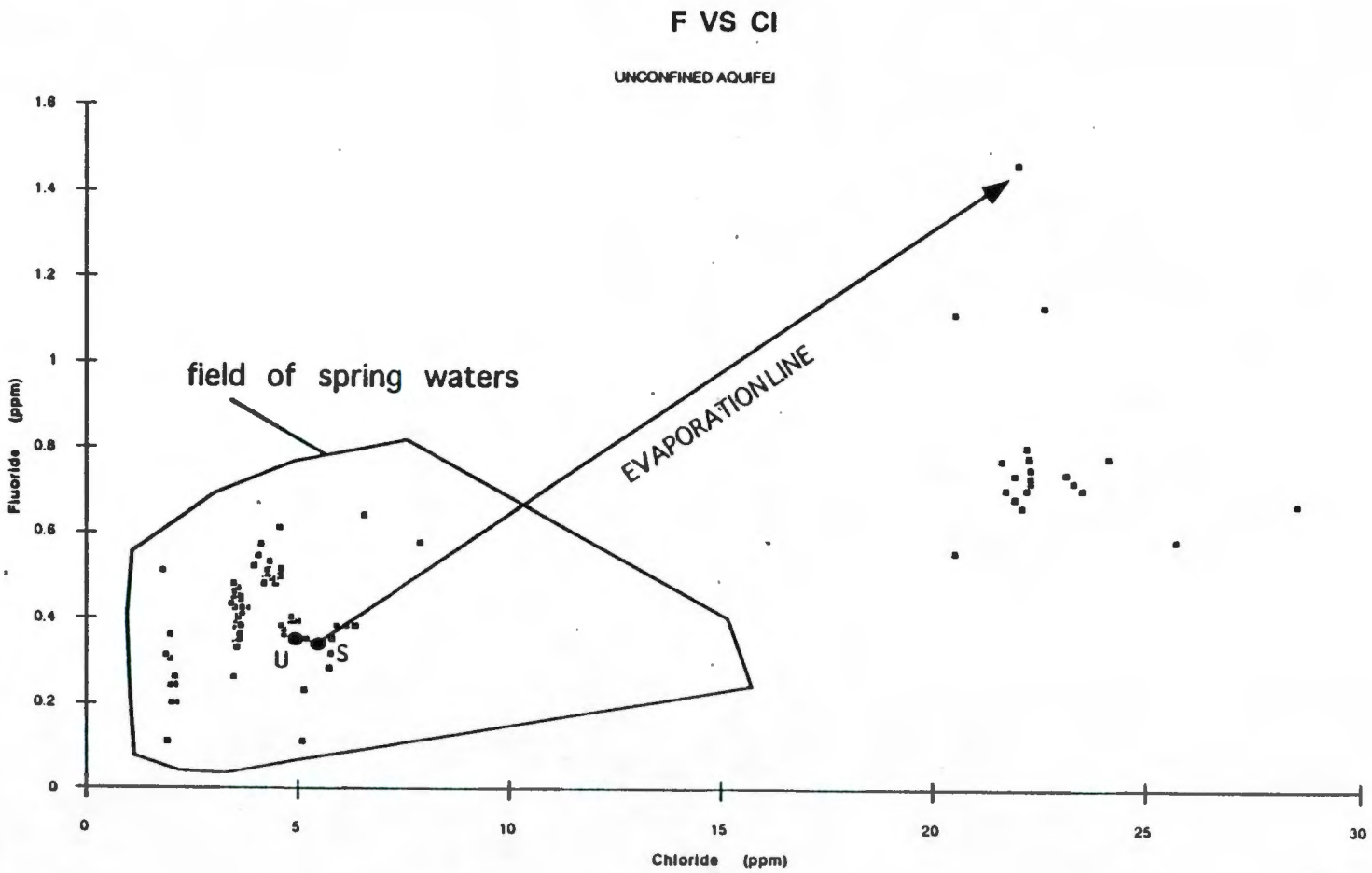


FIGURE D-6.5

Figure 6-5. Plot of Fluoride versus Chloride in the Unconfined Aquifer.

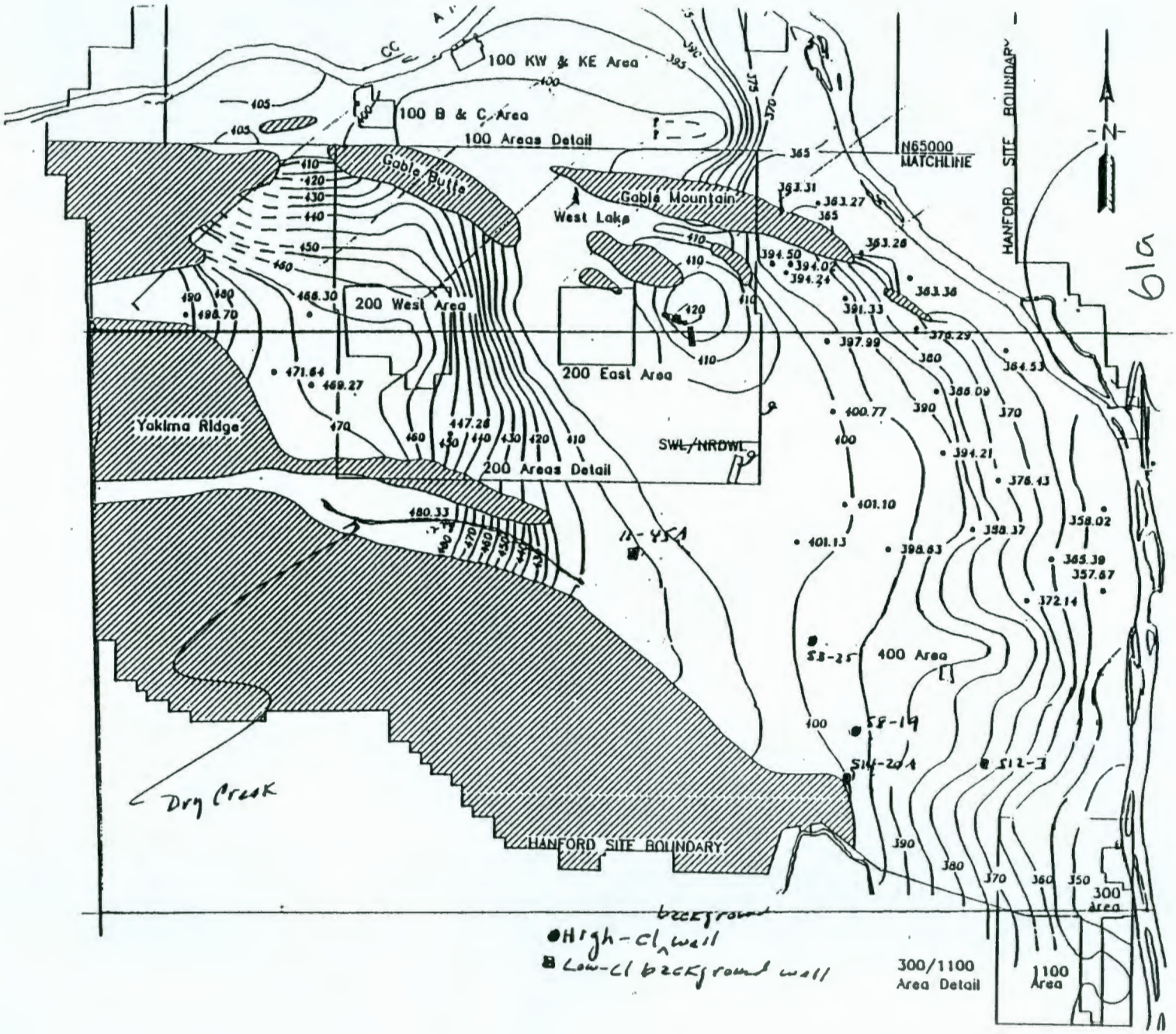


Figure 6-6. Water Table Map of the Southern Portion of the Study Area.

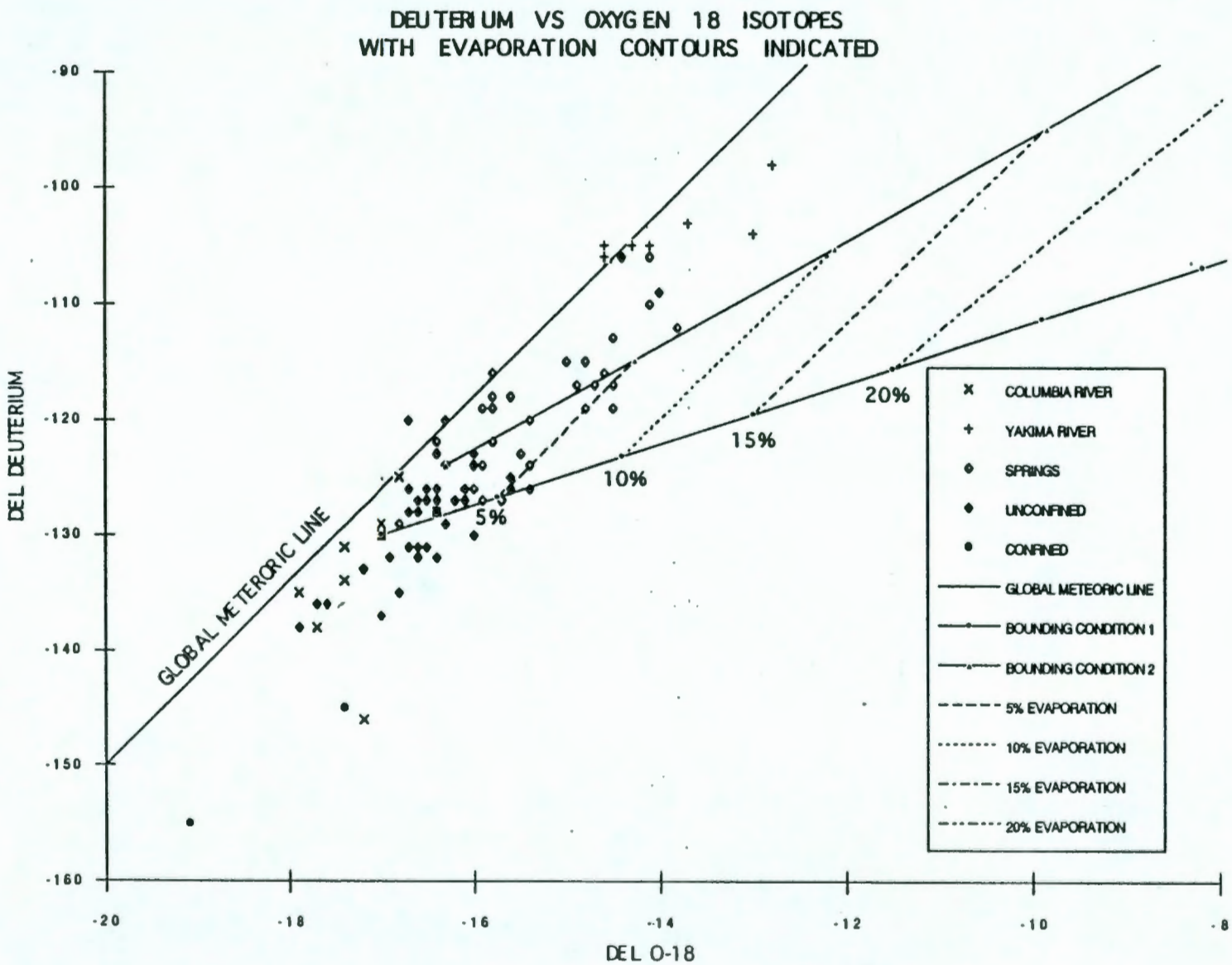


Figure 6-7. Isotopic Composition of Waters at the Hanford Site.

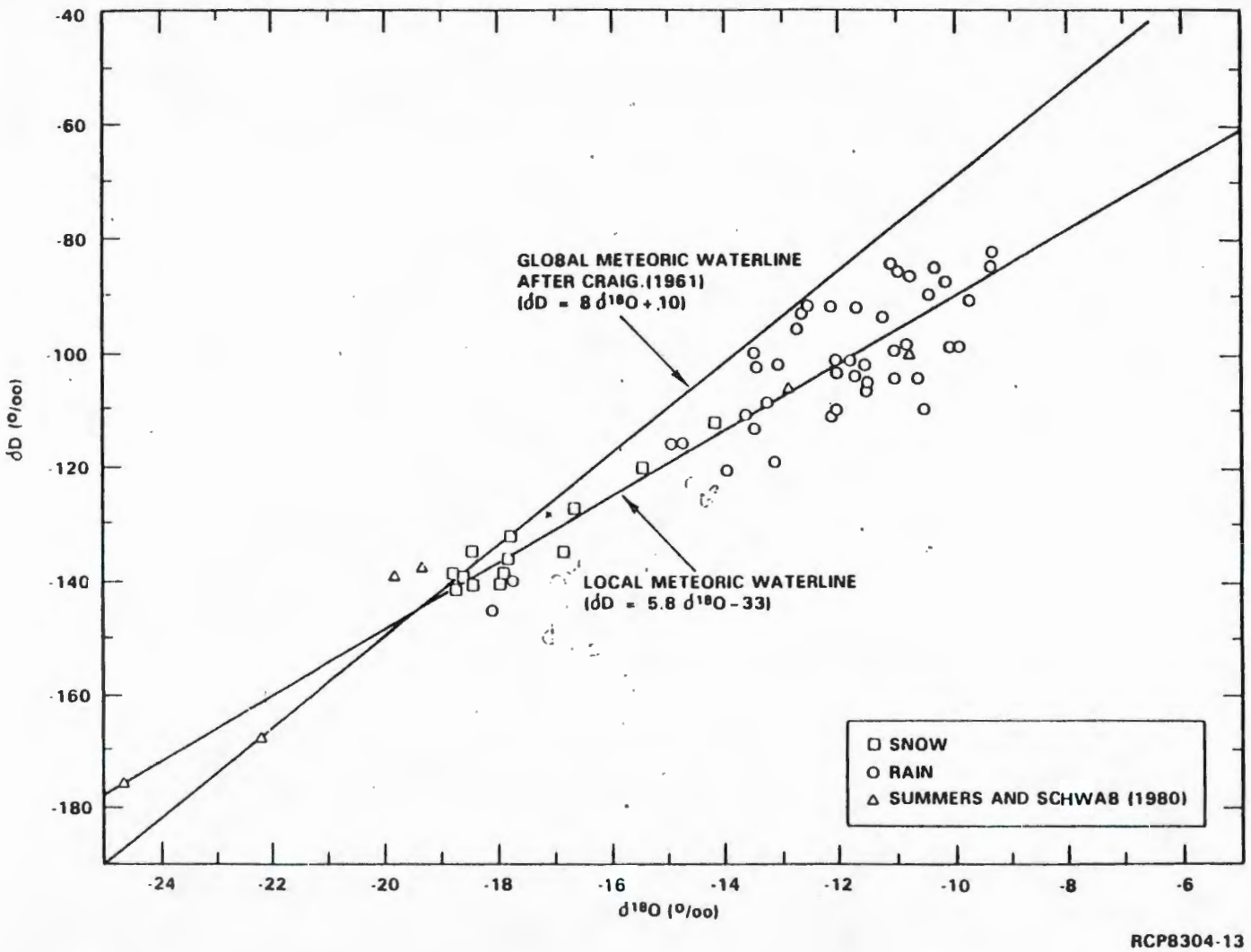


Figure 6-8. Isotopic Composition of Meteoric Waters at the Hanford Site (from Graham 1983).

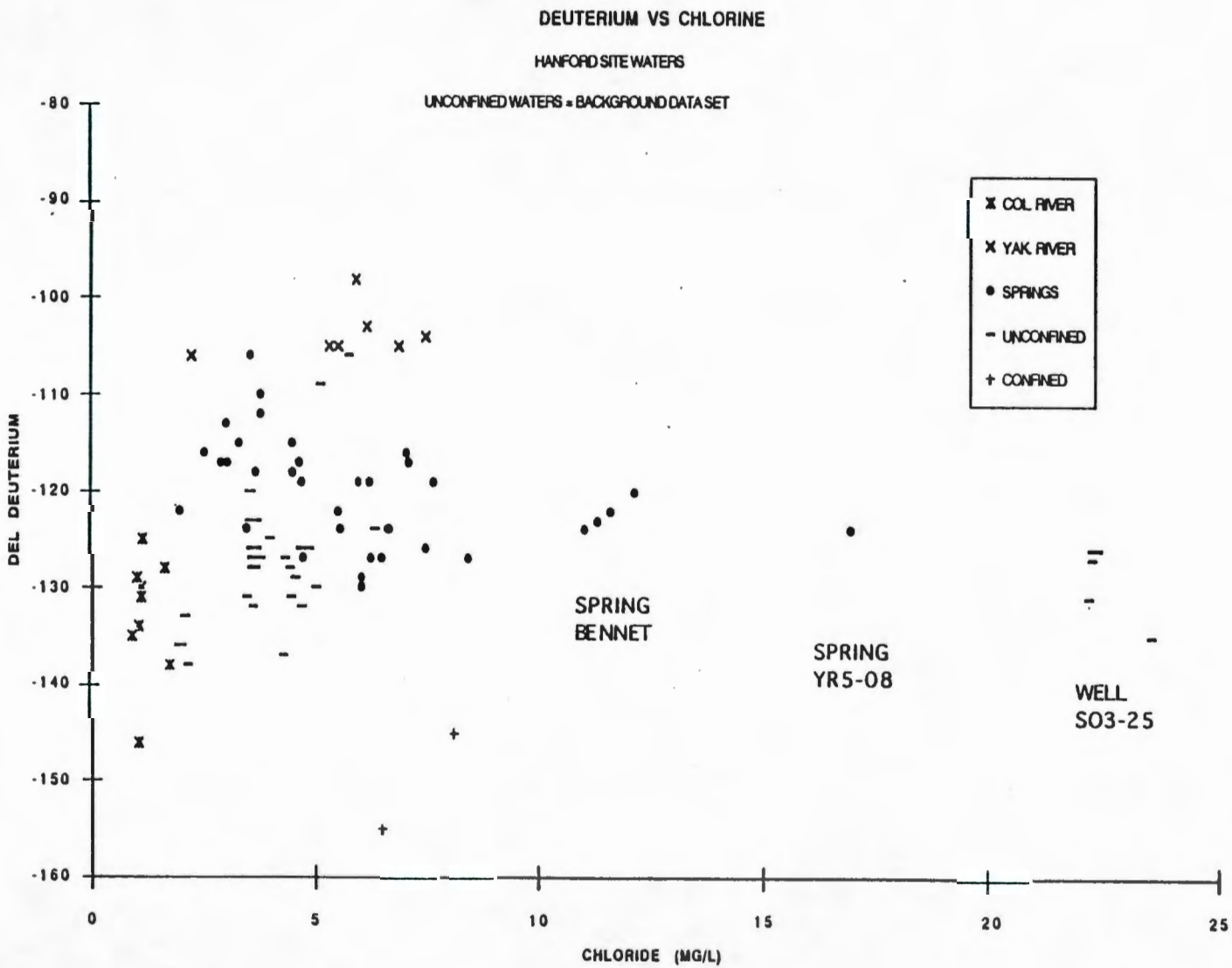


Figure 6-9. Del Deuterium versus Chloride in Hanford Site Waters.

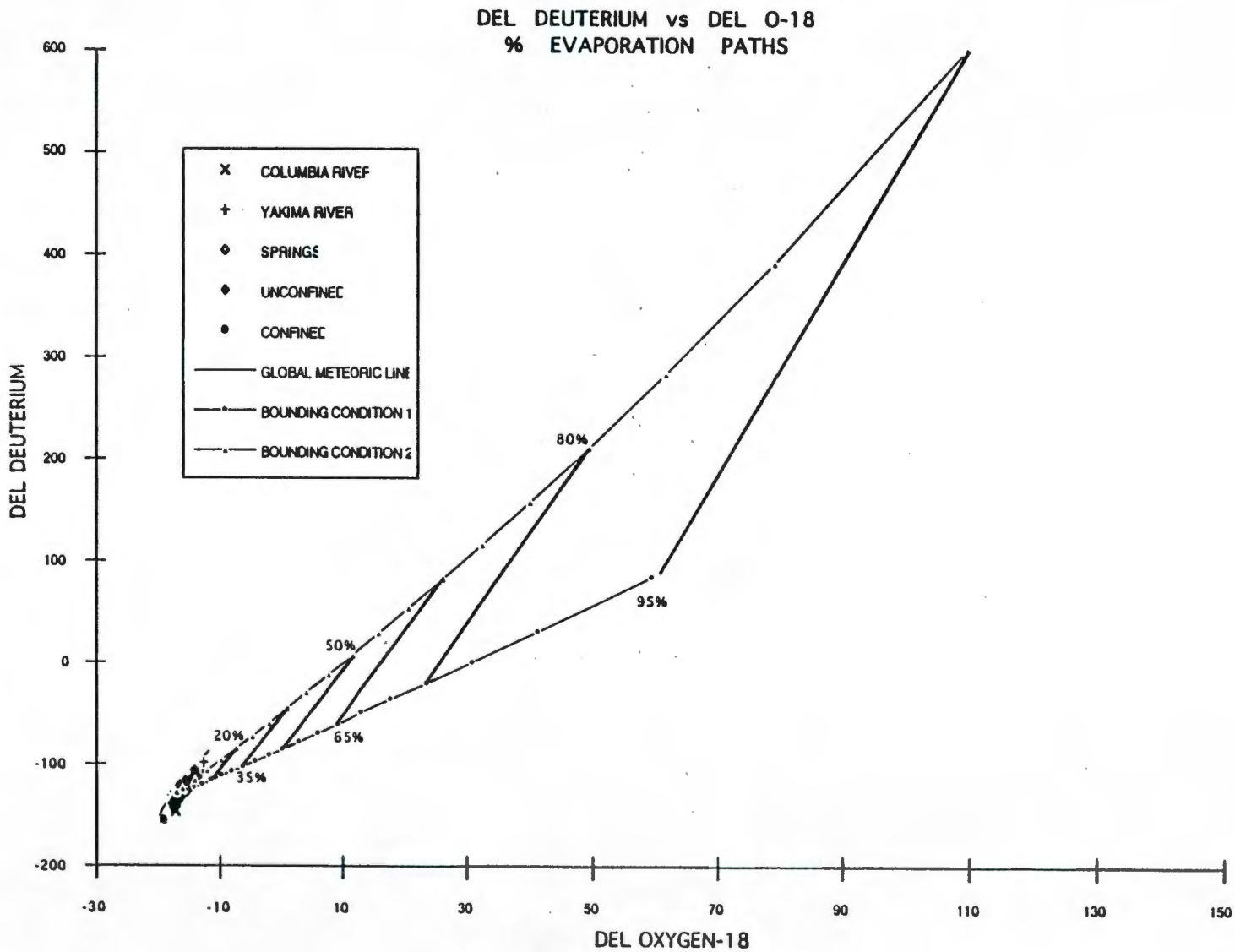


Figure 6-10. Plot of Isotopes in Hanford Site Groundwater Showing Evaporation Paths.

Table 3-1. Estimates of Modeled Recharge at the Hanford Site.

Source	Model	Prec., cm yr^{-1}	Rechrge, cm yr^{-1}
Wallace (1978)	Morton	15.9	1.2
Bauer and Vaccaro (1990)	USGS	16	0.25-1.27
Smoot et al. (1989)	UNSAT-H	16	1.1

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Table 3-2. Summary of Estimated Recharge from Lysimeter Facilities for Two Soil Types at the Hanford Site (from Murphy, Szecsody, and Phillips 1991).

Soil/Site/Vegetation	Time Period, yr	Water Content θ_{sat}[a]	Water Content θ_{res}[b]	Recharge Rate % of Precip.[c]	Recharge Rate cm/yr	Source
Warden silt loam/bare soil						
Computer simulation	20	0.45	0.040	1.1 ± 1.1	0.18 ± 0.17[d]	Smoot et al. 1989
Measured McGee Ranch	---[e]	0.41	0.0	---	---	Rockhold et al. 1988
Warden silt loam/vegetated						
McGee Ranch	2	---	---	---	<0.1	Gee 1987
FLTF Lysimeters	2	---	---		<0.1	Campbell et al. 1990
Quincy sand/bare soil						
BWTF, North Weighing	4	---	---	32.4	5.78	T. L. Jones 1989 and
BWTF, South Caisson	4	---	---	41.4	7.38	Rockhold et al. 1990[f]
CWTF Lysimeters	4	0.43	0.0	37.7	6.73	T. L. Jones 1989
Soil Moisture Characteristic Curves for Coarse Sand	---	0.42-0.52	0.032-0.096	---	---	Smoot et al. 1989
Quincy sand/vegetated						
BWTF, South Weighing Lysimeter	4	---	---	16.0	2.93	T. L. Jones 1989 and[f] Rockhold et al. 1990
BWTF Soils	---	0.30	0.096	---	---	Rockhold et al. 1988
200E Area Lysimeter	17	---	---	0.0	0.0	Rockhold et al. 1990
200 Area Moisture Profiles	---	---	---	<0.6	<0.1	Gee 1987
300 Area, cheatgrass	2	---	---	38	6.4	Gee 1987
USGS Model	---	---	---	1.6 - 8.0	0.25 - 1.27	Bauer and Vaccaro 1990

(a) Saturated water content (cm^3/cm^3). In some cases, the saturated water contents were fit with a retention function.
(b) Residual water content (cm^3/cm^3), either measured or model fit.
(c) Annual precipitation for the Hanford Site is 16.72 ± 4.87 cm for the years 1947 to 1988 (Stone et al. 1983).
(d) Statistical variation based on computer simulation of infiltration.
(e) Data were not reported in reference.
(f) Calculations performed by M. J. Fayer based on information in these two reports.
NOTE: The number cited in this table were used to estimate the pulse depths for various environmental tracers. The lysimeter numbers reflect the recharge for the period of measurement and not necessarily the long-term (e.g., >30 y) average rate that might more accurately apply to tracer movement. Chloride data in particular provides long-term (i.e. thousands of years) average recharge rates.

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TABLE 5-1. RESULTS OF CLOSED SYSTEM ROCK-WATER REACTION TESTS
(Water Concentrations in Milligrams per Liter)
(Sheet 1 of 2)

Starting Material	Atmosphere	Sample No.	Time (days)	Al	Ca	Fe	K	Mg	Na	Si	F	Cl	PO4	NO2	NO3	SO4	Oxylate	pH	TC	TOC	IC	HCO3
Detection Limit				0.1	0.1	0.02	1.5	0.1	0.3	0.2	0.15	0.1	0.2	0.1	0.1	0.1	0.2					
Basalt	Air	BA-A-1hr	0.04	0.24	44.7	0.27	64	12.9	20.2	10.2	4	12	8	<	83	193	<6	6.56	54.23	52.9	1.33	6.8
Basalt	Air	BA-A-6hr	0.25	0.22	84.9	0.07	26	20.4	29.1	23.8	4	9	<5	<	59	256	<6	7.39	61.9	55.6	6.3	32.0
Basalt	Air	BA-A-1	1	<	88.7	0.02	26	23.1	30.4	23.8	3.3	9.7	<	<2	54	277	<	7.56	54.5	46.2	8.3	42.2
Basalt	Air	BA-A-2	2	<	101.3	0.11	36	27.6	34.8	25.6	1.2	9.3	<	<2	83	285	<	7.63	71.5	49.2	22.3	113.4
Basalt	Air	BA-A-4	4	<	112	0.12	31	30.8	36.3	25.4	1.7	9.7	<	2	67	284	<	8.06	78.2	48.6	29.6	150.5
Basalt	Air	BA-A-8	8	<	121	0.02	32	34.7	40.7	24.5	1.6	8.7	<	2.6	61	289	<	7.97	73.4	31.2	42.2	214.5
Basalt	Air	BA-A-16	16	<	121	0.2	22	36.9	46.4	22.7	2.1	9	<	2	56	293	<	8.15	85	34.3	50.7	257.7
Basalt	Air	BA-A-32	32	0.32	115	0.02	22	37.4	53.4	24.1	2	8.2	<	<	44	275	<	8.13	86.7	35.7	51	259.3
Basalt	Air	BA-A-64	64	0.44	112	0.15	20	38.6	70.5	22.2	3.6	8.72	<.2	<	25.1	289	<.2	8.38	88	32.1	55.9	284.2
Basalt	Air	BA-A-128	128	<	80.7	0.07	20	29.1	106	19.5	3.5	9.1	<	<	5.7	322	<	8.51	78.5	32.5	46	233.8
Basalt	nitrogen	BA-N-1	1	0.22	93.1	<	28	25	32.1	26.1	1	9.9	<	<2	87	291	<	7.78	58.6	49	9.6	48.8
Basalt	nitrogen	BA-N-2	2	0.22	95.3	0.11	33	27.3	34.2	27.6	1.2	11.5	<	15.5	62	294	<	7.86	73.9	56.6	17.3	87.9
Basalt	nitrogen	BA-N-4	4	0.26	102	0.101	32	29.5	36.9	28.2	1.1	10.1	<	34	4	291	<	8.1	75.4	50.9	24.5	124.5
Basalt	nitrogen	BA-N-8	8	0.21	94	0.098	27	28.1	38.2	25.4	1.2	10	<	4.8	2	291	<	8.16	81.3	54.4	26.9	136.7
Basalt	nitrogen	BA-N-16	16	<	93.6	0.07	30	30.2	45.1	23.4	2.2	10.5	<	<2	3.3	296	<	8.06	84.4	49.9	34.5	175.4
Basalt	nitrogen	BA-N-32	32	0.26	94.7	<	23	33.6	54.4	23.5	2.5	9	<	<	1	259	<5	8.17	94.4	50.3	44.1	224.2
Basalt	nitrogen	BA-N-64	64	0.36	115	0.1	22	37	72.1	23	4	9.92	<.2	<	1.55	281	<.2	8.39	110	45	65	330.4
Basalt	nitrogen	BA-N-128	128	<	118	0.04	26	37.4	113	20.4	3.1	10.9	<0.5	<	1.5	326	<0.2	8.54	128	47	81	411.8
Ringold	Air	SO-A-1hr	1hr	0.1	32.4	0.04	12	12	9.9	16.6	4	11	<5	<	34	83	<6	7.25	52	49	3	15.3
Ringold	Air	SO-A-6hr	6hr	0.11	39.1	<	14	14.3	12.5	20.4	5	12	<5	<	45	94	<6	7.24	78.6	78	0.6	3.0
Ringold	Air	SO-A-1	1	<	45.2	<	11	15.4	17.2	18.2	1.5	13.6	<	<2	45	119	<	7.63	73.9	71.1	2.8	14.2
Ringold	Air	SO-A-2	2	<	35.3	<	8	15.5	14.2	17.9	1.6	10.5	<	<2	43	101	<	7.71	68.4	64.2	4.2	21.4
Ringold	Air	SO-A-4	4	<	45	<	14	19	17.3	19.2	1.6	11.2	<	<2	47	146	<	7.95	64.1	57.1	7	35.6
Ringold	Air	SO-A-8	8	<	50.3	<	24	20.4	17.7	19.2	1.9	13.4	<	<2	51	151	<	7.7	57.1	48.9	8.2	41.7
Ringold	Air	SO-A-16	16	<	58.6	<	33	23.3	20.6	19.8	1.9	11.9	<	<2	54	161	<	7.88	66.3	46.3	20	101.7
Ringold	Air	SO-A-32	32	<	68.3	<	13	27.7	24.1	21.8	1.5	11.6	<	<	68	162	<	8.06	79.7	60.1	19.6	99.6
Ringold	Air	SO-A-64	64	0.16	65.9	0.02	14	26.7	24	20.4	1.5	10.6	<.2	<	66.1	139	<.25	7.93	76.7	52.8	23.9	121.5
Ringold	Air	SO-A-128	128	<	66.3	<	18	27.5	29.2	18.9	<1.5	10	<	<	51.9	152	<	8.05	67.5	39.4	28.1	142.8
Ringold																						
Ringold	nitrogen	SO-N-1	1	<	39.6	<	39	16.3	16.1	18.4	0.9	10.4	<	<2	45	128	<	7.65	59.2	53.8	5.4	27.5
Ringold	nitrogen	SO-N-2	2	<	40.6	<	37	16.5	16.9	18.9	0.9	10.4	<	<2	46	128	<	7.98	48.4	40.4	8	40.7
Ringold	nitrogen	SO-N-4	4	0.96	50.4	<	32	20.6	19.3	19.2	1.1	11.4	<	<2	50	151	<	8.09	50.9	42.8	8.1	41.2
Ringold	nitrogen	SO-N-8	8	<	46.4	<	32	19.1	18.4	18.3	1.2	11.5	<	<2	48	121	<	8.11	56	47.1	8.9	45.2
Ringold	nitrogen	SO-N-16	16	<	44.8	<	16	18.6	19.4	18.6	1.3	10.1	<	<2	48	131	<	8	49.9	34.6	15.3	77.8
Ringold	nitrogen	SO-N-32	32	0.15	53.3	<	11	21.4	21.1	21.8	1.5	10.5	<	<	52	132	<	8.18	52.5	36.9	15.6	79.3
Ringold	nitrogen	SO-N-64	64	0.18	61.9	<	14	25.3	23.1	19.7	1.3	11.2	<.2	<	44	176	<.25	8.09	59.4	41.2	18.2	92.5
Ringold	nitrogen	SO-N-128	128	<	60.9	<	18	23.7	31.5	19.2	<1.5	12.1	<	<	38.3	178	<	8.4	81.8	55.6	26.2	133.2

N/A = NOT APPLICABLE
N/D = NO DATA ENTERED

Table 5-1. Results of Closed System Rock-Water Reaction Tests. (sheet 1 of 2)

TABLE 5-1. RESULTS OF CLOSED SYSTEM ROCK-WATER REACTION TESTS
(Water Concentrations in Milligrams per Liter)
(Sheet 2 of 2)

Starting Material	Atmosphere	Sample No.	Time (days)	Cu	Cr	Ni	Sr	Zn	Ag	As	B	Ba	Cd	Co	Li	Mn	Mo	P	Pb	Sb	Se	Sn	Tl	Ti
Detection Limit				0.02	N/D	0.03	0.01	0.01	N/D	0.02	0.01	0.02	N/D	N/D	0.05	0.01	0.1	0.1	0.1	0.2	0.1	0.1	0.05	0.1
Basalt	Air	BA-A-1hr	0.04	0.771	N/D	<	0.077	0.155	N/D	<	0.036	0.025	N/D	N/D	<	0.298	<	2.5	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-6hr	0.25	0.1	N/D	<	0.117	0.031	N/D	<	0.089	0.023	N/D	N/D	0.09	0.074	<	1.2	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-1	1	<	N/D	<	<	<	N/D	<	<	<	N/D	N/D	<	0.061	<	<	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-2	2	0.11	N/D	<	<	<	N/D	<	<	0.024	N/D	N/D	<	0.138	<	<	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-4	4	<	N/D	<	<	<	N/D	<	<	0.02	N/D	N/D	<	0.124	<	<	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-8	8	<	N/D	<	<	<	N/D	<	<	0.02	N/D	N/D	<	0.11	<	<	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-16	16	0.05	N/D	<	<	<	N/D	<	<	0.02	N/D	N/D	<	0.122	<	<	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-32	32	0.019	N/D	<	0.157	<	N/D	<	0.05	0.026	N/D	N/D	0.08	0.102	<	0.8	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-64	64	0.012	N/D	<	0.162	0.025	N/D	<	0.043	0.025	N/D	N/D	0.071	0.097	<	0.91	<	N/D	N/D	N/D	N/D	N/D
Basalt	Air	BA-A-128	128	<	N/D	<	0.123	<	N/D	<	0.077	0.023	N/D	N/D	<	0.046	<	<	<	N/D	N/D	N/D	N/D	N/D
					N/D				N/D				N/D	N/D						N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-1	1	0.112	N/D	<	0.121	0.092	N/D	<	0.06	0.025	N/D	N/D	<	0.125	<	0.97	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-2	2	0.167	N/D	<	0.128	0.061	N/D	<	<	0.026	N/D	N/D	<	0.222	<	1.2	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-4	4	0.126	N/D	<	0.133	<.05	N/D	<	0.059	0.024	N/D	N/D	<	0.234	<	1.09	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-8	8	0.081	N/D	<	0.125	<.05	N/D	<	0.057	0.024	N/D	N/D	<	0.176	<	1.06	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-16	16	<	N/D	<	<	<	N/D	<	<	0.021	N/D	N/D	<	0.262	<	<	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-32	32	<	N/D	<	0.135	<	N/D	<	0.05	0.023	N/D	N/D	<	0.233	<	1	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-64	64	<	N/D	0.02	0.164	0.034	N/D	<	0.049	0.024	N/D	N/D	<	0.139	0.1	1.5	<	N/D	N/D	N/D	N/D	N/D
Basalt	nitrogen	BA-N-128	128	<	N/D	<	0.171	<	N/D	<	0.11	0.028	N/D	N/D	<	0.106	0.057	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-1hr	1hr	0.016	N/D	<	0.154	0.042	N/D	<	<	0.029	N/D	N/D	<	<	<	1.2	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-6hr	6hr	0.024	N/D	<	0.189	0.053	N/D	<	0.028	0.042	N/D	N/D	0.062	<	<	2.2	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-1	1	<	N/D	<	<	<	N/D	<	<	0.038	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-2	2	<	N/D	<	<	<	N/D	<	<	0.032	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-4	4	<	N/D	<	<	<	N/D	<	<	0.042	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-8	8	<	N/D	<	<	<	N/D	<	<	0.041	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-16	16	<	N/D	<	<	<	N/D	<	<	0.045	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-32	32	<	N/D	<	0.352	<	N/D	<	0.045	0.059	N/D	N/D	0.11	0.035	<	0.8	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-64	64	<	N/D	<	0.347	0.029	N/D	<	0.037	0.053	N/D	N/D	0.117	0.029	<	1.3	<	N/D	N/D	N/D	N/D	N/D
Ringold	Air	SO-A-128	128	<	N/D	>	0.354	<	N/D	<	0.119	0.057	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold					N/D																			
Ringold	nitrogen	SO-N-1	1	<	N/D	<	0.198	<	N/D	<	0.206	0.054	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-2	2	<	N/D	<	0.199	<	N/D	<	0.203	0.045	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-4	4	<	N/D	<	0.306	<	N/D	<	0.211	0.076	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-8	8	<	N/D	<	0.229	<	N/D	<	<	0.043	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-16	16	<	N/D	<	<	<	N/D	<	<	0.038	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-32	32	<	N/D	<	0.273	<	N/D	<	0.059	0.042	N/D	N/D	0.13	<	<	0.3	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-64	64	<	N/D	<	0.327	0.036	N/D	<	0.048	0.052	N/D	N/D	0.067	0.039	<	0.93	<	N/D	N/D	N/D	N/D	N/D
Ringold	nitrogen	SO-N-128	128	<	N/D	<	0.316	<	N/D	<	0.139	0.056	N/D	N/D	<	<	<	<	<	N/D	N/D	N/D	N/D	N/D

N/A = NOT APPLICABLE
N/D = NO DATA ENTERED

TABLE 5-2. RESULTS OF OPEN SYSTEM ROCK-WATER REACTION TESTS
1/2 PORE VOLUME PER DAY
(Water Concentrations in Milligrams per Liter)
(Sheet 1 of 2)

Starting Material	Atmosphere	Sample No.	Time (days)	Al	Ca	Fe	K	Mg	Na	Si	F	Cl	PO4	NO2	NO3	SO4	Oxylate	pH	TC	TOC	IC	HCO3
Detection Limit				0.1	0.02	0.02	0.02	1.5	0.1	0.3	0.15	0.1	0.2	N/D	0.1	0.1	N/D	0.03	0.02	0.05	0.01	
Basalt	N/A	2-1437-01-01	1	<	32.4	<	16	7.4	34.2	19.6	1.5	8.6	<	N/D	27	81	N/D	8.02	51.2	38.0	13.2	67.1
Basalt	N/A	2-1437-01-02	2	<	13	0.053	6	3	22.4	21.1	1.2	2	<	N/D	4	20	N/D	8.02	35	13.6	21.4	108.8
Basalt	N/A	2-1437-01-03	3	<	10.2	0.052	7	2.4	19.1	20.9	1.1	0.53	<	N/D	1	6.9	N/D	7.81	26.6	7.4	19.2	97.7
Basalt	N/A	2-1437-01-04	4	<	9.5	0.036	4	2.2	19	21.4	0.8	0.43	<	N/D	0.9	4.2	N/D	8.09	24.1	7.3	16.8	85.2
Basalt	N/A	2-1437-01-05	5	<	8.89	0.029	4	2.1	18	21.3	0.7	0.4	<	N/D	1	3.3	N/D	8.1	23.5	6.8	16.7	84.7
Basalt	N/A	2-1437-01-06	6	<	8.53	0.027	4	2	16.9	21.1	0.55	0.38	<	N/D	0.8	2.7	N/D	8.06	23.1	8.3	14.8	75.1
Basalt	N/A	2-1437-01-07	7	<	7.9	0.022	4.01	1.84	15.5	21.9	0.36	0.36	<	N/D	0.4	2.3	N/D	7.94	23.5	8.1	15.4	78.3
Basalt	N/A	2-1437-01-08	8	<	7.69	<	4	1.78	14.7	21.7	0.34	0.37	<	N/D	0.6	2.1	N/D	7.91	22.2	7.0	15.2	77.4
Basalt	N/A	2-1437-01-09	9	<	7.23	<	4.5	1.73	14	21.9	0.32	0.38	<	N/D	0.8	2.2	N/D	7.93	21.1	6.7	14.5	73.5
Basalt	N/A	2-1437-01-10	10	<	7.02	<	5.3	1.66	12.9	21.9	0.3	0.45	<	N/D	0.9	2	N/D	7.9	19.8	6.7	13.1	66.7
Basalt	N/A	2-1437-01-11	11	<	6.85	<	5.2	1.62	12.2	22	0.33	0.36	4.2	N/D	0.9	2	N/D	8.07	20	7.3	12.7	64.6
Basalt	N/A	2-1437-01-12	12	<	6.57	<	5	1.55	11.2	21.9	0.32	0.4	0.9	N/D	0.9	1.7	N/D	8.04	19.5	7.3	12.2	61.9
Basalt	N/A	2-1437-01-13	13	<	6.46	<	5.5	1.47	10.7	22.2	0.23	0.48	<	N/D	0.4	1.5	N/D	7.92	19.6	7.6	12.0	81.1
Basalt	N/A	2-1437-01-14	14	<	6.48	<	1.5	1.52	10.2	22	0.26	0.4	<	N/D	0.8	1.5	N/D	7.66	18.8	7.4	11.4	57.8
Ringold	N/A	2-1438-01-01	1	0.84	1500	<	46.4	152	562	13.2	20	790	<	N/D	4190	833	N/D	7.54	211	195.0	16.0	81.3
Ringold	N/A	2-1438-01-02	2	<	35	<	2	4.55	93.1	14.1	2	21	<	N/D	76	107	N/D	7.54	52.7	26.7	26.0	132.2
Ringold	N/A	2-1438-01-03	3	<	14.3	<	3	1.88	57.2	14.1	1.4	5.4	<	N/D	12.5	33	N/D	7.7	43.2	9.8	33.4	169.8
Ringold	N/A	2-1438-01-04	4	<	12	<	4	1.74	50	14.8	1.6	3	<	N/D	8.1	24	N/D	7.95	40.4	10.1	30.3	154.0
Ringold	N/A	2-1438-01-05	5	<	10.4	<	2	1.51	43.6	14.7	1.8	2.3	<	N/D	5.5	19	N/D	8.06	36	9.8	26.3	133.4
Ringold	N/A	2-1438-01-06	6	<	9.42	<	2	1.39	38.2	14.5	2.2	2.6	<	N/D	4.3	15	N/D	7.93	32.7	8.8	23.9	121.4
Ringold	N/A	2-1438-01-07	7	0.1	8.97	0.031	2	1.29	34.7	15.2	1.7	1.5	<	N/D	3.3	12	N/D	7.94	30.9	8.7	22.2	113.0
Ringold	N/A	2-1438-01-08	8	0.31	8.94	0.12	2	1.35	31.6	15.3	1.5	1.4	<	N/D	3.9	11	N/D	7.96	28.8	7.9	20.9	106.0
Ringold	N/A	2-1438-01-09	9	0.36	8.71	0.2	2	1.36	28.4	15.6	1.5	1.5	<	N/D	3.3	9.7	N/D	7.94	28.4	7.7	20.7	105.1
Ringold	N/A	2-1438-01-10	10	0.33	8.64	0.24	2.9	1.25	24.8	15.4	1.9	2.3	<	N/D	2.8	9	N/D	7.97	24.8	7.7	17.1	87.0
Ringold	N/A	2-1438-01-11	11	0.28	8.84	0.19	2.8	1.29	21.8	15.3	1.1	2.2	<	N/D	2.6	8.4	N/D	8.08	25.7	9.3	16.4	83.5
Ringold	N/A	2-1438-01-12	12	0.23	8.9	0.17	2.7	1.2	18.8	15.2	0.7	0.5	<	N/D	1.2	6.2	N/D	8.13	22.4	7.8	14.6	74.4
Ringold	N/A	2-1438-01-13	13	0.24	8.68	0.15	2.8	1.35	15.9	15.4	0.8	0.6	<	N/D	2.2	7.1	N/D	7.89	23.6	8.8	14.8	75.3
Ringold	N/A	2-1438-01-14	14	<	6.23	<	3.8	1.51	10.1	21.8	0.7	0.8	<	N/D	1.3	6.3	N/D	7.68	20.8	8.0	12.8	65.2

N/A = NOT APPLICABLE
N/D = NO DATA ENTERED

Table 5-2. Results of 1/2 Pore Volume Per Day Open System Rock-Water Reaction Tests. (sheet 1 of 2)

TABLE 5-2. RESULTS OF OPEN SYSTEM ROCK-WATER REACTION TESTS
1/2 PORE VOLUME PER DAY
(Water Concentrations in Milligrams per Liter)
(Sheet 2 of 2)

Starting Material	Atmosphere	Sample No.	Time (days)	Cu	Cr	Ni	Sr	Zn	Ag	As	B	Ba	Cd	Co	Li	Mn	Mo	P	Pb	Sb	Se	Sn	Tl	Ti
Detection Limit				0.1	0.02	0.03	0.01	0.01		0.02	0.01	0.02				0.01	0.1	0.1						
Basalt	N/A	2-1437-01-01	1	<	<	<	<	<	<	<	<	0.01	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-02	2	<	<	<	<	<	<	<	<	0.008	<	<		<	<	<		N/D	N/D	0.101	N/D	N/D
Basalt	N/A	2-1437-01-03	3	<	<	<	<	<	<	<	<	0.006	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-04	4	<	<	<	<	<	<	<	<	0.005	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-05	5	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-06	6	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-07	7	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-08	8	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-09	9	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-10	10	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-11	11	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-12	12	<	<	<	<	<	<	<	<	0.003	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-13	13	<	<	<	<	<	<	<	<	0.004	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Basalt	N/A	2-1437-01-14	14	<	<	<	<	<	<	<	<	0.02	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-01	1	<	<	<	6.2	<	<	<	<	0.5	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-02	2	<	0.021	<	<	<	<	0.03	<	0.02	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-03	3	<	<	<	<	<	<	<	<	0.018	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-04	4	<	<	<	<	<	<	<	0.08	0.02	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-05	5	<	<	<	<	<	<	<	0.049	0.021	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-06	6	<	<	<	<	<	<	<	0.059	0.021	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-07	7	<	<	<	<	<	<	<	0.038	0.022	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-08	8	<	<	<	<	<	<	<	0.08	0.024	<	<		<	0.028	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-09	9	<	<	<	<	<	<	<	0.059	0.026	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-10	10	<	<	<	0.04	<	<	<	<	0.0237	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-11	11	<	<	<	0.04	<	<	<	<	0.0237	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-12	12	<	<	<	0.04	<	<	<	<	0.0256	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-13	13	<	<	<	<	<	<	0.08	<	0.026	<	<		<	<	<		N/D	N/D	<	N/D	N/D
Ringold	N/A	2-1438-01-14	14	<	<	<	<	<	<	<	<	<	<	<		<	<	<		N/D	N/D	<	N/D	N/D

N/A = NOT APPLICABLE
N/D = NO DATA ENTERED

Table 5-2. Results of 1/2 Pore Volume Per Day Open System Rock-Water Reaction Tests. (sheet 2 of 2)

TABLE 5-3. RESULTS OF OPEN SYSTEM ROCK-WATER REACTION TESTS
1/4 PORE VOLUME PER DAY
(Water Concentrations in Milligrams per Liter)
(Sheet 1 of 2)

Starting Material	Atmosphere	Sample No.	Time (days)	Al	Ca	Fe	K	Mg	Na	Si	F	Cl	PO4	NO2	NO3	SO4	Oxylate	pH	TC	TOC	IC	HCO3
Detection Limit				0.1	0.1	0.02	1.5	0.1	0.3	0.2	0.15	0.1	0.2	0.1	0.1	0.1	0.2					
Basalt	N/A	2-1440-02-01	4	<	37.7	<	6.0	8.58	37.6	21.8	<1.5	8.6	<	<	26	84	<	7.7	42.3	15.1	27.2	138.3
Basalt	N/A	2-1440-02-02	8	<	24.1	0.12	6.0	5.63	30.3	24.3	<1.5	1.7	<	<	1	40	<	7.84	39.9	15.8	24.1	122.5
Basalt	N/A	2-1440-02-03	12	<	18.2	<	7.0	4.24	24.9	23	0.9	1	<	<	<.1	14	<	7.99	38	10.9	27.1	137.8
Basalt	N/A	2-1440-02-04	16	<	14.2	<	7.0	3.4	22.5	25.3	0.8	0.6	<.02	<	<.1	5.9	<	8.05	32.91	8.38	24.53	124.7
Basalt	N/A	2-1440-02-05	20	<	13	<	6.0	3.01	19.3	23.6	0.7	0.5	<0.2	<	<.1	4	<	7.98	30.2	7.29	22.91	116.5
Basalt	N/A	2-1440-02-06	24	<	11.8	<	6.0	2.71	17.7	23.2	0.6	0.5	1	<	0.3	3.2	<	8.17	25.8	6.4	19.4	98.6
Basalt	N/A	2-1440-02-07	28	<	10.6	<	3.0	2.46	15.2	22.4	0.6	0.5	<.2	<	0.2	2.3	<	8.02	25.6	6.9	18.7	95.1
Basalt	N/A	2-1440-02-08	32	<	10.4	<	4.0	2.37	14.4	22.8	0.5	0.5	0.2	<	0.6	1.9	<	8.03	24.7	7.16	17.54	89.2
Basalt	N/A	2-1440-02-09	36	<	9.58	<	5.0	2.28	13.5	22.6	0.5	0.5	0.2	<	0.9	2	<	7.87	23.6	7.33	16.27	82.7
Basalt	N/A	2-1440-02-10	40	<	9.73	<	4.0	2.19	13.2	24	0.4	0.5	0.2	<	0.8	1.8	<0.2	7.8	23.4	7.31	16.09	81.8
Basalt	N/A	2-1440-02-11	44	<	9.46	0.027	5.0	2.09	12.1	23.2	0.26	0.48	<.2	<	0.6	1.74	<.25	7.88	23.4	8.11	15.29	77.7
Basalt	N/A	2-1440-02-12	48	<	8.9	<	3.0	2	11.7	23.3	0.3	0.48	<.2	<	0.78	1.58	<.25	7.74	22.6	8.46	14.14	71.9
Basalt	N/A	2-1440-02-13	52	<	9	<	3.0	2.1	11.1	24.1	0.25	0.44	<.2	<	1.08	1.47	<.25	7.93	22.3	8.17	14.13	71.8
Basalt	N/A	2-1440-02-14	56	<	8.6	<	4.0	1.95	9.6	22.3	0.22	0.45	<.2	<	1.13	1.33	<.25	7.88	21.8	7.75	14.05	71.4
Ringold	N/A	2-1439-02-01	4	<	1260	<	31.0	139	512	16.1	<30	740	<	95	3730	680	<	7.3	141	96	45	228.8
Ringold	N/A	2-1439-02-02	8	<	41.4	<	8.0	6.51	102.9	17.4	<.8	29	<	<	105	89	<	7.91	51.3	13.9	37.4	190.1
Ringold	N/A	2-1439-02-03	12	<	23.3	<	6.0	3.27	83.9	18.2	0.9	6.4	<	0.5	12	45	<	8.24	51.8	13.3	38.5	195.7
Ringold	N/A	2-1439-02-04	16	<	18.1	<	5.0	2.67	51.1	19	1.4	2.9	<.2	<	0.6	33	<	7.97	46.6	12.69	33.91	172.4
Ringold	N/A	2-1439-02-05	20	<	16.2	<	4.0	2.29	43	17.5	1.3	2.3	0.4	<	0.9	25	<	8.07	41.4	10.3	31.1	158.1
Ringold	N/A	2-1439-02-06	24	<	14.6	<	3.0	2.08	36.4	16.7	1.5	1.4	<.4	<	0.8	18	<	8.19	38	9.8	28.2	143.4
Ringold	N/A	2-1439-02-07	28	<	14.1	<	4.0	2.01	32	16.6	1.8	1.4	0.4	<	1.3	14	<	8.11	35.5	8.8	26.7	135.7
Ringold	N/A	2-1439-02-08	32	<	13.8	<	4.0	1.99	27.9	16.6	1.8	1.1	0.4	<	1.2	12	<	8.27	32.4	8.52	23.88	121.4
Ringold	N/A	2-1439-02-09	36	0.12	13.7	<	3.0	1.95	24.3	16.4	1.4	0.9	0.4	<	1	10	<	8	30.7	8.3	22.4	113.9
Ringold	N/A	2-1439-02-10	40	0.12	13.7	0.07	3.0	1.94	21.7	17.8	0.6	0.5	0.4	<	1	8.1	<0.4	7.91	29.6	8.74	20.86	106.0
Ringold	N/A	2-1439-02-11	44	0.485	12.8	0.284	3.0	1.91	16.7	16.5	0.86	0.89	0.23	<	0.87	6.58	<.25	8	27.8	9.08	18.72	95.2
Ringold	N/A	2-1439-02-12	48	<	13.4	0.2	4.0	2.1	14.3	15.8	0.71	0.85	<.2	<	0.9	5.63	<.25	7.7	26.4	9.04	17.36	88.2
Ringold	N/A	2-1439-02-13	52	<	13.7	0.1	3.0	2	11.2	15.6	0.48	0.81	0.22	<	1.54	5.13	<.25	7.98	25.7	8.44	17.26	87.7
Ringold	N/A	2-1439-02-14	56	0.2	14.2	0.1	2.0	1.9	8.9	14.2	0.37	0.73	0.23	<	1.83	4.22	<.25	7.87	23.9	8.7	15.2	77.3

N/A = NOT APPLICABLE
N/D = NO DATA ENTERED

TABLE 5-3. RESULTS OF OPEN SYSTEM ROCK-WATER REACTION TESTS
1/4 PORE VOLUME PER DAY
(Water Concentrations in Milligrams per Liter)
(Sheet 2 of 2)

Starting Material	Atmosphere	Sample No.	Time (days)	Cu	Cr	Ni	Sr	Zn	Ag	As	B	Ba	Cd	Co	Li	Mn	Mo	P	Pb	Sb	Se	Sn	Tl	Ti
Detection Limit				0.02	0.02	0.03	0.01	0.01	N/D	0.02	0.01	0.02	N/D	N/D	0.05	0.01	0.1	0.1	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-01	4	0.016	<	<	0.169	<	N/D	<	<	0.23	N/D	N/D	0.06	<	<	0.15	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-02	8	<	<	<	0.106	<	N/D	<	<	<	N/D	N/D	<	<	<	0.23	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-03	12	<	<	<	0.079	<	N/D	<	<	<	N/D	N/D	<	<	<	0.14	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-04	16	<	<	<	0.063	<	N/D	<	<	<	N/D	N/D	<	<	<	0.27	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-05	20	<	<	<	0.056	<	N/D	<	<	<	N/D	N/D	<	<	<	0.13	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-06	24	<	<	<	0.051	<	N/D	<	<	<	N/D	N/D	<	<	<	0.15	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-07	28	<	<	<	0.046	<	N/D	<	<	<	N/D	N/D	<	<	<	0.26	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-08	32	<	<	<	0.044	<	N/D	<	<	<	N/D	N/D	<	<	<	<.1	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-09	36	<	<	<	0.042	<	N/D	<	<	<	N/D	N/D	<	<	<	0.17	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-10	40	<	<	<	0.041	0.019	N/D	<	<	<	N/D	N/D	<	<	<	0.36	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-11	44	<	<	<	0.041	<	N/D	<	<	<	N/D	N/D	<	<	<	0.37	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-12	48	<	<	<	<	<	N/D	<	<	<	N/D	N/D	<	<	<	<	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-13	52	<	<	<	<	<	N/D	<	0.05	<	N/D	N/D	<	<	<	<	N/D	N/D	N/D	N/D	N/D	N/D
Basalt	N/A	2-1440-02-14	56	<	<	<	<	<	N/D	<	<	<	N/D	N/D	<	<	<	<	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-01	4	<	<	<	5.48	<	N/D	<	0.3	0.47	N/D	N/D	<	<	<	<	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-02	8	<	0.01	<	0.205	<	N/D	<	0.05	0.031	N/D	N/D	<	<	.25 ?	<	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-03	12	<	<	<	0.103	<	N/D	<	0.05	0.027	N/D	N/D	<	<	0.25	0.25	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-04	16	0.012	0.03	<	0.084	<	N/D	<	0.05	0.031	N/D	N/D	<	<	0.15	0.32	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-05	20	<	<	<	0.075	<	N/D	<	0.036	0.032	N/D	N/D	<	<	<	0.22	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-06	24	<	<	<	0.068	<	N/D	<	0.033	0.034	N/D	N/D	<	<	<	0.22	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-07	28	0.012	<	<	0.068	<	N/D	<	0.03	0.039	N/D	N/D	<	<	<	0.3	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-08	32	0.014	<	<	0.068	<	N/D	<	0.03	0.042	N/D	N/D	<	<	<	0.16	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-09	36	0.023	<	<	0.075	<	N/D	<	0.04	0.051	N/D	N/D	<	<	<	0.14	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-10	40	<	<	<	0.065	0.027	N/D	0.021	0.02	0.041	N/D	N/D	<	<	<	0.27	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-11	44	<	<	<	0.065	<	N/D	<	<	0.046	N/D	N/D	<	<	<	0.37	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-12	48	<	<	<	<	<	N/D	<	<	<	N/D	N/D	<	<	<	0.4	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-13	52	<	<	<	<	<	N/D	<	<	<	N/D	N/D	<	<	<	<	N/D	N/D	N/D	N/D	N/D	N/D
Ringold	N/A	2-1439-02-14	56	<	<	<	<	<	N/D	<	<	<	N/D	N/D	<	<	<	<	N/D	N/D	N/D	N/D	N/D	N/D

N/A = NOT APPLICABLE
N/D = NO DATA ENTERED

Table 5-4. Results of Hydrothermal Tests and Open-Closed Tests.

RESULTS OF HYDROTHERMAL TEST AND OPEN-CLOSED TESTS

ANALYTE	Sample Number 92-05985 8 days Basalt+H2O (105 degrees C) (mg/L)	Sample Number 2-1439-02-15 5 daus Open-Closed RINGOLD (mg/L)	Sample Number 2-1440-02-15 5 daus Open-Closed BASALT (mg/L)	Blank (mg/L)	Detection Limit (mg/L)
Al	0.294	<.1	<.1	<.1	0.1
Ca	102.4	40.3	28.4	0.09	0.1
Cu	0.988	<.02	<.02	<.02	0.02
Cr		<.02	<.02	<.02	0.02
Fe	0.3	<.02	<.02	<.02	0.02
K	130	5.4	3.4	<2.6	1.5
Mg	34.8	6.72	6.06	<	0.1
Na	116	20.8	9.6	0.78	0.3
Ni	0.01	<.03	<.03	<.03	0.03
Si	89.1	17.4	17.2	0.14	0.2
Sr	0.238	0.193	0.12	<.01	0.01
Zn	0.29	<.01	<.01	<.01	0.01
As		<.02	<.02	<.02	
B	0.257	0.127	0.302	0.051	0.01
Ba	0.065	0.096	0.039	<.02	0.02
Li	0.14		<.05	<.05	0.05
Mn	1.46	<.01	<.01	<.01	0.01
Mo	<.1	<.1	<.1	<.1	
P	10	<.1	<.1	<.1	0.1
pH	6.05	8.11	8.08	6.83	
F	32	3.14	1.84		
Cl	33	9.78	2.93	<.1	
PO4	30				
NO2		5.14			
NO3	124	25.3	6.14	<.1	
SO4	460	14.6	7.02	<.1	
Oxylate	<20				
TC	302	123	88.1	4.76	
TOC	296	95.5	64.6	4.64	
IC	6	27.5	23.5	0.12	
HCO3	30.5	139.8	119.5	0.61	

9 3 1 2 8 6 9 1 7 1 3

Table 5-5. Modal Proportions and Compositions of Constituent in Grande Ronde Basalts.

MODAL PROPORTIONS AND COMPOSITIONS OF CONSTITUENT MATERIAL IN GRAND RONDE BASALTS

Umtanum Basalt Starting Material		Cohassett Basalt				
			Modes (vol.%)			Observed Compositions (mol.%)
Constituent	Average Mode (vol.%)		Constituent	Entablature	Colonnade	
		Phenocrysts	plagioclase	3	3	An61
			augite	2	10	En76
			olivine	tr	tr	Fo64
plagioclase	41	Groundmass	plagioclase	37	41	An60-An39-Ab plag
pyroxene	25		augite	23	20	En75-En57-En0
			pigeonite			En68-En37-?
Fe-Ti oxide	5		Fe-Ti oxide	3	3	Usp80-Usp60
			apatite	tr	1	fluor-apatite
			sulfide	tr	tr	pyrrhotite
Glass	26		glass	21	17	
			mafic globules	4	<1	Mt/Px/Ap/Sulfide/Glass/?
			alteration	7	4	smectite/clinoptilolite/silica

Table 5-6. Composition of Umtanum Basalt Starting Material.

COMPOSITION OF UMTANUM BASALT STARTING MATERIAL

BULK ROCK (XRF ANALYSIS), expressed in weight percent of element

HEIS #	LAB #	WHC # Sample	PHI	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P
B01CN6	2751-26	BAS+0	0	25.74	1.33	3.51	10.05	0.16	2.07	5.10	1.22	0.77	0.09
B01CM6	2751-18	BAS+1	1	25.68	1.33	3.50	10.04	0.16	2.05	5.08	1.17	0.77	0.09
B01CM7	2751-19	BAS+2	2	25.61	1.31	3.52	10.00	0.16	2.09	5.09	1.16	0.76	0.09
B01CM8	2751-20	BAS+3	3	25.66	1.26	3.56	9.85	0.16	2.00	5.10	1.16	0.76	0.09
B01CM9	2751-21	BAS+4	4	25.73	1.23	3.62	9.63	0.16	1.95	5.04	1.20	0.77	0.09
B01CN0	2751-22	BAS+4.75	4.75	25.27	1.34	3.46	10.31	0.16	1.95	4.95	1.13	0.77	0.10
B01CN1	2751-23	BAS+PAN	PAN	24.90	1.42	3.23	11.08	0.16	2.21	5.00	1.05	0.76	0.11

		Ni	Cr	Sc	V	Ba	Rb	Sr	Zr	Y	Nb	Ga	Cu	Zn	Pb	La	Ce	Th
BAS+0	0	0	17	41	314	599	46	310	182	37	13.8	23	7	130	9	32	46	5
BAS+1	1	0	14	38	313	583	47	309	181	37	14	24	22	135	11	19	37	6
BAS+2	2	0	17	36	304	598	47	310	181	39	14.2	24	45	136	7	37	55	7
BAS+3	3	0	18	36	305	577	43	316	180	37	13.7	24	55	135	10	21	40	5
BAS+4	4	0	14	36	300	584	49	325	182	36	14	22	82	133	13	27	43	6
BAS+4.75	4.75	0	22	37	319	600	48	311	185	37	15.1	20	158	168	48	26	39	6
BAS+PAN	PAN	0	22	42	346	576	47	283	183	38	14.4	21	432	232	36	13	43	5

DIGESTATE COMPOSITION(CLP ANALYSIS), as weight percent

		Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K
BAS+0	0	0.0014	0.34	0.16	1.74	0.01	0.04	0.39	0.01	0.07
BAS+1	1	0.002	0.7	0.22	3.35	0.03	0.05	0.44	0.02	0.1
BAS+2	2	0.0028	0.55	0.25	2.58	0.02	0.05	0.45	0.03	0.12
BAS+3	3	0.0044	0.68	0.31	3.2	0.03	0.06	0.48	0.04	0.14
BAS+4	4	0.0059	0.75	0.44	3.54	0.03	0.08	0.55	0.07	0.16
BAS+4.75	4.75	0.0086	0.99	0.51	4.44	0.04	0.1	0.57	0.08	0.18
BAS+PAN	PAN	0.0208	0.96	0.82	4.33	0.04	0.12	0.87	0.12	0.2

DIGESTATE (CLP ANALYSIS)

		Ni	Cr	*As	V	Ba	*Be	Zr	*Co	Cu	Zn	Pb	NH3	Alkalinity	F	Cl	NO2	NO3	O-PO4	SO4
BAS+0	0	3.2	1.7	0.9	78.1	18.4	0.6	20.6	10.4	16.1	27.8	10.6	nd	452	2.37	57.1	0.85	298		
BAS+1	1	3.2	3	0.9	161	33.7	1.1	34.4	19.2	21.3	53.3	6.4	nd	402	0.75	8.73		46.9	2.9	84.3
BAS+2	2	3.2	2.5	0.9	124	37	0.9	30.9	14.7	45.4	43.5	8.6	nd	626	0.5	13.4	0.23	106	2.94	116
BAS+3	3	3.2	3.8	0.9	166	40.5	1	38.9	19.2	51.2	55.7	27.1	nd	453	0.53	12.6	0.25	96.2	5	163
BAS+4	4	3.2	6.1	0.9	177	53.5	1.2	40.2	21.1	73	63.9	14.9	nd	564	0.66	13.3	0.36	87.6	5.44	190
BAS+4.75	4.75	3.2	9.5	0.9	244	58.2	1.5	48.1	27.6	183	106	29.4	nd	404	2.27	17.4		116	149	260
BAS+PAN	PAN	3.2	11.2	0.9	237	71.7	1.5	48	30.3	326	140	30.7	nd	1280	3.48	27.7		123	129	407

nd Not determined
* No bulk-rock data

Table 5-7. Composition of Ringold Sediment Matrix Starting Material.

	Ringold Sediment Starting Material Bulk Composition (X-ray Fluorescence)	Ringold Sediment Starting Material Digestate Composition (EPA Protocol*)
SAMPLE #	KAL-Ring-Fm	2831-16
ID #		B06153
	(mg/kg)	(mg/kg)
Si	6.85E+05	29
Al	1.37E+05	7870
Sb		11.8
As		6.5
Ba	737	132
Be		1
Cd		0.61
Ca	3.34E+04	2880
Cr	136	10
Co		8
Cu	21	9.8
Fe	4.58E+04	22300
Pb	19	9.2
Mg	1.98E+04	3600
Mn	8.50E+02	201
Hg		0.1
Ni	34	6.5
K	2.58E+04	1500
Se		1.2
Ag		.2
Na	2.31E+04	202
Tl		0.61
V	86	53.9
Zn	73	38.8
Mo		2.9
Ti	7.58E+03	1070
Zr	296	24.1
Ammonia		3.01
Alkalinity		601
F		1.18
Cl		8.94
NO2		<.2
NO3		23
O-PO4		<.6
SO4		56.2
TOC		7669
P2O5	1.76E+03	
Sc	13	
Rb	100	
Sr	291	
Y	33	
Nb	16.3	
Ga	19	
La	44	
Ce	79	
Th	13	

TRACE ELEMENT ANALYSES OF SELECTED ROCK-WATER TESTS

(Concentrations in micrograms per Liter)

Analyte	ICP-MS Blank	Test System Material Atmosphere Analytical Method	Closed Basalt Air 16 days ICP-MS	Closed Basalt Nitrogen 16 days ICP-MS	Closed Ringold Air 16 days ICP-MS	Closed Ringold Nitrogen 16 days ICP-MS	Open Basalt Pore Volume 1 ICP-MS	Open Basalt Pore Volume 2 ICP-MS	Open Ringold Pore Volume 1 ICP-MS	Open Ringold Pore Volume 2 ICP-MS	Hydrotherma Basalt (105 degrees C) ICP-MS
Cr	0.55		1.98	1.98	4.25	2.32	2.5	1.5	5.87	2.31	8.37
Mn	0.62		116	65.9	54.7	28.5	20.1	1.24	77.4	1.01	1460
Cu	0.1		49.6	36.9	25.2	13.2	12.3	4.26	20.8	11	1020
Zn	0.5		11.3	7.59	4.6	0.5	15.6	1.74	17	0.5	465
As	0.05		4.24	4.97	16.3	12.9	9.11	11.1	40.3	19	29.4
Sr	0.02		186	147	704	341	174	115	4340	208	303
Mo	0.23		51.3	83.7	47.5	33.2	6.58	6.75	85.7	230	69.2
Cd	0.05		0.33	0.28	1.05	0.28	0.18	0.11	0.56	0.51	1.21
Ba	0.12		25.9	19.5	109	49.8	27.8	11.5	459	30.8	77
Pb	0.08		0.43	0.16	0.3	0.16	0.86	0.14	0.25	0.16	1.41

Analyte	ICP DL	Test System Material Atmosphere Analytical Method	Closed Basalt Air 16 days ICP	Closed Basalt Nitrogen 16 days ICP	Closed Ringold Air 16 days ICP	Closed Ringold Nitrogen 16 days ICP	Open Basalt Pore Volume 1 ICP	Open Basalt Pore Volume 2 ICP	Open Ringold Pore Volume 1 ICP	Open Ringold Pore Volume 2 ICP	Hydrotherma Basalt (105 degrees C) ICP
Cr	20		ND	ND	ND	ND	<	<	<	10	<
Mn	10		122	262	?	?	<	<	<	<	1460
Cu	20		50	<	<	<	16	<	<	<	290
Zn	10		<	<	<	<	<	<	<	<	988
As	20		<	<	<	<	<	<	<	<	<
Sr	10		<	<	<	<	169	106	5480	205	238
Mo	100		<	<	<	<	<	<	<	250	<
Cd	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND
Ba	20		20	21	45	38	<	<	470	31	65
Pb	10		<	<	<	<	<	<	<	<	<

Table 5-9. Summary of Rock-Water Reaction Tests.

	RINGOLD SEDIMENT-WATER REACTION TESTS			BASALT-WATER REACTION TESTS		
	Open	Open-Closed	Closed	Open	Open-Closed	Closed
Starting Material	Ringold	Ringold	Ringold (Air)	Basalt	Basalt	Basalt (Air)
Sample Number	2-1439-02-14 14 th Pore Volume	2-1439-02-15 5 days	SO-A-128 128 days	2-1440-02-14 14 th Pore Volume	2-1440-02-15 5 days	BA-A-128 128 days
Al	0.2	<.1	<	<	<.1	<
Ca	14.2	40.3	66.3	8.6	28.4	80.7
Cu	<	<.02	<	<	<.02	<
Cr	<	<.02	<	<	<.02	<
Fe	0.1	<.02	<	<	<.02	0.07
K	2	5.4	18	4	3.4	20
Mg	1.9	6.72	27.5	1.95	6.06	29.1
Na	8.9	20.8	29.2	9.6	9.6	106
Ni	<	<.03	>	<	<.03	<
Si	14.2	17.4	18.9	22.3	17.2	19.5
Sr	<	0.193	0.354	<	0.12	0.123
Zn	<	<.01	<	<	<.01	<
As	<	<.02	<	<	<.02	<
B	<	0.127	0.119	<	0.302	0.077
Ba	<	0.096	0.057	<	0.039	0.023
Li	<		<	<	<.05	<
Mn	<	<.01	<	<	<.01	0.046
Mo	<	<.1	<	<	<.1	<
P	<	<.1	<	<	<.1	<
Pb	<	<	<	<	<	<
F	0.37	3.14 (ck)	<1.5	0.22	1.84	3.5
Cl	0.73	9.78	10	0.45	2.93	9.1
PO4	0.23	<	<	<.2	<	<
NO2	<	5.14	<	<	<	<
NO3	1.83	25.3	51.9	1.13	6.14	5.7
SO4	4.22	14.6	152	1.33	7.02	322
pH	7.87	8.11	8.05	7.88	8.08	8.51
Oxylate	<.25	<	<	<.25	<	<
TC	23.9	123	67.5	21.8	88.1	78.5
TOC	8.7	95.5	39.4	7.75	64.6	32.5
IC	15.2	27.5	26.2	14.05	23.5	46
HCO3	77.3	139.8	133.2	71.4	119.5	233.8

Table 6-1. Average Fluoride and Chloride Concentrations in Meteoric Water, Spring Water, and Unconfined Aquifer Groundwater (mg/L).

	Meteoric water	Spring water	Unconfined aquifer groundwater	
			Low-Cl type	High-Cl type
Fluoride	<0.1	0.35	0.4	0.76
Chloride	0.5-1.0	6	4.4	22.9

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Table 6-2. Evaporation Enrichment Factors.

EVAPORATION ENRICHMENT FACTORS

% Evaporation	Enrichment Factor	Concentration Effect For Co = 0.5 (mg/L)	Concentration Effect For Co = 10 (mg/L)
10	1.1	0.6	11.1
20	1.3	0.6	12.5
30	1.4	0.7	14.3
40	1.7	0.8	16.7
50	2.0	1.0	20.0
60	2.5	1.3	25.0
70	3.3	1.7	33.3
80	5.0	2.5	50.0
85	6.7	3.3	66.7
90	10	5	100
95	20	10	200
99	100	50	1000

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Table 6-3. Comparisons of Average Compositions (ppm) of Spring Water, Low-Chloride Unconfined Aquifer, and High-Chloride Unconfined Aquifer.

CONSTITUENT	SPRING WATER	LOW-CHLORIDE GROUNDWATER	HIGH-CHLORIDE GROUNDWATER	EVAPORATION MODEL
Sodium	9.645 ± 2.825 (36)	13.220 ± 3.002 (9)	27.878 ± 4.750 (3)	36.161
Potassium	2.151 ± 0.810 (36)	4.720 ± 0.750 (9)	6.993 ± 0.930 (3)	8.065
Calcium	22.893 ± 4.427 (36)	35.791 ± 7.972 (9)	45.198 ± 10.669 (3)	85.830
Magnesium	10.293 ± 2.090 (36)	10.561 ± 2.638 (9)	11.461 ± 2.217 (3)	38.591
Iron	0.024 ± 0.007 (36)	0.140 ± 0.206 (9)	0.076 ± 0.051 (3)	0.090
Manganese	0.008 ± 0.002 (36)	0.033 ± 0.051 (9)	0.045 ± 0.065 (3)	.030
Zinc	0.035 ± 0.021 (36)	0.099 ± 0.138 (9)	0.031 ± 0.032 (3)	0.131
Barium	0.009 ± 0.005 (36)	0.036 ± 0.018 (9)	0.056 ± 0.008 (3)	0.034
Chloride	6.089 ± 3.194 (36)	5.468 ± 1.640 (10)	22.829 ± 2.134 (4)	(22.829)
Fluoride	0.353 ± 0.105 (36)	0.395 ± 0.070 (8)	1.038 ± 0.344 (3)	1.324
Sulfate	12.722 ± 3.137 (36)	24.505 ± 13.306 (9)	47.600 ± 27.779 (4)	47.697
Nitrate	6.387 ± 7.059 (36)	5.143 ± 3.236 (8)	5.043 ± 4.636 (4)	23.946

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