UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

GEOCHEMICAL CONTROLS ON DISSOLVED SODIUM IN BASALT AQUIFERS OF THE COLUMBIA PLATEAU, WASHINGTON

By P. P. Hearn, W. C. Steinkampf, G. C. Bortleson, and B. W. Drost

---

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 84-4304

★U.S. GOVERNMENT PRINTING OFFICE: 1985—597-397

Tacoma, Washington
1985

UNITED STATES DEPARTMENT OF THE INTERIOR
DONALD P. HODEL, Secretary

GEOLOGICAL SURVEY
Dallas L. Peck, Director

For additional information write to:

District Chief
U.S. Geological Survey
1201 Pacific Avenue - Suite 600
Tacoma, Washington 98402-4384

Copies of this report
can be purchased from:

Open-File Services Section
Western Distribution Branch
U.S. Geological Survey
Box 25425, Federal Center
Lakewood, Colorado 80225
(Telephone: (303) 234-5888)

CONTENTS

ILLUSTRATIONS

[Plate in pocket]

PLATE 1. Fence diagrams showing variation of sodium concentration, sodium-adsorption ratio, and water type in basalt aquifers, Columbia Plateau, Washington.

ILLUSTRATIONS - cont.

TABLES

METRIC CONVERSION FACTORS

Multiply	By	To obtain
inches (in.)----------------------	25.4	millimeters (mm)
	2.540	centimeters (cm)
	0.0254	meters (m)
feet (ft)-------------------------	0.3048	meters (m)
miles (mi)------------------------	1.609	kilometers (km)
square miles (mi^2)-----------------	2.590	square kilometers (km^2)

to change degrees Fahrenheit (°F) to degrees Celsius (°C):
°C = 5/9 (°F-32)

to change degrees Celsius (°C) to degrees Fahrenheit (°F):
°F = 9/5°C + 32

National Geodetic Vertical Datum of 1929 (NGVD of 1929): A geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "mean sea level." NGVD of 1929 is referred to as sea level in this report.

GEOCHEMICAL CONTROLS ON DISSOLVED SODIUM IN BASALT AQUIFERS OF THE COLUMBIA PLATEAU, WASHINGTON

By
P. P. Hearn, W. C. Steinkampf,
G. C. Bortleson, and B. W. Drost

ABSTRACT

Miocene basalt aquifers in the Columbia Plateau are the principal source of water for agricultural, domestic, and municipal use in Washington State. Irrigation using ground waters with relatively high sodium concentrations has been a cause for concern in recent years, because of the capacity of such waters to reduce soil permeability.

Chemical reactions involving ground water and the basalts are the primary mechanisms responsible for the input of sodium to ground water in the plateau. This conclusion is supported by the formation sequence of secondary alteration products in the basalts and by progressive changes in the chemistry of ground waters with increasing depth and position along regional flow paths.

In general, upgradient and shallow ground waters have low sodium concentrations and low sodium-adsorption ratios (SAR's), and are predominantly calcium sodium bicarbonate waters. In contrast, ground waters from deeper and downgradient locations have the highest sodium concentrations and SAR's, and are predominantly sodium bicarbonate waters.

Volcanic glass and cryptocrystalline matrix are the major sources of sodium to ground water, and are dissolved by a combination of silicate hydrolysis and dissolution by carbonic acid. Magnesium and calcium are removed from solution by the formation of an iron-magnesium smectite, calcite, and amorphous iron oxyhydroxide. The addition of sodium, silicon, and potassium by dissolution of basalt exceeds their removal by the precipitation of secondary minerals, and their concentrations increase in the initial stages of this process. In later stages of ground-water evolution, these continued increases produce a water apparently saturated with respect to clinoptilolite and silica phases, and these solid phases begin to precipitate. While the timing of these processes is unclear, the mineralogy of secondary alteration and estimated cooling rates of the basalt flows suggest that observed alteration products formed primarily at low temperature, under conditions similar to those existing at the present time.

INTRODUCTION

The Columbia River Basalt Group covers an area of approximately 77,000 square miles, about 25,000 of which are in Washington State (fig. 1) Within much of this area, basalt aquifers are the principal sources of water for agricultural, domestic, and municipal uses. Concern has been expressed in this agriculture-dependent region about problems associated with the use of ground waters with a high sodium concentration relative to calcium and magnesium. Continued irrigation with such waters can, without adequate management practices, reduce soil permeability to the point that water cannot effectively reach plant roots.

In 1982, the U.S. Geological Survey, in cooperation with the Washington State Department of Ecology, began a 2 1/2-year investigation of waters in the basalt aquifers in Washington State. The objectives of the study were to map the spatial and temporal variability of dissolved sodium in the aquifers and relate this variation to the geohydrologic system, and to identify the geochemical and geohydrologic factors controlling the occurrence of sodium in ground waters in the Columbia River Basalt Group.

The results of this work are being released as a series of map reports showing the spatial variations of the sodium-adsorption ratio (SAR) and dissolved-sodium concentrations and describing the geology and hydrology of the major basalt aquifers in the Columbia Plateau in Washington State (Bortleson and Cox, 1985; Drost and Whiteman, 1985; Bauer and Vaccaro, 1985). This report discusses the geochemical factors controlling the occurrence of high-sodium ground waters in the Columbia Plateau.

Water Quality for Irrigation

Although all natural waters contain some dissolved solutes, the suitability of water for irrigation generally depends on the types and amounts present. Use of irrigation water with a high ratio of sodium to calcium plus magnesium can, without mitigating treatment, saturate the exchange sites on soil clays with sodium ions. When such sodic soils are wetted, the clays can disperse, reducing permeability, and can harden on drying to the point where cultivation is difficult.

Because it is the sodium concentration relative to calcium and magnesium that determines the effect on soils, the concentrations of all three ions must be considered. A common measure of sodium loading potential is defined by the expression

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{(\mathrm{Ca} + \mathrm{Mg})/2}} ,$$

where the concentrations of sodium (Na), calcium (Ca), and magnesium (Mg) are expressed in milliequivalents per liter (U.S. Department of Agriculture Salinity Laboratory, 1954). For waters of medium salinity, SAR values below 8 reflect a low sodium hazard, between 8 and 14 a medium hazard, and above 14 a high sodium hazard.

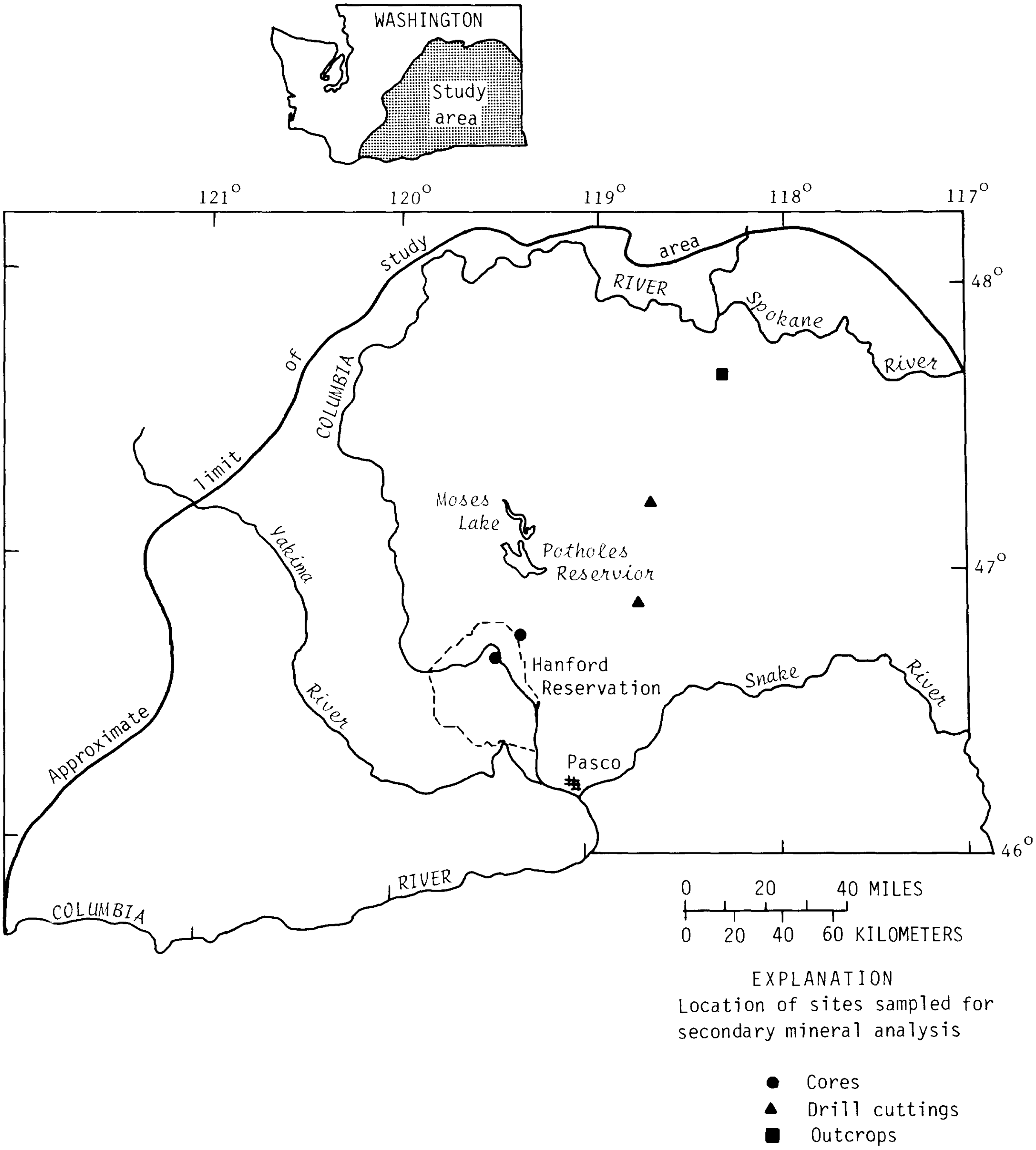

FIGURE 1.--Locations of study area and rock sample sites of Columbia River Basalt Group.

Methods

Records of about 2,500 wells, including geophysical logs, were compiled and reviewed to define the vertical and areal extent of the three major freshwater-bearing geologic formations in the Columbia River Basalt Group (Drost and Whiteman, 1985). From these records, 418 wells with identified stratigraphic completion intervals were selected for sampling at least once during one of the following periods: summer 1982, spring 1983, and summer 1983 (Bortleson and Cox, 1985).

Values of pH, dissolved oxygen, specific conductance, and dissolved inorganic carbon species were determined at each sampling site. Where possible, samples were collected at wellheads, and a flow chamber was used to isolate the samples from the atmosphere. Samples and field data were obtained only after the water temperature had stabilized. Analyses of inorganic constituents were made by the U.S. Geological Survey Central Laboratory in Arvada, Colo., using procedures described by Skougstad and others (1979). Unaerated samples were collected at selected sites for carbon-14 analysis by the University of Arizona Isotope Geochemistry Laboratory.

Two outcrop samples and 13 samples of drill cuttings from wells in the central and northeastern parts of the study area were obtained in order to investigate secondary alteration in the basalt aquifers. Ten core samples were obtained from two test wells within or near the Hanford Reservation (fig. 1). Samples that showed visible alteration under a binocular microscope were selected for analysis. Polished thin-sections or polished chips embedded in epoxy were carbon-coated and examined with an ETEC Autoscan scanning electron microscope equipped with an EDAX model 9100 Energy Dispersive X-ray Spectrometer (SEM/EDS)*. Separate phases within altered zones were discriminated by means of a backscattered electron detector. EDS analyses were made on 10 X 10-micrometer areas using an accelerating voltage of 18.5 Kv and a count time of 30 seconds. Glass reference standards were prepared by fusing U.S. Geological Survey standard rock powders. The mineralogy of the major secondary alteration products was initially determined on hand-picked samples by powder X-ray diffraction. Subsequent identifications were made by referencing EDS analyses to the compositions of these samples. Silicon was not present in any sample in sufficient quantity to facilitate identification of a specific phase; consequently, phases containing only silicon, based on EDS analyses, are referred to simply as silica.

Acknowledgments

The authors extend their gratitude to farmers, ranchers, and others who made their wells available for water sampling and water-level measurement. Also acknowledged are agencies that provided personnel and special assistance to gain access to publicly owned wells. Appreciation is expressed to Rockwell-Hanford Operations of Rockwell International for providing core samples from selected wells.

---

*Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

GEOHYDROLOGIC SETTING

Geology

The Columbia Plateau is that area underlain by the Columbia River Basalt Group. It is both a structural and topographic basin with its lowest point near Pasco, Wash. The rocks of the plateau are primarily flat-lying Miocene flood basalts, with relatively minor amounts of interbedded Miocene sediments and overlying fluvial sediments and loess of Pliocene to Holocene Age (fig. 2). Geologic structure and topography are more complex in the southwestern part of the study area, due to pre-eruptive topography and post-emplacement folding and faulting. Along the borders of the plateau the basalts are underlain primarily by volcanic and metamorphic rocks of Precambrian to early Tertiary age. In the interior of the plateau the nature of the rocks underlying the basalts is not known.

The lavas which formed the Columbia River Basalt Group issued largely from a system of northwest-trending linear vents in southeastern Washington and northeastern Oregon between 6 and 16.5 million years ago. Although flows were emplaced from early to late Miocene, most of the basalts erupted during the first 3.5 million years. The average thickness of the entire sequence of basalts in the plateau is more than 1/2 mile, but individual flows range in thickness from a few inches to more than 300 feet. The total volume of the group has been estimated at about 48,000 cubic miles (Hooper, 1982).

The Columbia River Basalt Group has been subdivided into five formations (fig. 2). The Grande Ronde, Wanapum, and Saddle Mountains Basalts comprise most of the total volume of basalt. The underlying Imnaha and Picture Gorge Basalts are of limited areal extent and minor geohydrologic import, and as such, are not addressed here.

The Grande Ronde Basalt underlies virtually all of the study area, and makes up about 85 percent by volume of the basalt in the plateau. It is exposed along the northern margin and in a few deeply incised stream channels in the central and southwestern parts of the study area. Its thickness ranges from a few feet along the northern margin, where it pinches out against "basement" rocks, to more than 4,000 feet in the Pasco area. The Grande Ronde comprises at least 30 and perhaps as many as several hundred individual flows. Sedimentary interbeds are extremely rare and are generally only a few feet thick. These interbeds are typical of those formed in the Columbia River Basalt Group, and range in composition from clay to sand and gravel. The boundary between the Grande Ronde and the overlying Wanapum Basalt is marked by a sedimentary interbed, the Vantage member of the Ellensburg Formation, throughout much of the study area. The Ellensburg Formation is not part of the Columbia River Basalt Group. This interbed averages 25 feet in thickness, but ranges from 0 to more than 100 feet.

Series	Group	Formation
Holocene Pleistocene Pliocene		Surficial deposits
Miocene	Columbia River Basalt Group	Saddle Mountains Basalt
		Mabton interbed of Ellensburg Formation
		Wanapum Basalt
		Vantage Member of Ellensburg Formation
		Grande Ronde Basalt
		Picture Gorge Basalt Imnaha Basalt
Basement rock		

FIGURE 2.--Generalized stratigraphic section of Columbia River Basalt Group and interbedded Ellensburg Formation.

The Wanapum Basalt underlies almost all of the study area and is exposed or is covered by a veneer of sediments throughout most of the northern half. In the southern half it is generally covered by thick sequences of sediments or by the Saddle Mountains Basalt. The Wanapum comprises about 10 individual flows and averages about 400 feet in thickness, ranging from a few feet where it pinches out against exposures of the Grande Ronde to more than 1,000 feet in the southwestern part of the study area. Sedimentary interbeds are more common in the Wanapum than in the Grande Ronde, but are still relatively rare and commonly thin. The Wanapum and the overlying Saddle Mountains Basalt are separated by the Mabton interbed of the Ellensburg Formation in the southwestern part of the study area. This interbed averages 50 feet in thickness, and ranges from 0 to more than 150 feet.

The Saddle Mountains Basalt is the youngest formation in the Columbia River Basalt Group, and accounts for less than 1 percent of the total basalt accumulation. It is present only in the southwestern part of the study area, where it is either exposed or is covered by sediments. The Saddle Mountains averages 400 feet in thickness, but exceeds 800 feet in some locations. Sedimentary interbeds are common and many are more than 50 feet thick.

Basalt Mineralogy and Physical Characteristics

The Columbia River Basalt Group lavas are classified as tholeites; the rocks consist chiefly of plagioclase feldspar, pyroxene, and opaque metal oxides. The most abundant crystalline components are (1) plagioclase with compositions between labradorite and andesine, (2) pyroxene with compositions between augite and sub-calcic augite, (3) and minor titanium-iron oxides of the ilmenite-magnetite solid solution series (Ames, 1980). These minerals are present in a matrix of cryptocrystalline material and volcanic glass. Plagioclase is generally the most abundant mineral component, and is commonly present as microscopic crystal laths surrounded by smaller and less numerous pyroxene grains. A suite of accessory minerals, including apatite, olivine, and metallic sulfides, is present in varying amounts. Also present are suites of minerals that were formed either late in the cooling stages of flow emplacement or some time after meteoric water began circulating through the rock framework. These secondary minerals are discussed further in a subseqent section of this report.

Flood basalts characteristically have low silica contents, high emplacement temperatures, and high volatile contents. These characteristics result in low-viscosity lavas that flow readily. This fluidity, combined with the large volumes of lavas extruded, the relatively flat pre-eruption topography, and the uplift in the southeastern part of the region that was contemporaneous with eruption are the primary reasons for the extensive areal coverage of the Columbia River Basalt Group.

The internal structure of basalt flows is largely a function of their cooling rate, which, in turn, depends largely on their emplacement temperature and environment. Flows that solidified under relatively static conditions developed a fairly characteristic infrastructure (fig. 3). The terms colonnade and entablature were taken from classical architectural terminology to describe the two most commonly observed structural zones (Tomkieff, 1940). The slowly cooled flow interiors developed distinctive columnar jointing patterns. Columns in the colonnade zone are mostly straight and tightly jointed, averaging about 3 feet in diameter. Columns are generally smaller and more irregular in the entablature zone; the presence of irregular cross-joints produces a hackly or friable structure (fig. 3). The entablature commonly accounts for 70 percent of the total volume of flows, but proportions can vary from 0 to 100 percent (Swanson and Wright, 1978).

Differences in cooling rates within flows also controlled the composition and relative abundance of glassy and crystalline components, and individual crystal size. Sudden chilling, caused, for example, when lava flowed into a lake, prevented significant crystal growth. Such rapidly cooled flows typically have distinctive "pillow" structures at their bases, are fine grained and glass-rich, and are commonly filled with vesicles from the rapid exsolution of volatiles. In contrast, slower cooling promoted crystal growth and the gradual release or incorporation of volatile components into solid phases. The resultant rock tends to contain more coarse-grained, crystalline phases and less glass.

In general, the basalt flows in the Columbia Plateau are characterized by vesicular tops and bottoms that are relatively glassy, with crystallinity increasing toward the flow center. Thick flows, and those largely restricted to drainage features, such as some of the Saddle Mountains Basalt flows, generally reflect lower overall cooling rates in flow interiors. Such flows tend to have coarser grained and more crystalline interiors than flows of similar volume but greater lateral extent. The central colonnade zones of flows, which cool more slowly, contain a more "evolved" assemblage of minerals and less glass than the overlying entablature zone. In contrast, the faster cooling occurring in entablature zones produces more glassy material; entablature glasses may also contain a cryptocrystalline matrix which solidified in an intermediate stage between crystalline and glassy (Long and Strope, 1983).

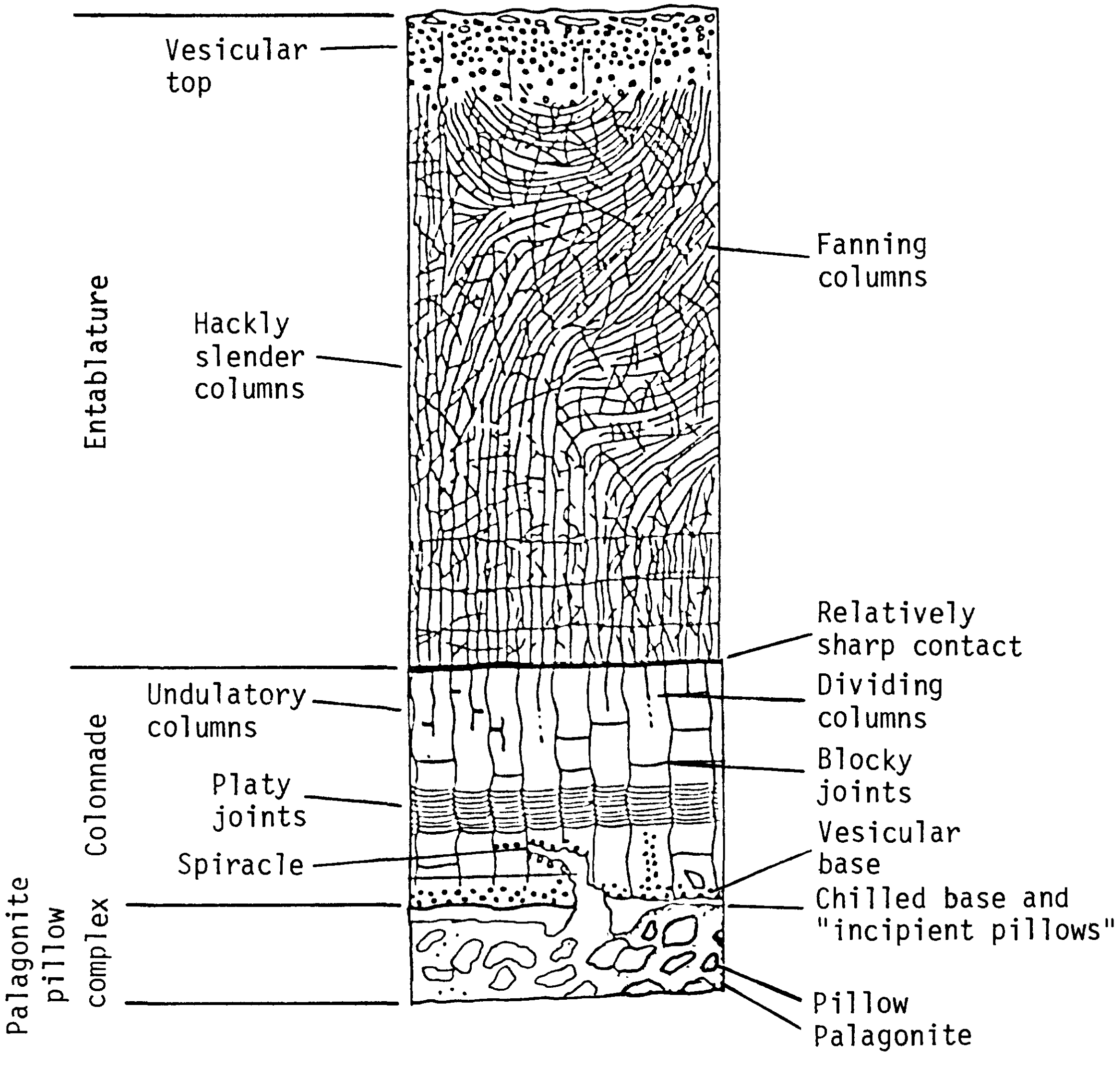

FIGURE 3.--Idealized basalt-flow structure. Modified from Swanson (1967).

Hydrology

The Columbia River basalt geohydrologic system is bounded on the north by the Columbia River, on the east by the Washington-Idaho border, on the south by the Blue Mountains, and on the west by a line midway between the Columbia River and the Cascade Range. These boundaries roughly correspond to the outcrop limits of the basalts. The system is overlain by a discontinuous mantle of Holocene to Pliocene loess and alluvial sediments, which in some locations is sufficiently thick and saturated to comprise an aquifer. The base of the flow system is the contact with the underlying igneous and metamorphic rocks and suspected marine sediments, the depth of which is unknown. Because of the extensive areal coverage of the basalts and the relatively recent initiation of agricultural ground-water withdrawals there is a paucity of information regarding the hydraulic characteristics of individual basalt flows and formations and the geohydrologic system as a whole.

Precipitation in the study area ranges from about 6 to 22 inches per year, generally increasing with altitude and with proximity to the Cascade or the Rocky Mountain Ranges. Natural recharge to the basalts occurs in some places along the plateau margins and in roughly that part of the plateau interior where more than about 8 inches of annual precipitation falls. A significant amount of artificial recharge occurs in the Columbia Basin Irrigation Project (CBIP) (fig. 4), where ground-water elevations rose as much as 300 feet between 1952 and 1968 as a result of irrigation and canal leakage (Tanaka and others, 1974). The upper part of the system is also recharged in those areas where pumping has sufficiently reduced heads to facilitate upward flux from deeper units.

Ground-water flow in the basalt aquifers is controlled to a large extent by the structural characteristics of individual flows. Flow takes place in vesicles, joints, fractures, and intraflow structures that create permeable zones. Flow is both vertical and lateral in the brecciated and vesicular tops and bottoms of flows, but primarily vertical in the thick central flow portions (fig. 5). Within the flow centers, the entablature and most of the colonnade are dense and less jointed and tend to have much lower porosities and permeabilities. In general, permeability is increased by the presence of joints and fractures caused by structural activity such as folding or faulting. Sedimentary interbeds serve as aquifers in those areas where their lithologies and extent facilitate the storage and transmission of significant quantities of water; they otherwise serve as semi-confining beds.

Ground water generally flows toward the major streams, including lower Crab Creek and the Yakima, Palouse, Columbia, and Snake Rivers (fig. 4 and 6). Over much of the area, ground-water movement is downward, and the individual basalt formations tend to become hydraulically semi-confined. Interformational flow is primarily downward from the Saddle Mountains to the Wanapum and from the Wanapum to the Grande Ronde throughout most of the study area. Upward flow from or within the Grande Ronde occurs in the vicinity of the Columbia and Snake Rivers, Crab Creek, and major surface-water bodies (fig. 4). The Columbia and Snake are major ground-water discharge sites. Significant local variations from these general patterns are caused by structural and stratigraphic barriers, major surface drainage features, irrigation recharge, and ground-water withdrawals. Agricultural pumpage is likely the most significant factor in reversing the natural direction of vertical flow in the central part of the plateau roughly east of the CBIP.

The movement of ground water in the basalts has also been affected by numerous uncased wells in the study area that function as conduits between flows by allowing water to move freely from one flow to another without having to travel through intervening layers. The magnitude of the total flux through these wells is largely a function of head difference between the connected permeable zones, and is likely significant in comparison to the natural downward flow. The movement of ground water is also affected by the large withdrawal-induced water-level declines that have been recorded east of the CBIP (Cline, 1984).

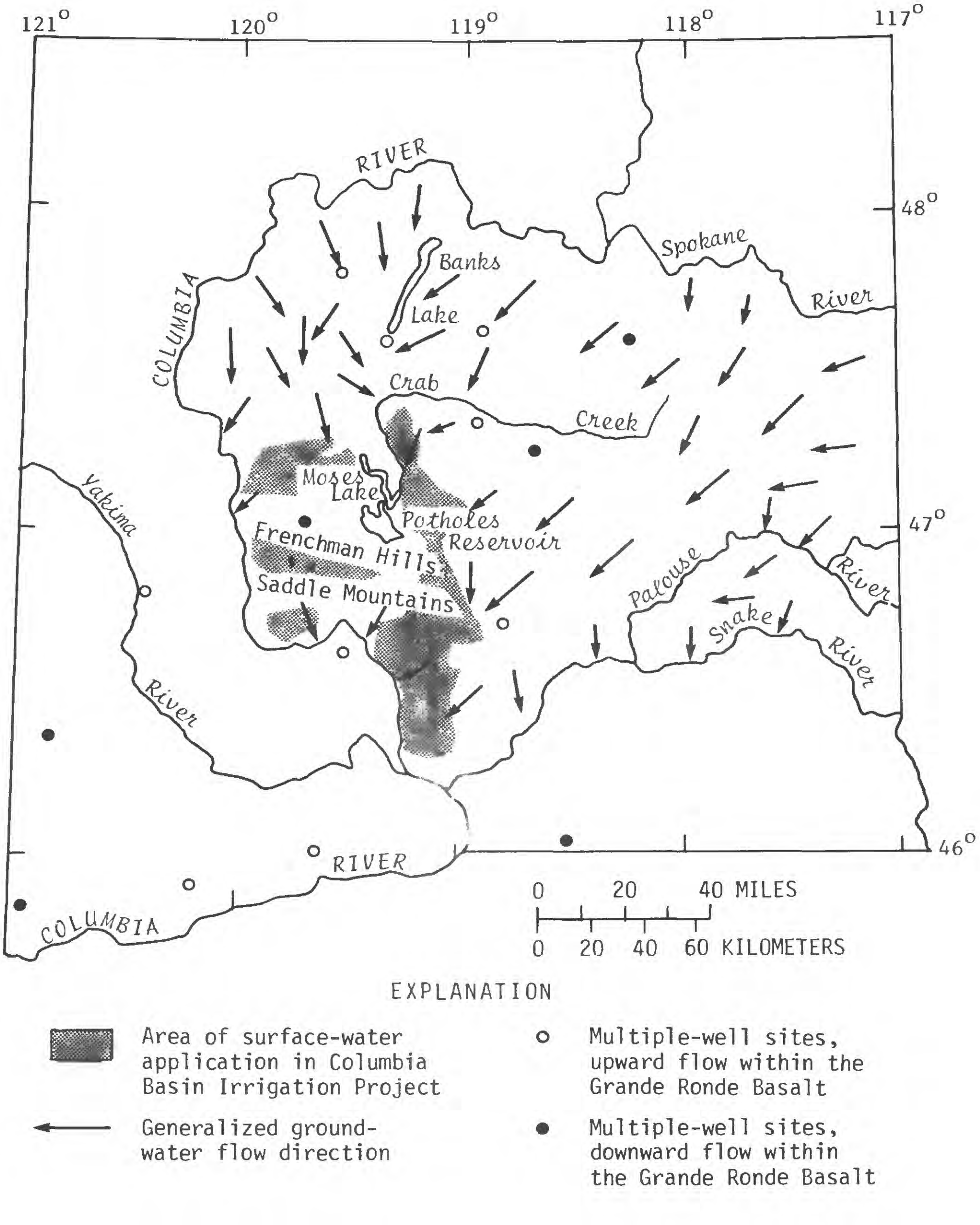

FIGURE 4.--Generalized ground-water flow in Wanapum and Grande Ronde Basalts in part of the study area. Flow direction inferred from potentiometric maps (Bauer and others, in press) and from ground-water elevations at multiple-well sites (D. R. Cline, unpublished data).

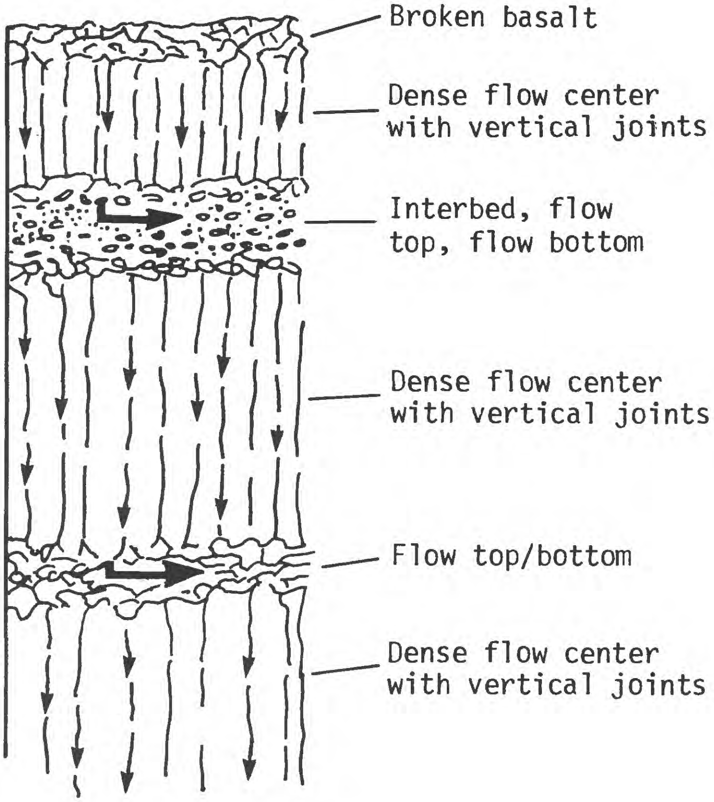

FIGURE 5.--Ground-water flow directions in generalized basalt section. Arrow size indicates generalized relative magnitude of flux.

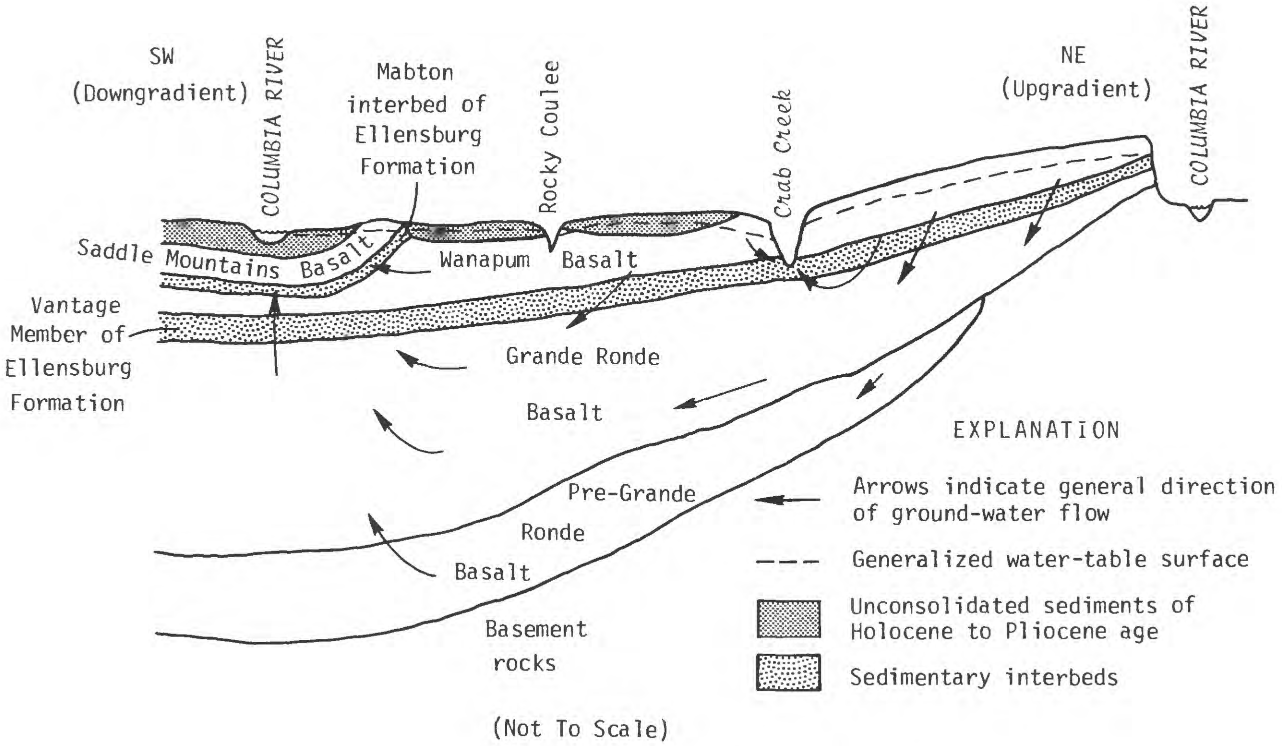

FIGURE 6.--Idealized geologic cross section, showing directions of ground-water flow.

BASALT-GROUND WATER INTERACTION

The assemblage of minerals and amorphous glass in a given basalt flow represents the components that were stable at or near the temperature of transition from molten lava to solid rock. As the rock cooled toward earth-surface temperature, however, these components became thermodynamically unstable. Hydrothermal reactions with meteoric water began shortly after emplacement; further reaction with meteoric water and carbonic acid continued as cooling progressed.

As a result of these reactions, the concentrations of solutes in the ground water increased, and mineral phases stable at the newly established conditions could begin to form. Depending on the residence time and travel path of the ground water, its composition could have evolved through several stages over time. The population and distribution of secondary minerals within the aquifer therefore provides insight into the geochemical evolution of the ground water.

Secondary Alteration

Early studies of secondary alteration in the Columbia River Basalt Group were confined to surface weathering at only a few locations (Allen and Scheid, 1946; Wise and Tschernich, 1975; Summers, 1976). Ames (1980) described in detail the nature and distribution of secondary alteration in five drill cores from the Hanford Reservation, but provided only a limited interpretation of his findings. The first attempt to develop a conceptual model of the alteration process was made by Benson and Teague (1982), who combined new data with Ames' findings to identify the major alteration products and establish a general sequence for their formation.

Secondary minerals are found primarily in the fractured and vesicular zones of flows, which are the major paths of ground-water flow. Although as many as 16 different secondary minerals have been identified, only a few species are found in significant quantities. The findings of this study, as well as the results reported by Ames (1980) and Benson and Teague (1982) show the major secondary phases to include smectite, primarily nontronite (fig. 7); the zeolite clinoptilolite (fig. 8); iron oxide of indeterminate crystallinity; and various forms of silica. Although other secondary minerals are common, they occur mostly in minor or trace amounts.

Both Benson and Teague (1982) and Ames (1980) noted differences between the suites of secondary minerals observed in vesicles and those found in open fractures. Fractures generally contained smectite, clinoptilolite, and silica, with sparse illite, pyrite, and calcite. Some vesicles, on the other hand, contained minor amounts of several other secondary phases, including chabazite, erionite, phillipsite, analcime, apatite, gypsum, and vermiculite. Fractures were commonly filled with alteration products, whereas vesicles were only partially filled. Benson and Teague (1982) attributed these differences primarily to volumetric differences and rates of mass transfer; fractures filled more rapidly because of their smaller size. In contrast, the rate of secondary mineral formation was slower in vesicles because of their isolation from the flow system, relative to fractures.

FIGURE 7.--Scanning electron micrograph of smectite lining a vesicle. Secondary electron image. Scale bar is 100 micrometers.

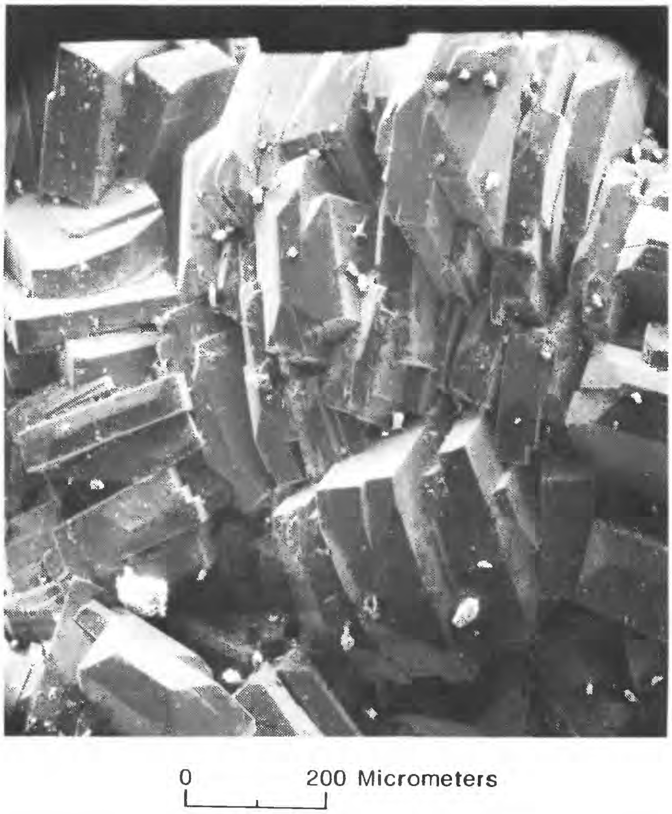

FIGURE 8.--Scanning electron micrograph of clinoptilolite crystals lining a vesicle. Secondary electron image. Scale bar is 100 micrometers.

Although the process of secondary alteration may have been accelerated by the elevated pressures and temperatures associated with lava flow emplacement, most of the alteration appears not to have been hydrothermal, but to have occurred at low temperatures (less than 100°C) by reactions with ground water. This conclusion is supported primarily by the mineralogy of the alteration assemblage. Silica is present as opal, quartz, cristobalite, and tridymite (Benson and Teague, 1982). If these rocks had been exposed to temperatures above 100°C for a substantial period of time, the amorphous opaline silica would have been converted to a more ordered phase or phases; this has not occurred. Further, the iron- and magnesium-rich smectite found in these rocks is common in volcanic rocks that have not been exposed to post-emplacement temperatures above 100°C (Walton, 1975; White and others, 1980), but not in basalts exposed to hydrothermal conditions. Finally, hydrothermal alteration of Icelandic basalts has produced a zeolite assemblage largely free of clinoptilolite (Walker, 1960), whereas this mineral is the dominant zeolite species in the Columbia River Basalt Group.

Although the available evidence appears to rule out a high-temperature hydrothermal origin for the suites of secondary alteration products in the Columbia River Basalt Group, the role of reactions at lower epithermal temperatures (50°-100°C) is less clear. The presence of quartz, cristobalite, and tridymite can be construed to indicate alteration at slightly elevated temperatures; however, these phases can also be the products of solid-state ordering of amorphous silica that precipitated at low temperatures. Studies of modern analogues to the Columbia River flood basalts indicate that even the thickest individual flows cooled to normal surface temperatures within a few hundred years (Rosalind Helz, U.S. Geological Survey, personal commun., 1984). Thus, while alteration in the lower epithermal range might have occurred, these rocks were exposed to such temperatures for only an extremely short period during their history.

Alteration Sequence

A general vertical distribution of secondary alteration products was observed by Benson and Teague (1982), and is also evident in the data from this study. Smectite is ubiquitous in both shallow and deep samples, but appears to be somewhat less common in samples from depths greater than 2,000 feet below land surface. In contrast, clinoptilolite was found only in samples from below 1,000 feet. Benson and Teague reported silica phases to be ubiquitous, with quartz the dominant species in samples from above 2,000 feet. No discrete silica was detected in this study in samples from above 1,500 feet. Discrete iron oxide was found in this study in most samples above 1,000 feet, but was largely absent below that depth.

On the basis of the sequence of alteration observed in vesicles and fractures, and vertical differences in the relative amounts of secondary species, Benson and Teague (1982) proposed the following general sequence of formation: clay (mostly nontronite) —> clinoptilolite —> silica and/or clay. The iron oxide observed in shallow samples in this study suggests that this phase precipitates together with nontronite. A scanning electron micrograph of a vesicle containing this sequence of alteration is shown in figure 9.

Smectite and Clinoptilolite Compositions

Because smectite and clinoptilolite are the only major alteration products that are not simple oxides, an effort was made to determine if variations in their compositions reflect changes in their environment of formation. EDS analyses of smectite and clinoptilolite were used to compute mean chemical formulae, based on unit cells with 10 and 36 oxygens, respectively. Smectite analyses were rejected if the computed formula did not satisfy structural criteria for total silicon and concentration criteria for octahedral and exchange ions. Mean compositions and computed formulas are given in table 1. Total iron is reported as Fe_2O_3, because ferric and ferrous states cannot be distinguished using EDS analysis.

The composition of clinoptilolites within a single sample is generally fairly constant, but smectites with different compositions commonly occur in proximity. Multiple generations of compositionally distinct smectites are found as linings (fig. 10) in many vesicles within a single sample. These sequences indicate episodic changes in local physico-chemical environments, although the precise mechanism is not apparent.

Although the low sample density in this study precluded the evaluation of lateral variations in smectite and clinoptilolite compositions, some trends are apparent as a function of depth. A plot of smectite octahedral ion concentrations shows samples from depths shallower than 1,000 feet to be slightly higher in iron than samples from below 1,000 feet (fig. 11). Further, analyses that did not yield an acceptable formula are predominantly from shallow samples, and generally fall between the mean composition and the iron corner of the diagram. This suggests that the shallow smectites contain discrete but finely admixed particles of amorphous iron oxide. If present in sufficient quantity, this excess iron would result in an erroneous formula.

A trend with depth is also apparent in the molar plot of exchange ions in clinoptilolite (fig. 12). The data show a progressive increase in sodium and an attendant decrease in potassium within the depth interval from 1,000 to 3,000 feet. A similar sodium enrichment was noted by Benson and Teague (1982) for clinoptilolite in samples from deeper than about 3,300 feet. In contrast, no systematic variations with depth were noted for smectite exchange ions.

TABLE 1.--Mean mineral composition and computed formula

Mineral	Mean composition (normalized to 100 weight percent)							Number of Analyses
	Na_2O	CaO	K_2O	MgO	Fe_2O_3	Al_2O	SiO_2	
Smectite	1.5	1.7	0.9	9.4	12.6	11.4	62.5	40
Clinoptilolite	5.6	1.6	2.7	0.4	0.5	16.4	72.8	30

	Computed Formula
Smectite	$\overset{\text{[exchange ions]}}{(Na_{0.07}\ Ca_{0.15}\ K_{0.09})}\ \overset{\text{[octahedral ions]}}{(Mg_{0.71}\ Fe_{1.11}\ Al_{0.43})}\ Al_{0.33}\ Si_{3.67}\ O_{10}\ (OH)_2$
Clinoptilolite	$\overset{\text{[exchange ions]}}{(Na_{0.88}\ Ca_{0.48}\ K_{0.94})}\ Mg_{0.10}\ Fe_{0.20}\ Al_3\ (Al_{0.66}\ Si_{1.34})\ Si_{13}\ O_{36}$

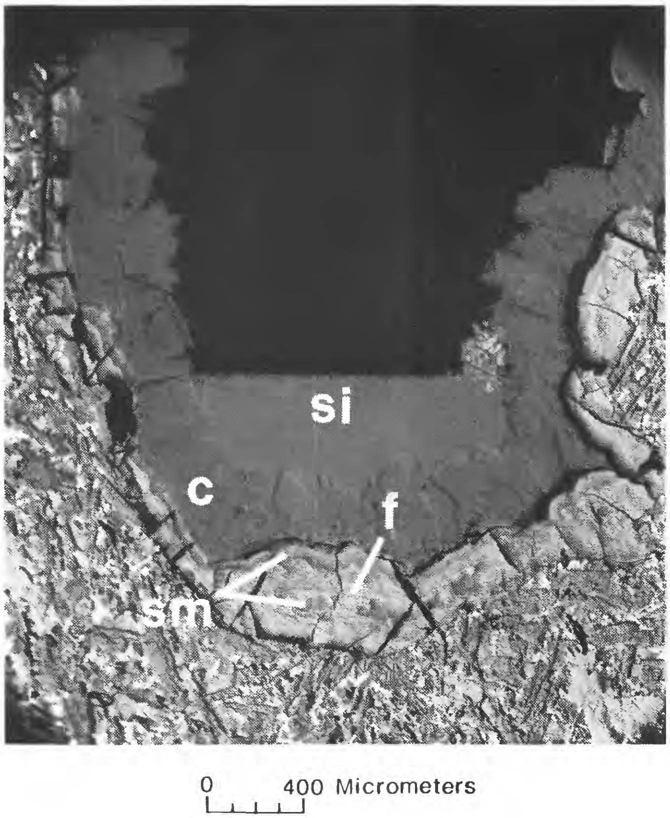

FIGURE 9.--Scanning electron micrograph of a vesicle lining showing sequence of secondary alteration: smectite (sm) plus amorphous iron oxide (f) → clinoptilolite (c) → silica (si). Backscattered electron image. Scale bar is 100 micrometers.

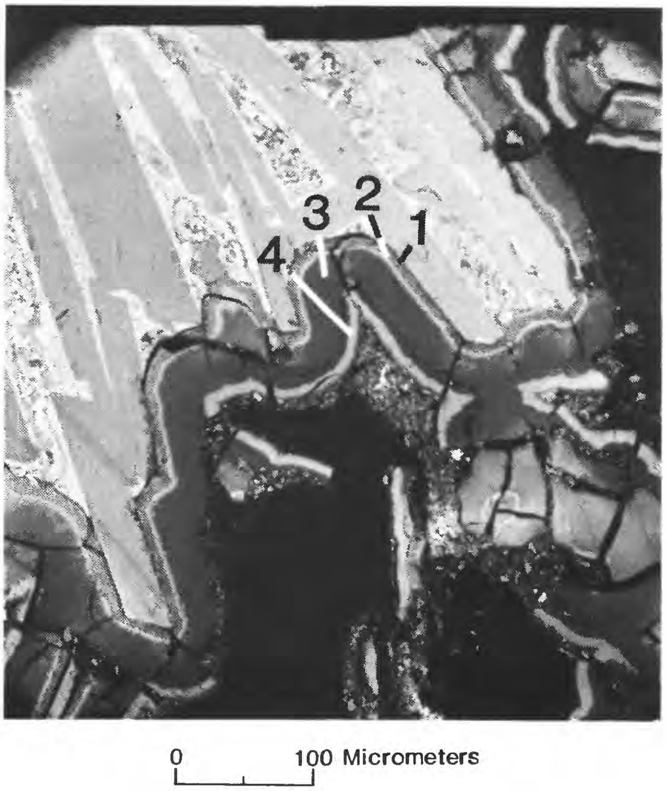

FIGURE 10.--Scanning electron micrograph of vesicle lining showing multiple generations of smectite (labelled 1-4, oldest to youngest). Backscattered electron image. Scale bar is 100 micrometers.

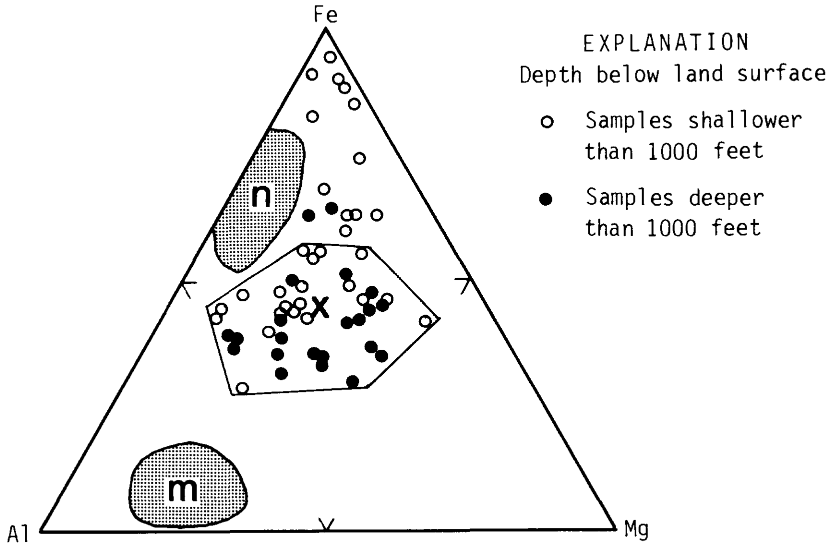

FIGURE 11.--Plot of smectite octahedral ion concentrations (mole percent). Polygon encloses analyses used to compute average composition, denoted by "X". Shaded zones indicate ranges of composition reported in literature for montmorillionites (m) and nontronites (n); data from Grim (1968) and Deer and others (1967a).

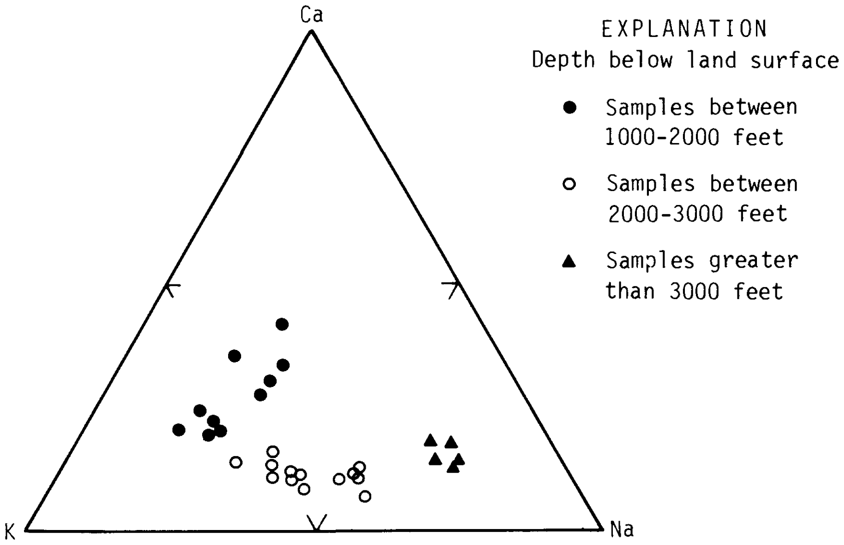

FIGURE 12.--Plot of clinoptilolite exchange ion concentrations (mole percent).

Relative Phase Solubility

The absolute solubilities of the major crystalline and glassy components of Columbia River Basalt Group formations are not known; previous studies, however, suggest some relative differences. Volcanic glass is much more soluble than crystalline silicate minerals, due to its lack of crystal structure and extensive surface area (Jones, 1966). On the basis of qualitative observations, Benson and Teague (1982) suggested that pyroxene and iron-titanium oxide minerals are more easily altered than plagioclase feldspar. One could therefore possibly expect the major components to react with ground water in the following order: glass, poorly crystalline matrix, pyroxene and titano-magnetite, then plagioclase feldspar. Sodium oxide concentrations in plagioclase feldspar and entablature glasses are approximately 5 weight percent; pyroxenes and titano-magnetites contain less than one-tenth this amount (fig. 13). These data, together with the higher solubility of glass, suggest that glass is the major source of dissolved sodium in ground water. Plagioclase is perhaps a significant source, but the magnitude of its contribution cannot be determined without further investigation.

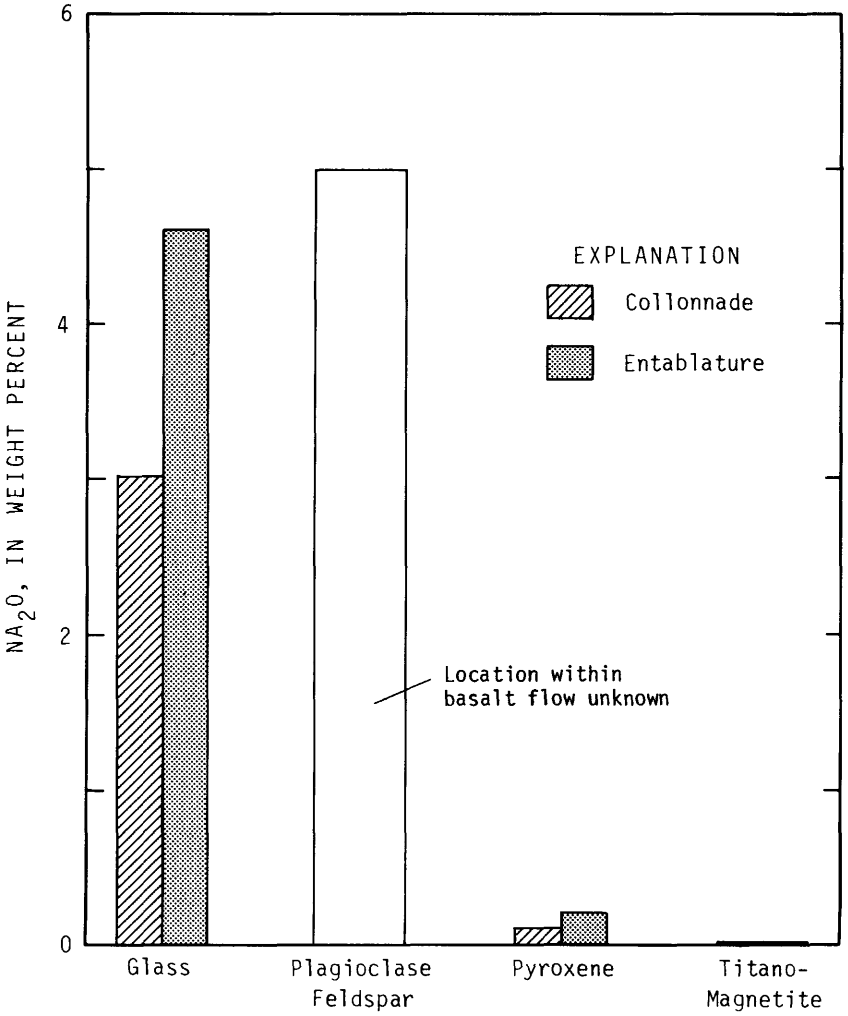

FIGURE 13.--Relative sodium contents of major phases in basalt. Basaltic glass and pyroxene data from Allen and Strope (1983) and Long and Strope (1983), respectively; plagioclase and titanomagnetite data from Deer and others (1967b).

CHEMICAL EVOLUTION OF GROUND WATER

The solutes present in a given ground water are determined by several factors: 1) the composition of the water when it entered the aquifer; 2) the solid phases the water encountered, and their respective solubilities; and 3) the residence time of the water in the aquifer. In this study, the chemical evolution of Columbia Plateau ground waters was examined with respect to residence time and position along regional flow path. Both methods revealed progressive changes in the chemical character of ground waters sampled.

In order to evaluate changes in solute chemistry with increasing residence time, carbon-14 determinations were made on 70 samples from 50 wells distributed throughout the plateau. The results of these analyses are expressed as percent modern carbon. No attempt was made to correct the data for the possible dilution of the dissolved radiocarbon by isotopically "dead" older carbon from the rocks. Percent modern carbon, however, should indicate relative age differences, while avoiding the uncertainty of correction procedures. The data were divided into three general groups for consideration: those with less than 35 percent modern carbon (oldest waters), those with 35 to 65 percent, and those with more than 65 percent (youngest waters).

The cation plot of dissolved sodium, magnesium, and calcium in figure 14 shows a general progressive enrichment of sodium with residence time, and a concurrent depletion of calcium and magnesium; the concentration of calcium relative to magnesium remains fairly constant. Progressive changes are also apparent in several other constituents. The pH and mean concentrations of dissolved silicon and potassium all increase with time, whereas dissolved oxygen is progressively depleted (fig. 15). No corresponding trends are apparent in the anion plot of dissolved bicarbonate, sulfate, and chloride (fig. 16). Although bicarbonate is the most abundant anion in all but one sample, changes in the anionic suite with time appear largely random.

The effects of the progressive reactions are also illustrated by examining data along approximate ground-water flow lines in the central part of the plateau, where the basalt layers are basically horizontal, have few structural deformities, and where data from numerous sampled wells are available. The parallel cross sections presented on plate 1 were prepared from topographic maps and structure contour maps of the Grande Ronde, Wanapum, and Saddle Mountains Basalts (Drost and Whiteman, 1985). Superimposed on the cross sections are shaded depictions of spatial variations of sodium concentration, SAR, and cation water type, based on analyses of water from 199 wells.

Shallow ground waters throughout the plateau tend to have low sodium concentrations and low SAR values. Both properties increase downgradient and with depth. A progressive enrichment of sodium is also reflected in the cation type of ground waters along the regional flow path. The predominantly calcium sodium ground waters in shallow and upgradient locations evolve to sodium calcium and sodium potassium ground waters in deeper and downgradient locations. Typical analyses of waters along the flow paths are listed in table 2.

TABLE 2.--Selected analyses of waters from Grande Ronde, Wanapum, and Saddle Mountains Basalts

[Values in milligrams per liter unless otherwise indicated]

Location[a]	Cross section	Index No.	Date of collection	Depth of well (ft below land surface)	Specific conductance (micromhos at 25°C)	pH, in units	Temperature (°C)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Sodium-adsorption ratio (SAR)	Potassium (K)	Bicarbonate (HCO_3)	Carbonate (CO_3)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Nitrate (NO_3)	Silica (SiO_2)	Dissolved iron (ug/L)
							Grande Ronde Basalt													
25/37-21L4	B-B'	413	7-21-82	975	288	8.2	22.3	15	5.8	40	2.3	4.8	174	0.0	11	4.3	0.9	0.1	50	18
25/32-35P1	A-A'	407	9- 9-82	1,140	270	8.2	21.3	12	5.3	39	2.4	4.8	151	.0	7.0	4.6	.8	.1	57	21
24/41-14D1	C-C'	400	7-19-82	775	213	7.7	15.7	19	8.4	17	.8	3.1	136	.0	8.0	2.0	.4	.1	50	91
23/41-24P2D1	D-D'	377	7-20-82	300	481	7.7	14.7	48	26	22	.7	2.5	336	.0	5.0	2.4	.3	.1	51	94
23/31-33E1	A-A'	367	8- 9-82	685	315	8.9	19.4	9.0	3.7	56	4.1	5.6	151	8.0	12	8.0	1.2	.1	59	6
21/30-23J1D1	A-A'	331	9- 8-82	1,335	372	8.6	23.1	16	2.4	55	3.5	11	130	3.0	35	20	.9	.1	68	8
21/38-23L1	C-C'	342	7-21-82	502	248	8.4	21.4	15	3.6	34	2.1	5.0	145	3.0	5.0	3.0	.9	.2	63	11
19/33-7R1	B-B'	290	5-25-83	1,730	310	8.8	24.3	4.4	1.7	62	6.6	8.0	172	5.0	7.8	6.8	2.6	.1	66	17
18/31-33D1	B-B'	257	5-19-83	2,400	400	9.3	36.6	1.8	.1	89	18	7.1	172	22	12	13	4.1	.1	110	62
17/33-12F2	C-C'	232	8-10-82	1,020	300	7.8	19.2	9.0	2.2	52	4.2	7.5	160	.0	7.0	10	1.9	.2	66	3
15/32-7J1	C-C'	170	5-20-83	1,900	348	8.3	25.4	9.3	4.9	57	3.9	7.0	172	.0	18	9.8	1.8	.2	66	12
15/36-33A2	D'D'	177	9- 8-82	510	410	7.7	19.9	29	19	40	1.5	7.1	281	.0	11	6.1	.8	.1	76	8
							Wanapum Basalt													
23/43-6G1	D-D'	379	7-19-82	125	196	7.4	11.8	30	6.7	8.1	.4	1.4	116	.0	5.0	1.1	.3	2.2	51	4
22/38-2D1D1	C-C'	359	7-21-82	300	315	7.7	12.9	37	11	14	.5	2.3	156	.0	11	6.1	.3	4.7	47	7
24/38-2D1	C-C'	396	7-20-82	85	430	7.2	9.7	38	12	26	1.0	2.9	177	.0	28	15	.2	7.6	38	20
25/35-3E1D1	A-A'	410	7-22-82	200	400	6.7	11.6	37	11	23	.9	3.8	150	.0	19	13	.2	12	48	6
15/35-2D1	D-D'	175	8- 7-82	342	301	8.1	15.1	17	13	25	1.1	7.1	177	.0	7.0	4.2	.4	.5	44	3
18/33-12C2	C-C'	259	8-11-82	500	325	8.0	17.7	21	10	27	1.3	9.1	148	.0	22	6.1	.5	3.2	47	3
20/32-15D2	B-B'	311	8-13-82	220	353	8.2	14.4	37	12	19	.7	3.8	153	.0	31	17	.4	.5	45	3
19/36-5B1	C-C'	293	8- 9-82	155	804	7.4	12.6	63	25	69	1.9	3.5	285	.0	70	49	.3	10	39	3
10/32-3R1	D-D'	74	7-19-83	540	728	7.9	19.1	46	25	61	1.8	9.4	139	.0	92	74	.4	11	58	10
14/30-10P1	C-C'	142	8-31-82	433	375	7.7	16.5	30	19	22	.8	4.8	190	.0	28	7.7	.4	1.2	53	3
17/29-24C1	B-B'	225	8-11-82	210	590	7.8	16.6	13	15	86	3.9	7.4	226	.0	67	22	.5	5.5	47	3
							Saddle Mountains Basalt													
14/29-5A1	B-B'	140	8-31-82	305	560	8.2	18.8	38	30	32	1.0	5.9	190	.0	76	32	.5	4.0	57	3
13/30-31N1	C-C'	117	9- 1-82	235	925	7.9	16.1	86	41	52	1.2	4.8	280	.0	150	49	.3	8.0	48	4
12/28-23H1D1	C-C'	105	8-30-82	413	395	8.2	18.5	15	3.7	62	3.9	9.6	193	.0	11	19	.8	.1	62	35
11/30-36M1	D-D'	87	5-17-83	237	830	7.8	16.3	60	57	25	.6	2.1	248	.0	120	55	.3	8.1	50	14
9/29-2G2	D-D'	55	5-18-83	473	445	7.9	22.1	5.2	2.4	90	8.4	12	262	.0	.2	26	1.5	.1	62	73
9/30-2R1	D-D'	57	8-27-82	211	575	8.0	17.6	47	24	31	.9	4.8	206	.0	76	26	.5	4.0	41	3

[a] Location, cross section, and index number shown on sheet 6.

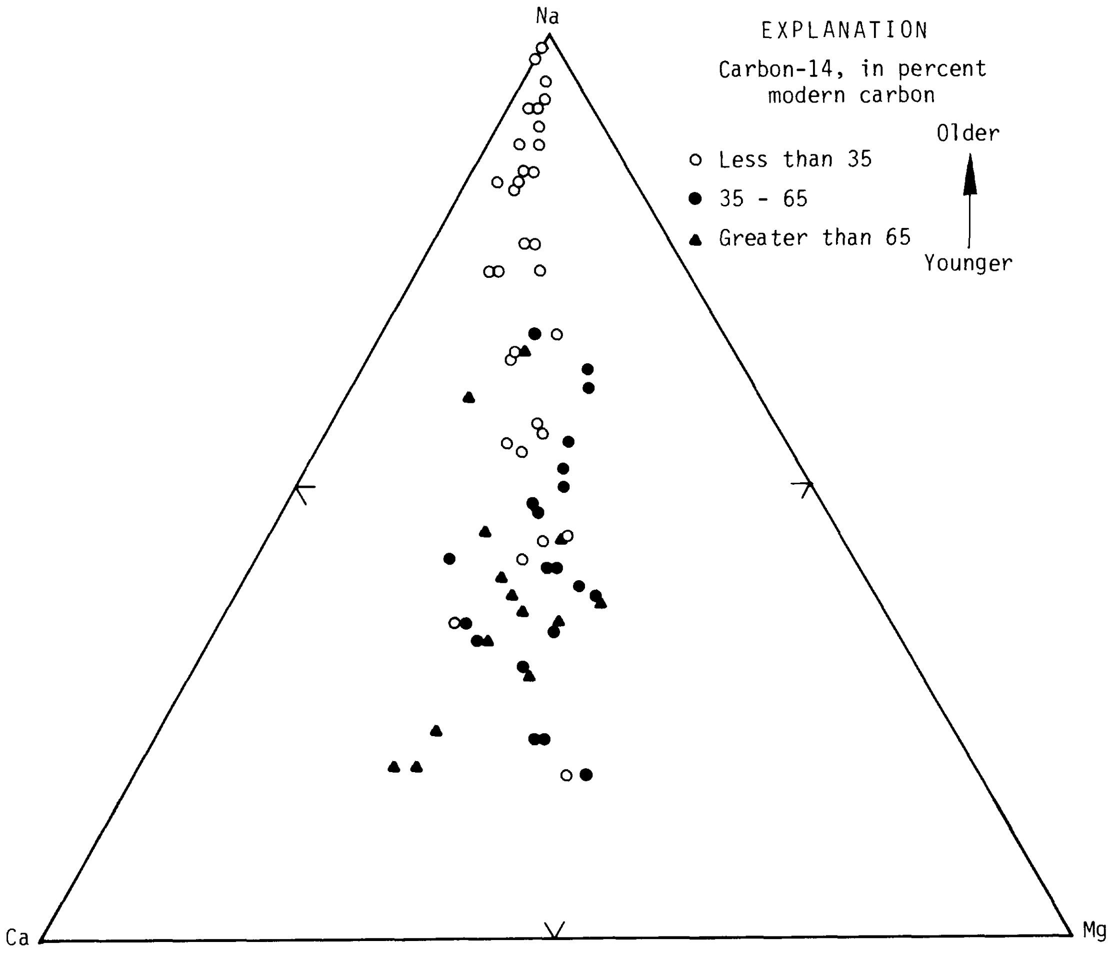

FIGURE 14.--Molar plot of dissolved sodium, calcium, and magnesium concentrations in ground water, grouped by carbon-14 values.

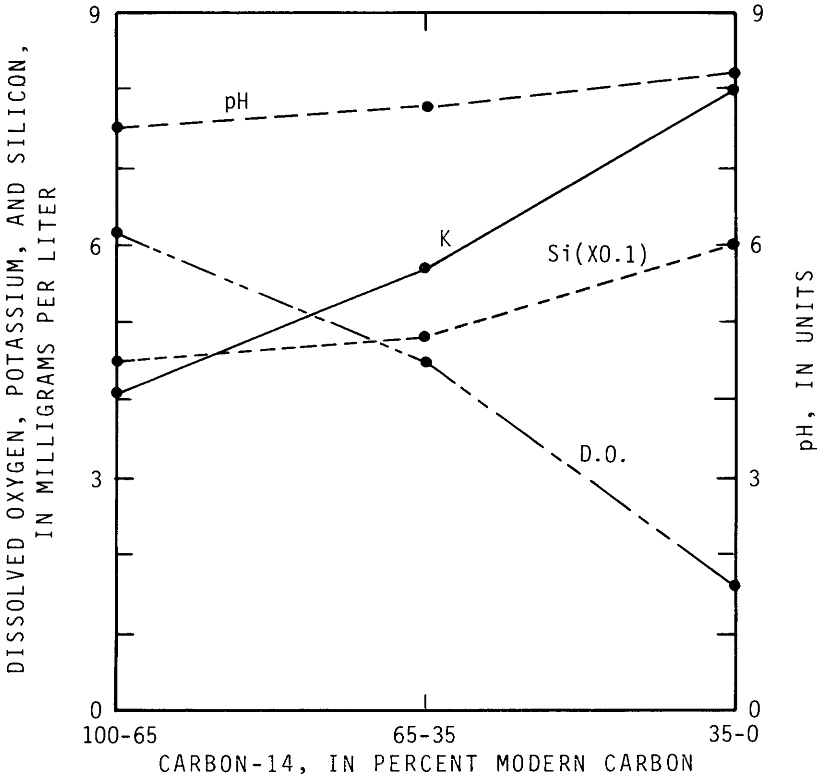

FIGURE 15.--Average concentrations of dissolved oxygen (D.O.), hydrogen ion, potassium (K), and silicon (Si) versus range of carbon-14. Average hydrogen ion concentration plotted as pH, in pH units. Silicon value plotted in 0.1 times actual concentration.

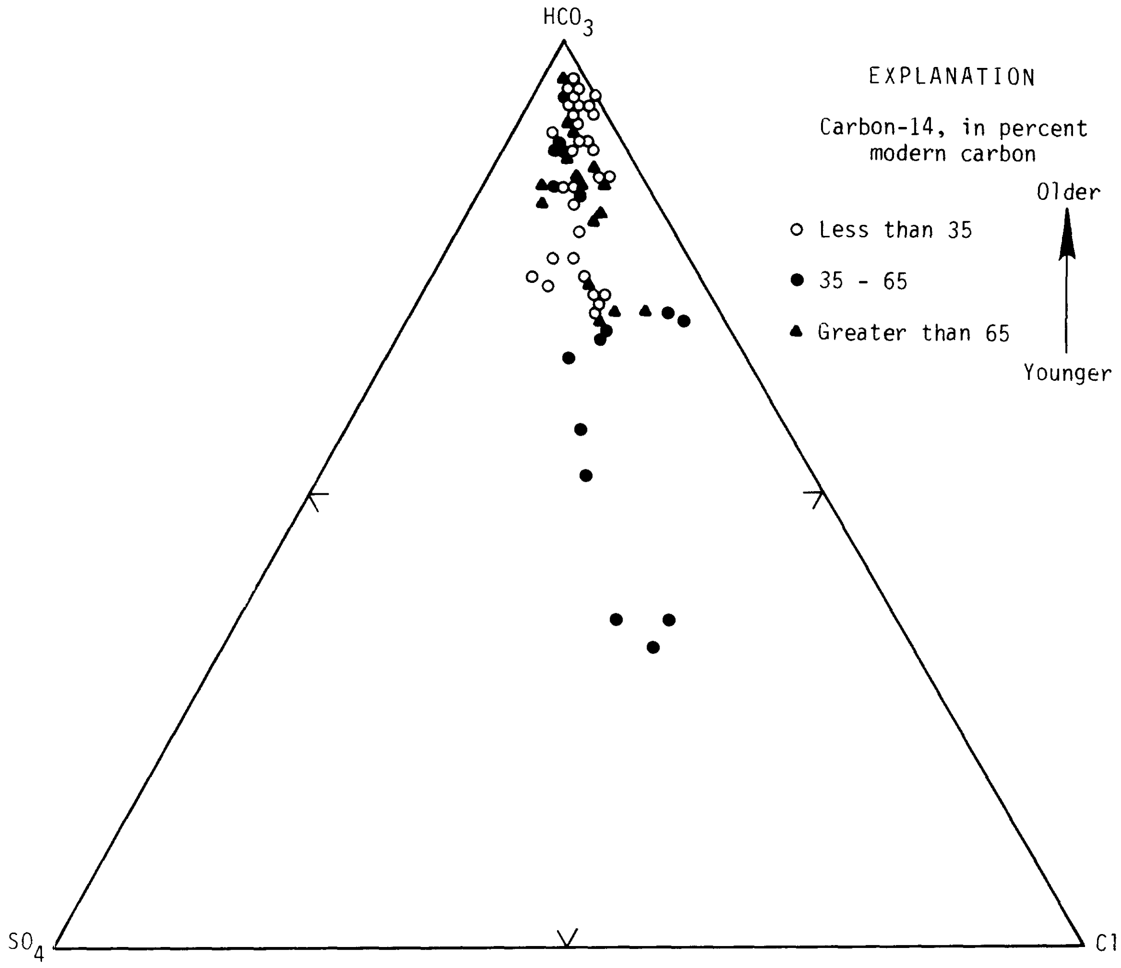

FIGURE 16.--Molar plot of dissolved bicarbonate, sulfate, and chloride concentrations in ground water, grouped by carbon-14 values.

Although many of the deep wells in the downgradient parts of the flow paths are completed in aquifers in both the Grande Ronde and Wanapum Basalts, the SAR's, sodium concentrations, and cation types are more typical of waters from the Grande Ronde. This formation is generally the source of most of the water produced by these composite wells.

Mineral-Water Equilibria

Efforts to determine whether the observed assemblage of alteration products is in equilibrium with present-day ground waters have been impeded in large part by a lack of thermochemical data. Free energy data for ideal and specific zeolites and montmorillonites have been published, but data for clinoptilolite and smectites similar in composition to those found in the Columbia River Basalt Group are not available. Deutsch and others (1982) used the speciation-solubility models WATEQ2 (Ball and others, 1979) and EQ3 (Wolery, 1979) to analyze ground-water quality data from basalts primarily within the Hanford Reservation. Although the clay mineral solubility data they used probably are not representative of the phases actually present in the basalts, their results are in reasonable agreement with observed alteration products. Most of the ground waters they considered were computed to be in equilibrium with calcite and an amorphous silica phase essentially equivalent to a silica glass. Samples for which aluminum data were available were computed to be generally undersaturated with halloysite, saturated to supersaturated with allophane, and supersaturated with other secondary clay minerals, as represented by montmorillonite. They suggested that the apparent supersaturation of ground waters at the low end of the observed pH range with amorphous and crystalline clays indicates that the formation of clay minerals lags behind the dissolution of primary phases. This is in accord with Pačes' (1978) hypothesis that silicon and aluminum concentrations in low-temperature natural waters are controlled by equilibrium with a metastable cryptocrystalline aluminosilicate of variable composition. They also suggested that an amorphous ferric hydroxide is the primary control on dissolved iron concentrations, rather than the prevalent secondary nontronitic smectite found.

The results of Deutsch and others (1982) suggest that dissolution of basalt and precipitation of secondary phases are continuing in the Columbia Plateau today. This conclusion is supported by this study, which shows an overall correspondence between changes in solute chemistry and sequences of secondary alteration. The progressive enrichment of sodium, silicon, and potassium in ground waters is consistent with the formation of a smectite depleted in sodium and potassium, relative to basaltic glass, followed by the precipitation of a sodium-potassium zeolite and silica. Although the chronology of secondary alteration has yet to be established, the available evidence suggests that the observed alteration products are the result of processes which are presently continuing.

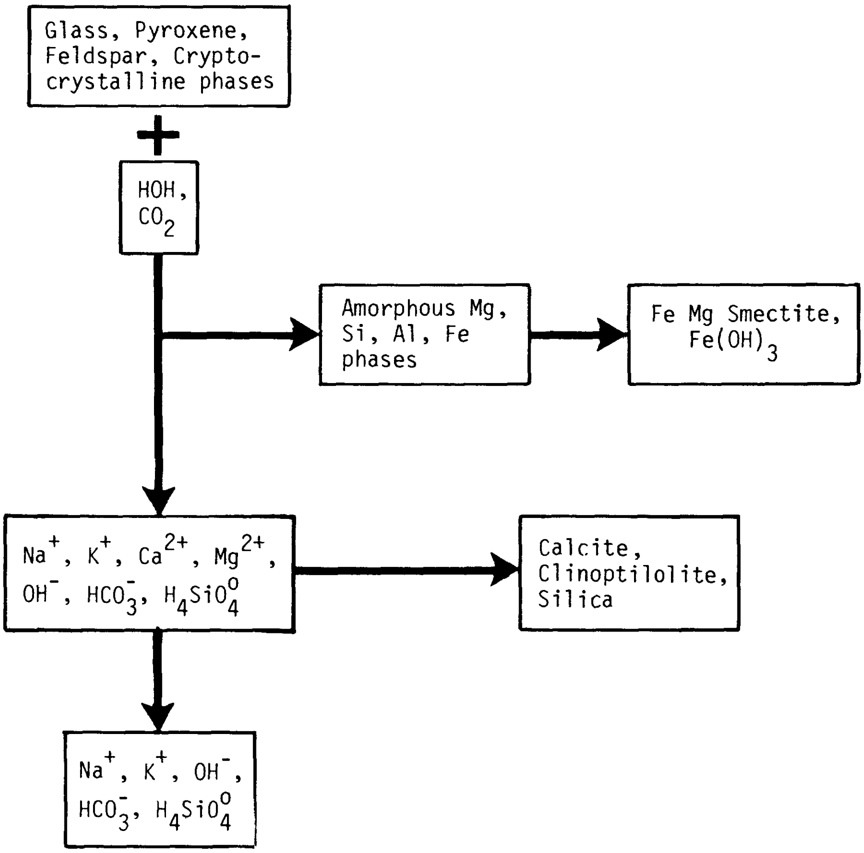

FIGURE 17.--Conceptual geochemical model of basalt alteration and sodium enrichment.

Geochemical Model of Sodium Enrichment

A conceptual model describing the chemical evolution of ground water in the Columbia Plateau was developed from the results of this study. The model derives largely from the work of Jones (1966) and is as follows. The dissolution of volcanic glass, cryptocrystalline matrix, and pyroxene proceeds by a combination of hydrolysis and attack by soil-derived carbonic acid (fig. 17). The initial solid products of this process are probably amorphous compounds of aluminum, iron, magnesium, and silicon. Smectite forms from these metastable phases as they age and become structurally more ordered. Dissolved oxygen is consumed by the oxidation of ferrous iron from glass and pyroxene. As the hydrolysis reaction proceeds, the release of hydroxyl ions causes the pH to rise. The pH increase facilitates calcite precipitation, removing calcium and additional magnesium and iron from solution and effectively buffering the ground-water pH. Because the rates of release of sodium, potassium, and silicon exceed their removal by precipitation, the concentrations of these species increase. The water eventually becomes supersaturated with clinoptilolite and silica, and these phases can precipitate. Additional sodium is perhaps added to solution by the replacement of exchangeable sodium on clays by calcium and magnesium. Upward flow of deeper chloride sulfate waters higher in sodium and silica should also be considered as a locally significant factor (White, 1983).

SUMMARY

The occurrence of relatively high sodium concentrations and SAR values in many deep and downgradient ground waters of the Columbia Plateau can be explained by ground water-basalt reactions. This conclusion is consistent with progressive changes in solute chemistry with increasing ground-water age and depth, and by the compositions and sequences of formation of secondary alteration products. Ground waters in general evolve from a calcium magnesium bicarbonate type in shallow and upgradient locations to a sodium potassium bicarbonate type in deeper and downgradient locations.

Dissolved sodium derives primarily from the dissolution of basaltic glass and cryptocrystalline matrix, and to a lesser extent from plagioclase feldspar. The dissolution of these phases occurs through a combination of silicate hydrolysis and attack by soil-derived carbonic acid. The release of hydroxyl by the hydrolysis reaction drives the pH higher; this increase is buffered to some extent by the precipitation of calcite. The precipitation of calcite and an iron-magnesium smectite lower calcium and magnesium concentrations, leaving a solution richer in sodium, silicon, and potassium. When these concentrations exceed the solubility limits of clinoptilolite and silica, these phases can begin to precipitate.

The mineralogy of the alteration assemblage suggests that alteration occurred at temperatures below 100°C. Although the role of lower epithermal reactions is less clear, the estimated cooling rates of the basalt flows indicate that such temperatures were in effect for only a brief period during the total history of these rocks. Although the temporal aspect of alteration is unknown, the agreement of the changes in ground-water chemistry and the secondary alteration sequence observed in this study with the results of a published thermochemical study (Deutsch and others, 1982) suggests that the observed alteration products were formed by low-temperature processes still active.

REFERENCES

Allen, C. C., and Strope, M. B., 1983, Microcharacterization of basalt--considerations for a nuclear waste repository: in R. Gooley, ed., Microbeam analysis: San Francisco Press, p. 51-53.

Allen, V. T., and Scheid, V. E., 1946, Nontronite in the Columbia River region: American Mineralogist, v. 31, p. 294-377.

Ames, L. L., 1980, Hanford basalt flow mineralogy: Battelle Institute Pacific Northwest Laboratory, report no. PNL-2847, 447 p.

Back, William, 1961, Techniques for mapping of hydrochemical facies, in Short papers in the geologic and hydrologic sciences: U.S. Geological Survey Professional Paper 424-D, p. D380-382.

Ball, J. W., Jenne, E. A., and Nordstrom, D. K., 1979, WATEQ2 - A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters: U.S. Geological Survey Water-Resources Investigations Report 78-116, 109 p.

Bauer, H. H., and Vaccaro, J. V., 1985, Ground-water levels in the Columbia River Basalt Group and overlying materials, Spring 1983, southeastern Washington State: U.S. Geological Survey Water-Resources Investigations Report 84-4360, 4 sheets (in press).

Benson, L. V., and Teague, L. S., 1982, Diagenesis of basalts from the Pasco Basin, Washington - I. Distribution and composition of secondary mineral phases: Journal of Sedimentary Petrology, v. 52, p. 595-673.

Bortleson, G. C., and Cox, S. E., 1985, Occurrence of dissolved sodium in ground waters of basalts underlying the Columbia Plateau, Washington: U.S. Geological Survey Water-Resources Investigations Report 85-4005, 6 sheets (in press).

Cline, D. R., 1984, Ground-water levels and pumpage in east-central Washington, including the Odessa-Lind area, 1967 to 1981: Washington State Department of Ecology Water-Supply Bulletin 55, 34 p.

Deer, W. A., Howie, R. A., and Zussman, J., 1967a, Rock forming minerals, v. 3 - Sheet silicates: London, Clowes and Sons, 270 p.

----1967b, Rock forming minerals, v. 4 - Framework silicates: London, Clowes and Sons, 435 p.

Deutsch, W. J., Jenne, E. A., and Krupka, K. M., 1982, Solubility equilibria in basalt aquifers: The Columbia Plateau, Eastern Washington, USA: Chemical Geology, v. 36, p. 15-34.

Drost, B. W., and Whiteman, K. J., 1985, Surficial geology, structure, and thickness of selected geohydrologic units in the Columbia Plateau, Washington: U.S. Geological Survey Water-Resources Investigations Report 84-4326, 10 sheets (in press).

Grim, R. E., 1968, Clay mineralogy, New York, McGraw, 596 p.

Hooper, P. R., 1982, The Columbia River Basalts: Science, v. 215, p. 1463-1468.

Jones, B. F., 1966, Geochemical evolution of closed basin water in the western Great Basin, *in* J. L. Rau, ed., Second Symposium on Salt: Northern Ohio Geological Society, v. 1, p. 181-200.

Long, P. E., and Strope, M. B., 1983, Composition of augite and pigeonite in basalt flows that are candidates for a nuclear waste repository: *in* R. Gooley, ed., Microbeam Analysis: San Francisco Press, p. 57-60.

Pačes, Tomáš, 1978, Reversible control of aqueous aluminum and silica during the irreversible evolution of natural waters: Geochimica et Cosmochimica Acta, v. 42, p. 1487-1493.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., 1979, Methods for determination of inorganic substances in water and fluvial sediments: chapter A1, Book 5, Techniques of Water-Resources Investigations of the United States Geological Survey, 626 p.

Summers, K. V., 1976, The clay component of the Columbia River palagonites: American Mineralaogist, v. 61, p. 492-494.

Swanson, D. A., 1967, Yakima Basalt of the Tieton River area, south-central Washington: Bulletin of the Geological Society of America, v. 78, p. 1077-1110.

Swanson, D. A., and Wright, T. L., 1978, Bedrock geology of the northern Columbia Plateau and adjacent areas: *in* V. R. Baker and D. Nummedal, eds., The channeled scabland - A guide to the geomorphology of the Columbia Basin, Washington: National Aeronautics and Space Administration, 186 p.

Tanaka, H. H., Hansen, A. J., Jr., and Skrivan, J. A., 1974, Digital model study of ground-water hydrology, Columbia River Basin Irrigation Project area, Washington: Washington State Department of Ecology Water-Supply Bulletin 40, 60 p.

Tomkeieff, S. I., 1940, The basalt lavas of the Giant's Causeway district of northern Ireland: Bulletin Volcanologique, v. 6, p. 90-143.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkaline soils: U.S. Department of Agriculture Handbook 60, 160 p.

Walker, G. P. L., 1960, Zeolite zones and dike distribution in relation to the structure of the basalts of eastern Iceland: Journal of Geology, v. 68, p. 515-528.

Walton, A. W., 1975, Zeolite diagenesis in Oligocene volcanic sediments, Trans-Pecos, Texas: Bulletin of the Geological Society of America , v. 96, p. 615-624.

White, A. F., Claassen, H. C., and Benson, L. V., 1980, The effect of dissolution of volcanic glass on the water chemistry in a tuffaceous aquifer, Rainier Mesa, Nevada: U.S. Geological Survey Water-Supply Paper 1535-Q, p, Q1-Q34.

White, D. E., 1983, Background paper for assessment of basalt lava flows (BWIP), Washington: Richland, Washington, Rockwell Hanford Operations, 29 p.

Wise, W. S., and Tschernich, R. W., 1975, Cowelsite, A new Ca-zeolite: American Mineralogist, v. 60, p. 951-956.

Wolery, T. J., 1979, Calculation of chemical equilibrium between aqueous solution and minerals: The EQ3/6 Software Package. Lawrence Livermore Lab., Livermore, California, report no. UCRL-52558.