Water Information Bulletin No. 30

Geothermal Investigation in Idaho

Part 14

Geochemical and Isotopic Investigations of Thermal Water Occurrences of the Boise Front Area, Ada County, Idaho

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Boise, Idaho 83720

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Thermal Water Occurrences of the
Boise Front Area, Ada County, Idaho

by

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I. INTRODUCTION

Purpose and Scope

The purpose of this report is to further examine and evaluate the geothermal potential of the Boise area. To accomplish this, a limited chemical and isotopic investigation was undertaken and pertinent geological, geophysical, and hydrogeological data in the published and unpublished literature were reviewed. It is anticipated that information contained in the report may be used to help formulate regulatory strategies for the development of the region's geothermal potential.

Well- and Spring-Numbering System

The numbering system used by the Idaho Department of Water Resources (IDWR) and the U.S. Geological Survey (USGS) in Idaho indicates the location of wells or springs within the official rectangular subdivision of the public lands, with reference to the Boise base line and meridian. The first two segments of the number designate the township and range. The third segment gives the section number, followed by three letters and a numeral which indicate the quarter section, the 40-acre tract, the 10-acre tract, and the serial number of the well within the tract, respectively. Quarter sections are lettered a, b, c, and d in counter-clockwise order from the northeast quarter of each section (Figure 1). Within the quarter sections, 40-acre and 10-acre tracts are lettered in the same manner. Well 3N-2E-10aad1 is in the SE1/4 of the NE1/4 of the SE1/4 of Section 10, T3N, R12E, and was the first well inventoried in that tract. Springs are designated by the letter "S" following the last numeral, for example 3N-2E-12cdd1S.

Use Of Metric Units

The metric or International System (SI) of units is used in this report to present water chemistry and most other data. Concentrations of chemical substances dissolved in the water are given in milliequivalents per liter (meq/l) and in milligrams per liter (mg/l), rather than in parts per million (ppm) as in some previous Water Information Bulletins. Numerical values for chemical concentrations are essentially equal, whether reported in mg/l or ppm, for the range of values in this report. Milli-equivalents per liter is a measure of the equivalent charge of an ion available in solution. Data may be converted from mg/l to meq/l by the expression
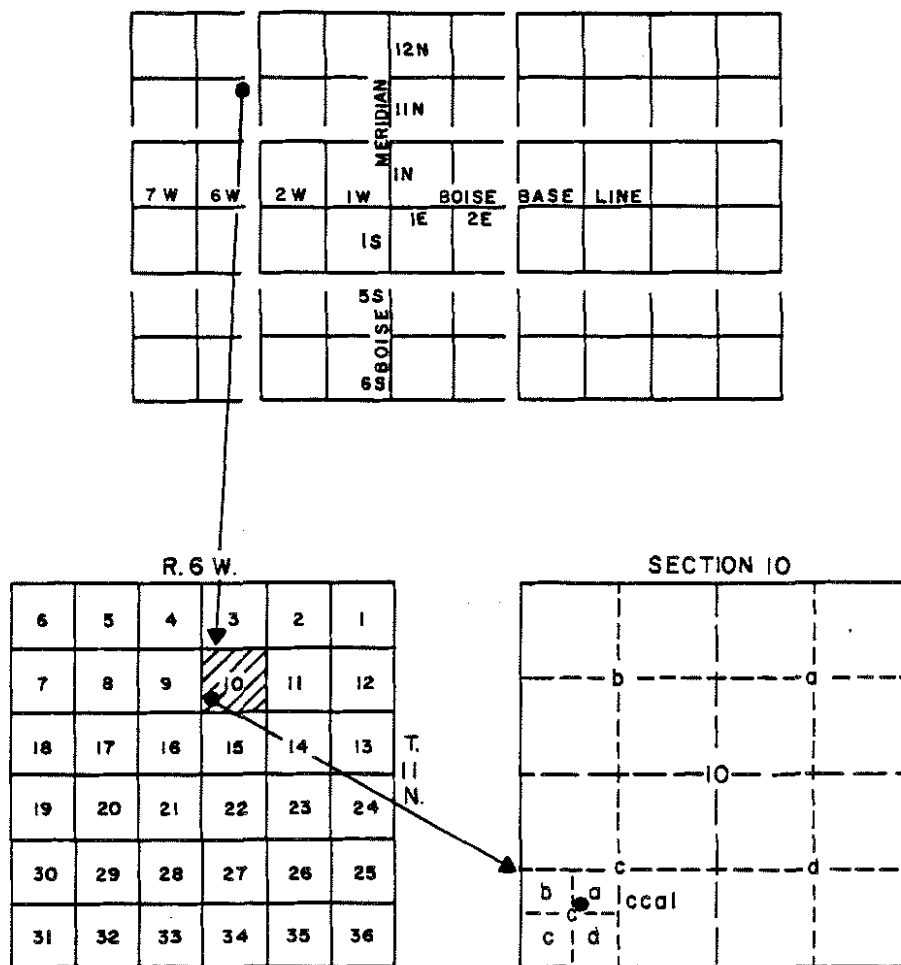
$$(meq/l) = (mg/l) \ (v/FW)$$

FIGURE 1. Diagram showing the well-and spring-numbering system.
(Using well 11N-6W-10 ccal.)

where v is the valence of the ion and FW is its gram formula weight. Water temperatures are given in degrees Celsius (^{O}C). Figure 2 shows the relation between degrees Celsius and degrees Fahrenheit.

Linear measurements (inches, feet, yards, miles) are given in their corresponding metric units (millimeters, meters, kilometers), as are weight and volume measurements.

Previous Work

Many significant earlier studies of the Boise Front and adjacent areas are regional reconnaissance investigations dealing primarily with defining and correlating rock units. Lindgren (1898) published a geologic description of the Boise quadrangle. Russell (1903) described the artesian basins in southeastern Oregon and southwestern Idaho. Lindgren and Drake (1904) published a description of the geology of the Nampa area. Kirkham (1931a) revised the Payette and Idaho formations and treated the Boise area. Kirkham (1931b) also wrote on the Snake River downwarp and published information on the igneous rocks of southwestern Idaho (Kirkham, 1931c). In 1957, Nace and others published information on studies in the Mountain Home Plateau area. The geology and mineral resources of Canyon and Ada Counties were described by Savage (1958). Malde (1959) described the fault zone along the northern margin of the western Snake River Plain. Mundorff and others (1964) studied ground water for irrigation in the Snake River Plain. A M.S. thesis by Mohammed (1970) described hydrologic conditions of the Boise Ridge area. Ross (1971) included information on thermal waters in the Boise area in her report on the geothermal potential of Idaho, as did Young and Mitchell (1973). The U.S. Geological Survey (1971) open filed an aeromagnetic map of southwestern Idaho, and Mabey and others (1974) published a preliminary gravity map of southern Idaho which included the Boise area. Mabey (1976) published interpretations of gravity and magnetic patterns from the maps. Brott and others (1976) reported on heat flow studies in the western Snake River Plain. Mink and Graham (1977) studied the geothermal potential of the west Boise area. Kimmel (1979) investigated the stratigraphy and paleoenvironment of the Chalk Hills and Glenns Ferry formations in the western Snake River Plain. Nelson and others (1980) reported on their geothermal resource exploration efforts in the Boise area. Burnham (1979) reported on ground-water investigations south of Boise for the Ada County Planning Association, and published results of well testing on the Boise Capitol Mall wells (Kelly 1981). A comprehensive report on geological, hydrological, geochemical, and geophysical investigations of the Nampa-Caldwell and adjacent areas, southwestern Idaho (Mitchell, 1981) includes valuable information on the Boise Front area. Wood and others (1982) included much new geologic information and also parts of older reports in a field trip guide to the Boise Foothills.
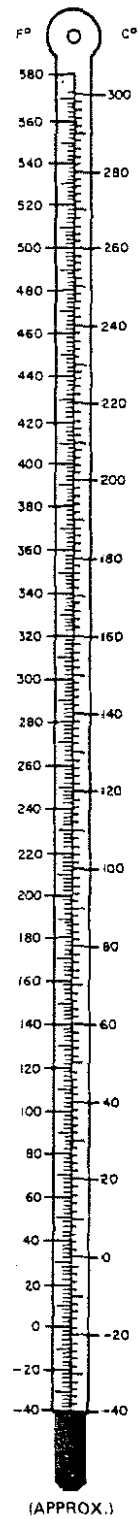
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FIGURE 2. Temperature conversion graph

II. HYDROGEOLOGIC SETTING

Geology

The Boise area is situated along the boundary of the western Snake River Plain and the foothills of the highlands of the Idaho Batholith (Figure 3). The northwest-trending Frontal Fault System forms the boundary between these two provinces. Thermal springs and wells are concentrated near the fault system and the warmest waters are found in the Boise area.

The western Snake River Plain is a relatively featureless major northwest-trending structural basin about 65 km wide and 250 km long. The basin was formed by downwarping and faulting in late Cenozoic time. Details of the subsurface geology of the basin have not been worked out; however, the general subsurface conditions are known (Mabey, 1976; Armstrong and others, 1975). Mabey (1976) suggests the basin may contain as much as 7 km of basin fill volcanic flows, tuffs, sands, clays, and silts. The J.N. James No. 1 exploratory well, located in the basin near Meridian, 20 km east of Boise, encountered 4.3 km of Pleistocene to Miocene volcanics and sediments and did not penetrate to basement rocks (Wood and Anderson, 1981). It is thought that the granitic and metamorphic rocks of the Idaho Batholith are the basement beneath the basin because these rocks form the mountains both north and south of the Plain.

The southern margin of the western Snake River Plain has been described as a zone of rifting near the present course of the Snake River. Warner (1975) first postulated the existence of a left-lateral, strike-slip fault with some 80 km of relative displacement of the northern and southern blocks. Wood and others (1982) thought the fault had a major, down to the north, normal component of slip. In reality, both strike- and dip-slip displacement could have occurred along this rift system. South of the rift system Miocene-age Columbia River Basalts, Tertiary silicic volcanic rocks, and Cretaceous granitic rocks crop out in the Owyhee Mountains.

The northern margin of the western Snake River Plain was described by Malde (1959) as having at least 2700 m of aggregate throw along a zone of northwest-trending, high-angle faults that displaced the Plain downward relative to the highlands on the north. The work of Wood and others (1982) shows that, in general, the Frontal Fault System consists of several stepwise dislocations of down to the southwest movement. Horst and graben structures have been identified within the Plain proper (Wood and Anderson, 1981).

Deep seated faults of the Frontal Fault System have been mapped for distances of about 20 km to the northwest and 65 km
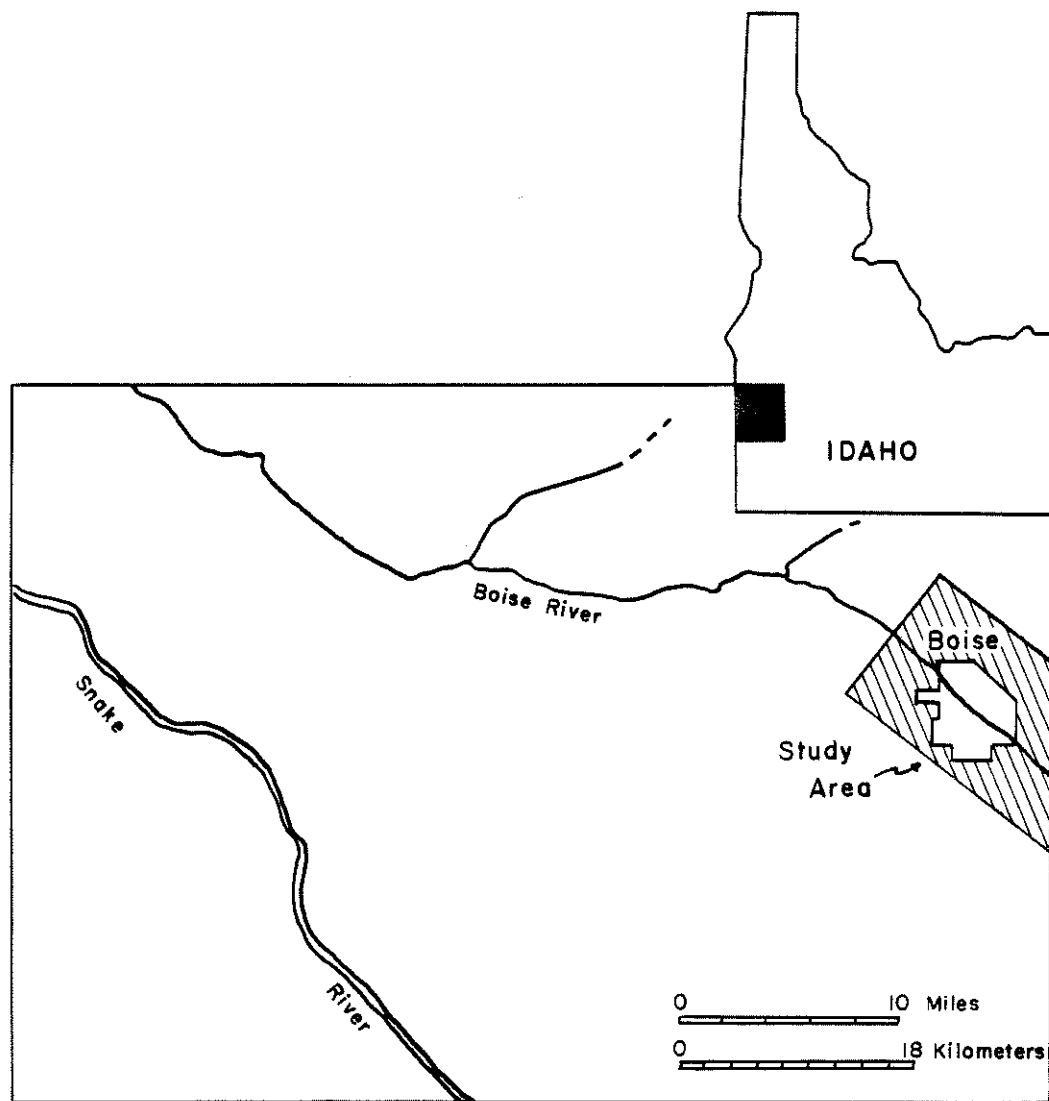
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FIGURE 3. Index map showing study area

to the southeast of Boise (Bond, 1978). Width of the fault system is uncertain. A structural profile based on a seismic reflection profile suggests it may be as much as 8 to 10 km wide in the Boise area. Surfical mapping and correlation of lithologic and geophysical borehole logs have extended the width of the zone at least 1.5 km into the Boise Foothills (Wood and others, 1982; Burnham, 1981; Wood and Vincent, 1980).

Recent alluvial deposits obscure possible fault traces in the Boise Valley southwest of the Boise Foothills. Faults in the system commonly have normal displacements. Depth to basement rock in the fault zone increases in a stepwise fashion, becoming progressively deeper southwestward toward the Snake River Plain. Although the Frontal Fault System appears to be quite wide, fault spacing appears to be closer in a zone of intense faulting along the base of the Boise Foothills. The zone is commonly referred to as the Foothills fault, and is the focus of highest ground water temperatures.

The stratigraphy in the vicinity of the Frontal Fault System in the Boise area is under reorganization. Most of the previously published and unpublished geologic literature concerning the area recognized the Glenns Ferry Formation of the Idaho Group as the fluvial and lacustrine sedimentary sequence of clay and silt with interbeds of sand and clayey to gravely sand which are encountered in the upper 200 meters in boreholes in the Boise Valley and which crop out in the Boise Foothills (Dion, 1972; Hollenbaugh, 1973; Mink and Graham, 1977; Nelson and others, 1980; Savage, 1958). Malde and Powers (1962) redefined and described the Idaho Group as seven overlapping formations. In descending order, the formations are:

> Black Mesa Gravel
> Bruneau Formation
> Tuana Gravel
> Glenns Ferry Formation
> Chalk Hills Formation
> Banbury Basalt
> Poison Creek Formation

In the Nampa-Caldwell area west of Boise, Wood and Anderson (1981) defined the Glenns Ferry and younger formations as the upper Idaho Group, and the Chalk Hills and older formations as the lower Idaho Group. A seismic reflection profile between the Boise Foothills and the Caldwell area suggests the Glenns Ferry and Chalk Hills Formations dip away from the Boise Foothills, beneath the Snake River Plain, at 7° to 10°. The profile identifies the approximate boundary between the upper and lower Idaho Groups as reflecting horizon "I." The profile suggests horizon "I" surfaces 8 to 15 km southwest of the Boise Foothills. Seismic reflection data for the upper 300 meters were not available for construction of the upper portion of the profile. However, the

profile does indicate the strata below 300 meters near the foot-hills also dip away from the foothills, thus suggesting the Glenns Ferry Formation is not present in the area.

Occurrence of the Glenns Ferry Formation in the Boise area remains unresolved. Wood and Anderson (1981) suggest the wide-spread "blue clay" and overlying coarse sandy facies encountered in many wells in the upper 180 meters in the Boise Valley may be part of the Glenns Ferry Formation. Wood and others (1982) label the upper 150 meters of a section exposed in the Dry Creek area of the Boise Foothills as possible Glenns Ferry Formation. The Glenns Ferry-Chalk Hills issue cannot be resolved as part of this investigation. However, based on the seismic data, most strata assigned to the Glenns Ferry Formation by previous investigators are considered to be Chalk Hills Formation in this report. A generalized stratigraphic column of the Frontal Fault Zone in the Boise area is shown in Figure 4. Additional detailed surface and subsurface geologic investigations need to be undertaken before final resolution of the stratigraphy can be achieved.

In the Boise Foothills, the sedimentary and volcanic section thins northeastward, exposing basement rocks of the Idaho Batholith at higher elevations. Lithologic descriptions and borehole correlations by Burnham (1981), Wood and others (1982), Wood and Vincent (1980), and others suggest that most of the stratigraphic section underlies the Boise Foothills. Formation names have not been applied to most of the lithologic mapping units, although Wood and Anderson (1981) suggest about 200 meters of Chalk Hills Formation rest on an irregular erosional surface of silicic volcanics of the Idaho Group or upon weathered, eroded flows and tuffs of the Banbury Basalt in the Boise Foothills.

Lithologies that appear to be the Chalk Hills Formation, Banbury Basalt, and Idavada Volcanic Group have been encountered in numerous wells and boreholes in the Boise Valley near the Boise Foothills. The widespread "blue clay" layer encountered in the upper portion of most boreholes and wells may belong to the Glenns Ferry or the Chalk Hills formations. An oolitic limestone has been described near the base of the Glenns Ferry Formation at numerous localities and may define the Base of the Formation (Kimmel, 1979). Oolitic limestones have been mapped in the Boise Foothills (Wood and others, 1982), but they have not been reported in borehole data taken near the "blue clay" layer in the Boise Valley. The absence of oolitic limestone may be evidence that the "blue clay" is part of the Chalk Hills Formation, or oolitic limestone may not be a basal layer of the Glenns Ferry Formation in the area, or it simply may have been overlooked by those lithologically logging wells and boreholes. The deepest wells in the area, Capitol Mall No. 1 and Capitol Mall No. 2, have penetrated depths of 656 and 924 meters below land surface, respectively. Both wells were terminated in silicic volcanics of the Idavada Volcanic Group (Anderson, 1981; and Kelly, 1981).

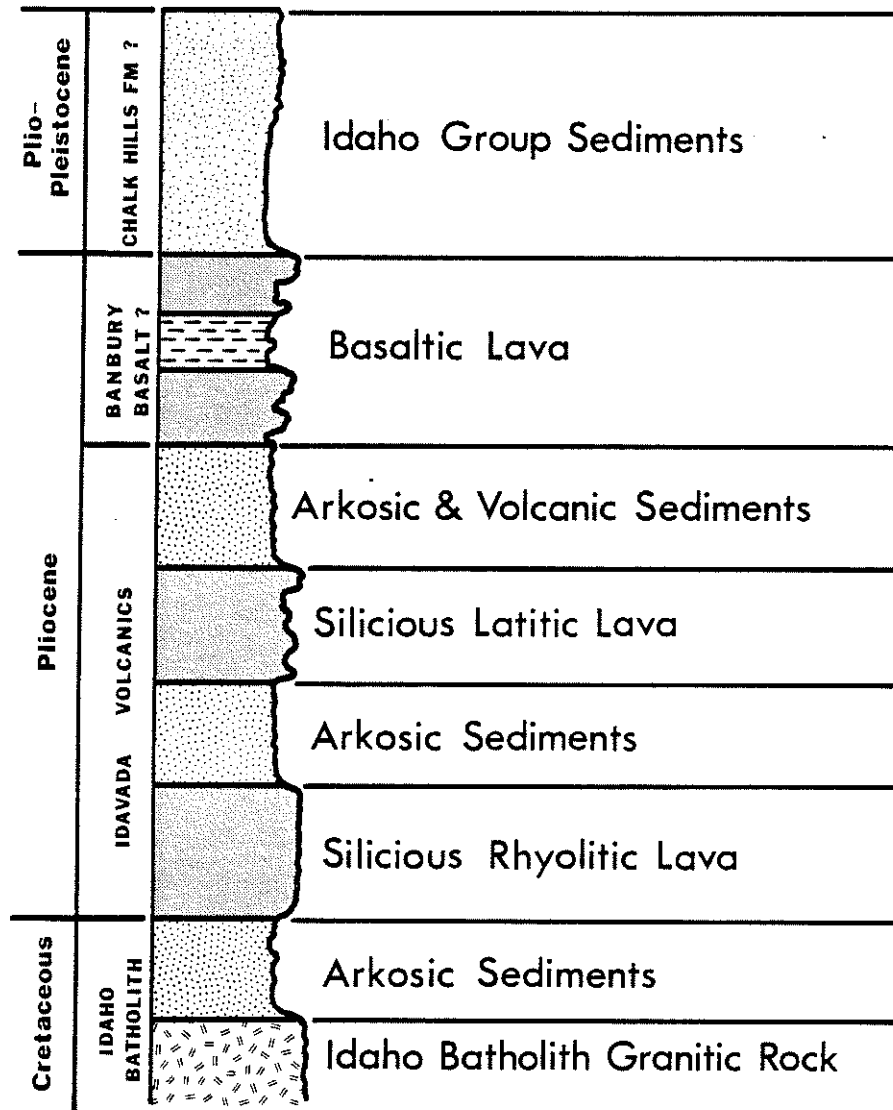|		
Plio-Pleistocene	CHALK HILLS FM ?	Idaho Group Sediments
Pliocene	BANBURY BASALT ?	Basaltic Lava
	IDAVADA VOLCANICS	Arkosic & Volcanic Sediments
		Silicious Latitic Lava
		Arkosic Sediments
		Silicious Rhyolitic Lava
Cretaceous	IDAHO BATHOLITH	Arkosic Sediments
		Idaho Batholith Granitic Rock

FIGURE 4. Generalized stratigraphic column for the Foothills Fault Zone

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Strata between the bottom of these wells and the crystalline basement rocks is unknown; it probably includes an interval of older volcanic and sedimentary rocks.

Hydrogeology

Two ground-water regimes have been identified in the Boise area. Shallow water table or unconfined aquifers generally occur in the older terrace gravel, basalt, younger terrace gravel of the Snake River Group and Recent alluvium in the Boise Valley (Burnham, 1979; Dion, 1972; and Ralston and Chapman, 1969), and in the upper portion of the Chalk Hills Formation in the Boise Foothills (Mink and Graham, 1977; and Mohammed, 1970). A deeper ground-water regime of confined (artesian aquifers) occurs in the lowermost Chalk Hills and older formations. Water temperatures in the artesian aquifers are commonly thermal, whereas temperatures in the unconfined aquifers are not.

In the Boise Valley, the shallow aquifers generally occur within 30 to 50 meters of the land surface. Water level in these aquifers responds to seasonal recharge, including leakage from canals (Burnham, 1979; and Dion, 1972) and from irrigation infiltration (Burnham, 1979). The shallow aquifers are an important water supply source for many individual wells in the area. A thick sequence of interbedded clay, silt, and sand in the upper portion of the Chalk Hills Formation (?) known as the "blue clay" appears to separate hydraulically the shallow aquifers from the deeper confined aquifers.

Water table contours of the shallow aquifers in the Boise Ridge and Dry Creek areas are roughly coincident with the topography, and depth to the water surface exhibits seasonal and meterologic variations (Mohammed, 1970). In the foothills, the shallow ground-water system appears to occur in the upper portion of the Chalk Hills Formation and is hydraulically connected with the unconfined ground-water system in alluvial deposits in the Dry Creek area. The relationship between the shallow systems and the "blue clay" zone is unknown in the Boise Foothills. However, a confined system of aquifers is found below the shallow aquifers.

Considerable geologic and hydrogeologic data have been collected from lithologic and borehole geophysical well logs and by detailed geologic mapping in the State Capitol - Old Military Reservation - State Penitentiary area--referred to in this report as the State Capitol area (Anderson, 1981; Burnham, 1980; Kelly, 1981; Nelson and others, 1980; Wood and Vincent, 1980; Wood and others, 1982). Burnham (1982) constructed a generalized lithologic column for the area and a northeast-southwest geophysical correlation section between several wells in the area. The column and section are thought to be representative of the principal lithologic units and are of major significance because

they may depict hydrostratigraphic units of the deeper aquifer. A hydrostratigraphic unit is a body of rock having considerable lateral extent and composes a geologic framework for a reasonably distinct hydrologic system. In other words, hydrostratigraphic units are aquifers, aquitards, etc.

A geologic structure section depicting the possible hydro-stratigraphic units in the State Capitol area is shown in Figure 5. The section is based largely on Burnham's (1982) stratigraphic column and correlation section. Interbed and volcanic hydrostratigraphic units have tentatively been assigned to the section. However, these assignments are made with limited knowledge of the water-bearing properties of the lithologic units on which they are based. The major deep thermal aquifers appear to be contained primarily in the Idavada Volcanics. Wood and others (1982) report Interbed (1) and Siliceous Volcanics (1) to be the principal aquifers supplying thermal water to the Boise Geothermal Ltd. wells. These intervals also appear to be the major production zones in the Capitol Mall wells, although the production zones in Capitol Mall No. 2 are difficult to isolate because the well is open over the lower 525 meters, which includes the lowermost Banbury Basalt and Interbeds (1) and (2) and Siliceous Volcanics (1) and (2) of the Idavada Volcanics. Capitol Mall No. 1 is open to the Idavada Volcanics intervals Siliceous Volcanics (1) and the uppermost Interbed (2).

Extensive hydrothermal alteration has been noted in the lower part of the Banbury Basalt and in the Idavada Volcanics from cuttings taken from thermal wells in many locations. Zeolites have also been noted in cuttings from the Foothills Fault Zone, but have not been noted at other locations.
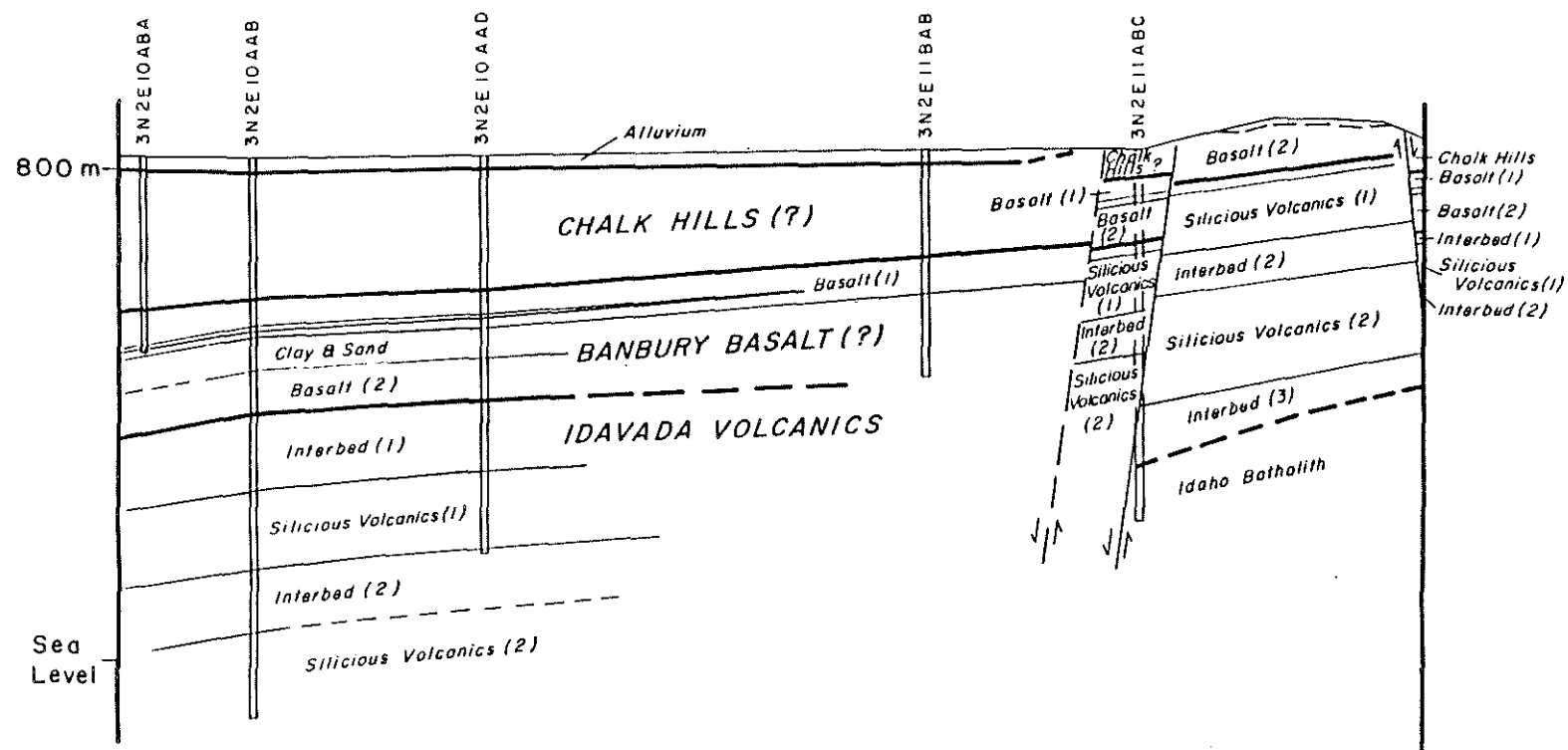
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FIGURE 5. Geologic section showing possible hydrostratigraphic units

III. DATA COLLECTION

Sampling Strategy and Well Descriptions

Water quality samples were collected from ten wells to determine representative physical, chemical, and isotopic characteristics of the hydrogeologic regimes of the Frontal Fault Zone in the Boise area. Samples were collected for analysis for major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, HCO_3 and SO_4^{2-}), minor solutes (F^-, PO_4^{3-} and SiO_2), stable isotopic ratios ($^2H/^1H$, $^{13}C/^{12}C$ and $^{18}O/^{16}O$), and radioisotope contents (^3H and ^{14}C). Major ion analyses for an additional six wells were obtained from Mitchell and others (1980). See Figure 6 for sampling locations. The complex rock-water interactions and ground-water flow patterns that occur in ground-water flow systems may often be better understood by an analysis of these geochemical characteristics. Rock-water interactions often change the chemical composition of the ground water as it moves along the flow path from recharge to discharge areas. Such changes are indicative of changes in the lithology and thermal regime of the flow path. Analyses of the concentration of major and minor ions may lead to an understanding of the lithologic characteristics of the aquifers and to an understanding of ground-water mixing patterns. Evaluation of stable and radioactive environmental isotopes may provide insight into the flow pattern of an aquifer by providing information on the thermal history, mixing patterns, and the mean subsurface residence time of the ground water sampled. Specific sampling methods employed in this investigation are described in the following section.

A strategy was developed to collect representative samples from:

1) the shallow (unconfined) and deeper (artesian) aquifer systems;

2) the several apparently thermal regimes in the deeper aquifers; and

3) the Boise Foothills, the zone of intense faulting near the base of the foothills and the Boise Valley near the foothills.

Selected physical data from the wells sampled are listed in Table 1.

Samples were collected from wells drawing water from the shallow aquifers in two locations: one site in the Boise Foothills (4N 2E 22BCD2) and one site in the Boise Valley 4N 2E 29ACD1). These wells were selected because they are associated with wells thought to draw water from the deeper
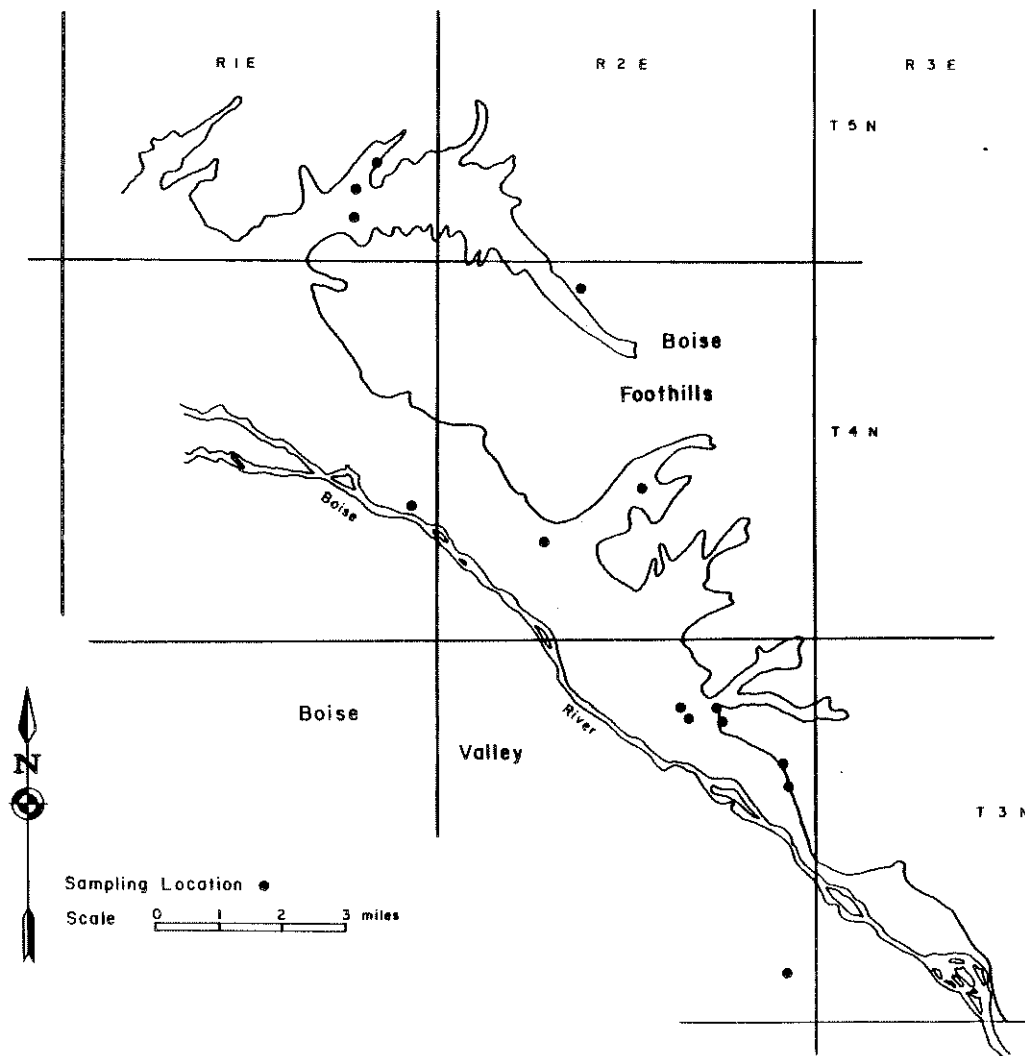
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R 1 E   R 2 E   R 3 E

T 5 N

Boise

Foothills

T 4 N

Boise

Boise

Valley

River

N

T 3 N

Sampling Location ●

Scale   0   1   2   3 miles

FIGURE 6. Sample locations

TABLE 1. PHYSICAL DATA OF WELLS SAMPLED

Well Number	Aquifer Sampled	Date Sampled	Discharge Temperature (°C)	Depth to Water (m)	Well Depth (m)	Well Head Elevation (m)
5N 1E 35ACA1	Deep; Boise Foothills– Dry Creek Valley	13 Aug. '81	40.0	Flowing	121	829
4N 1E 24DCC1	Deep; Boise Valley	13 Aug. '81	27.2	Flowing	310	794
4N 2E 22BCD1	Deep; Boise Foothills	18 Aug. '81	42.5			902
4N 2E 22BCD2	Shallow; Boise Foothills	18 Aug. '81	28.0	Flowing	150	902
4N 2E 29ACD1	Shallow; Intense Fault Zone	03 Dec. '81	15.5	Flowing		815
4N 2E 29ACD2	Deep; Intense Fault Zone	03 Dec. '81	47.2	Flowing	364	815
3N 2E 11BAA1	Deep; Intense Fault Zone	12 Aug. '81	74.0	Flowing	270	847
3N 2E 12CDD1	Deep; Intense Fault Zone	10 Aug. '81	79.5	Flowing	121	841
3N 2E 10AAD1	Deep; Boise Valley	19 Oct. '81	65.0	Flowing	655	847
3N 2E 10AAB1	Deep; Boise Valley	21 Sep. '81	70.5	Flowing	924	846

underlying aquifers. It was anticipated that sampling the deeper wells would allow direct comparison of the chemical and isotopic characteristics of the shallow and deep aquifers. Well 4N 2E 22BCD1 has a discharge temperature of 28° C which may be the result of leakage from the deeper aquifer as the well is doubly constructed. Well logs are not available for these wells.

Two wells thought to draw water from the deeper aquifer system in the Boise Foothills were sampled. One well (4N 2E 22BCD2) is doubly constructed with the shallow well (4N 2E 22BCD1) in Stewart Gulch. A drilling log is not available for the deep well, but a log from another well (4N 2E 28ABB1) located about 1.5 km downstream suggests a clay horizon may partially or com- pletely hydraulically separate the shallow and deep aquifer systems. Lithologic descriptions on the well log are interpreted to be the Chalk Hills Formation (?), Banbury Basalt(?), and the Idavada Volcanics. Water was first encountered in a sandy zone 90 to 102 meters below land surface thought to be part of the Chalk Hills Formation. Water was also encountered in volcanic and sedimentary interbeds 122 to 220 meters below land surface thought to be the Banbury Basalt and Idavada Volcanics. A multi-colored zone of clays and mudstones, which may be the "blue clay" horizon, separated the two water bearing zones. A double casing arrangement in the borehole appears to have partially or totally hydraulically isolated the two water-bearing horizons in the well. At the time of well completion in 1978, the water level rose to within 13 meters of the land surface from the deeper aquifer and to within 69 meters of the land surface from the shallow aquifer. Water temperatures of the two aquifers were not recorded on the well log.

Limited information is available on the second deep aquifer well sampled in the Boise Foothills. The well (5N 1E 35ACA1) is located in Dry Creek and reportedly is 121 meters deep. It is thought to draw water from the deep aquifer system because it has a discharge temperature of 40° C and it free flows about 100 l/min.

Four of the approximately twenty geothermal wells and test holes in the State Capitol area were sampled. This area is of particular interest because it has the highest known ground- water temperatures along the Frontal Fault Zone. Wells commonly discharge water in the 70 to 80° C temperature range. Two of the wells sampled, Warm Springs Water District (3N 2E 12CDD1) and Boise Geothermal Ltd. No. 2 (3N 2E 11BAA1), are located at the base of the Boise Foothills in the Foothills Fault zone. The other two wells, Capitol Mall No. 1 (3N 2E 10AAD1) and Capitol Mall No. 2 (3N 2E 10ABB1), are located in the Boise Valley, 600 to 900 meters from the base of the Boise Foothills.

Boise Geothermal Ltd. No. 2 is one of a cluster of four wells drilled along the Foothills Fault Zone. In the well field area,

displacement along the fault zone occurs on at least four normal faults. Brecciation in the fault zone was identified in Boise Geothermal Ltd. No. 4. At all well sites, the Banbury Basalt (?), and Interbed (1) and the upper part of Siliceous Volcanics (1) of the Idavada Volcanics have been extensively altered to montmorillonite (?) clay, and zeolites are abundant (Wood and others, 1982). Boise Geothermal No. 2 is thought to receive water from Siliceous Volcanics(1).

Also sampled were two wells penetrating the deep aquifer system along the edge of the Boise Valley northwest of the State Capitol well cluster. One well (4N 2E 29ACD2) was selected because it is located adjacent to a shallow well (4N 2E 29ACD1). The other well (4N 1E 24DCC1) was selected because it appears to represent a cooler deep thermal regime along the edge of the Boise Valley.

Field Procedures

Though the wells sampled (except 4N 2E 22BCD1) flow under artesian pressure, they are capped and valved off. Water standing in the column may therefore interact with casing materials and may change in Eh (oxidation-reduction potential). The well cap is not necessarily gas tight, potentially allowing gas exchange which results in an increase in Eh. To prevent sampling water which is not representative of the formation being sampled, the wells were allowed to flow freely for one half to one hour before sampling, depending on flow rate. Well 4N 2E 22BCD1 was pumped for a similar period. This allowed several bore-volumes of water to be flushed from the system.

Samples were taken from each well for solute analysis. Samples for metal analyses were passed through 0.45 filters and stored in rinsed, Nalgene (tm) bottles. The chemical speciation of solutes in ground water is dependent on the temperature and redox conditions in the aquifer. When removed from this environment, these conditions change, causing a redistribution of solute speciation. In some cases, this may involve the precipitation of some solid phase (such as ferric hydroxide) within the sample. This alters the composition of the water, resulting in misleading chemical analyses. To prevent this, the samples were acidified with approximately 3 ml of nitric acid. This lowered the pH of the sample to below 2, where such precipitation is inhibited. The resulting sample has been altered in NO_3^{-2} and H^+ (pH) content. Previous analyses have shown that the ground waters have negligible nitrate concentrations, so the addition of this poorly interacting species does not alter the resulting analysis. The pH of the sample is altered by this treatment, but is also altered by exchange of carbon dioxide through the gas-permeable walls of the sample container. The pH of a sample can thereby be seriously altered before analysis in the laboratory. The

pH of the sample is therefore determined immediately in the field, allowing minimum opportunity for alteration from aquifer conditions.

The exchange of atmospheric carbon dioxide through the sample container also alters the carbonate/bicarbonate content of the sample before it can be analyzed in the laboratory. The analysis for these major ions must therefore be made in the field. Various methods for this procedure are possible, but the procedure recommended here is considered easy, accurate, and least error-prone under field conditions. A 100 ml sample of filtered water is titrated with 1/10 normal sulfuric acid. The sample is first titrated to an end point of pH = 8.3 with phenolphthalen as the indicator. In all cases in this study, the indicator remains colorless, showing that the pH < 8.3 and that carbonate ion is not present. The sample is then titrated to an end point of pH = 4.6 with bromocresol green/methyl red (Rand and others, 1979) as the indicator. The number of ml of acid consumed in this titration to the light pink (blue free) end point corresponds directly to the number of meq/l bicarbonate ion in solution.

The remaining chemical analyses were made in the laboratory by the Idaho Department of Health and Welfare in Boise. The samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), chloride (Cl^-), flouride (F^-), and silicate (SiO_2). The results of these analyses are reported in Table 3. Samples collected for an ion analysis were not filtered or acidified.

A filtered 100 ml sample was taken in a glass bottle for stable isotopic analysis. This bottle was sealed with paraffin on site to assure that no evaporation could take place which could alter the deuterium and oxygen-18 content of the sample. These stable isotopic analyses were made by Geochron, Inc.

A miniumum of five grams of elemental carbon are required for routine radiocarbon analysis. This would require a sample of over 50 liters for samples containing as little bicarbonate as that from well 4N 2E 22BCD1. Since this presents great problems in sample transportation and great potential for sample contamination, the carbon is extracted from the sample, concentrated, and then sent to the laboratory for analysis. This is done by first adjusting the pH of the 60-liter sample to greater than 11.5. This is done by adding sodium hydroxide pellets to the sample, forcing all carbon in solution to take the form of carbonate ion. This carbonate ion is susbsequently precipitated by overdosing the sample with barium chloride. This causes the precipitation of barium carbonate. This is collected in a one-liter container with some supernatant fluid and sent for analysis. During the preparation of the sample in the laboratory, the barium carbonate is acidified to release carbon dioxide

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gas. An aliquot of this gas is retained for ^{13}C analysis by mass spectrometry while the remainder is used in the ^{14}C analysis. These analyses were also done by Geochron, Inc.

Additional samples of one liter were collected at wells 3N 2E 10AAD1 and 3N 2E 10AAB1 for tritum (^3H) analysis. These analyses were done by Teledyne Isotopes, Inc.

IV. DATA ANALYSIS

Geothermal Temperatures and Heat Flow

Brott and others (1976) and Smith (1981) found high heat flow values associated with fault zones along the margins of the Snake River Plain and low values near the center. They attributed these values to:

1) Refraction of heat by low heat conductive sedimentary rocks in the central regions of the Plain toward high heat conductive crystalline rocks in the bounding struc- tures north and south of the plain.

2) Upward flow of thermal water along the marginal fault zone.

3) Lowering of heat flow values measured in shallow wells by downward percolating irrigation water near the central portions of the Plain.

Thermal aquifers of large areal extent have been identified in the Boise River Basin (Lewis and Young, 1982), the central Nampa-Caldwell area (Anderson and Wood, 1981), and in the southern Bruneau-Grand View area (Littleton and Crosthwaite, 1957; Ralston and Chapman, 1969; and Young and Whitehead, 1975) of the western Snake River Plain. Limited drilling away from the Foothills Fault by the state of Idaho has shown laterally con- tinuous aquifers exist along the northern margin of the Snake River Plain. Thermal water here appears to be obtained from the same rock units, that is the Banbury Basalt and the Idavada Volcanics, as in the Bruneau-Grand View area (Wood and others, 1982). Similar isotopic and chemical composition of the thermal waters add evidence to that established from stratigraphic studies and geologic mapping that the aquifers in the Boise and Bruneau-Grand View areas are similar. In the Nampa-Caldwell area, the absence of the Siliceous Volcanics of the Idavada Volcanics in the J.N. James No. 1 well makes correlation with units in the Boise area uncertain.

Many ground-water temperatures recorded in wells and from well discharges in the Boise area are anomalously high. Discharge temperatures are generally highest along the base of the Boise Foothills, with the highest temperatures clustered in the vicinity of the State Capitol. Geothermal gradients of 80° to nearly 200° C/km, well above regional values, may be calculated from borehole temperature logs taken from the deeper geothermal wells and test boreholes in the State Capitol well cluster (Anderson, 1981; and Nelson and others, 1980). Mink and Graham (1977) reported a geothermal gradient of 47° C/km in a 378 meter deep well in the Boise Foothills. Smith (1981) found a linear region,

coincident with the Foothills Fault, to have the highest heat flow values in and around the western Snake River Plain. Heat flow is a measure of heat energy passing through a unit area of the earth per unit of time. The greater reliability of heat flow measurements over simple temperature gradient measurements or calculations in assessing an areal geothermal potential is well known. The geothermal gradient may be viewed as the thermal difference between the earth's deeper layers and those found at the surface, and is dependent on the ability of the intervening rock layers to conduct heat (thermal conductivity). Heat flow measurements take this thermal conductivity into account, and therefore are uniform with depth, while abrupt and sometimes large variations in geothermal gradient occur with depth due to changes in thermal conductivity. A high heat flow, therefore, may indicate the presence of an intense heat source (regional and local) in the subsurface, while a high geothermal gradient may only reflect a lower thermal conductivity.

The deep aquifer systems have higher discharge water temperatures than do the shallow systems. Temperature variations across the "blue clay" or other strata hydraulically separating the two systems are often substantial. In the Boise valley, shallow ground water temperatures are typically in the 12° to 15° C range (Dion, 1972). Deeper aquifer temperatures are usually 30° C or greater. Doubly constructed wells, which draw water from both aquifer systems, may have water temperature variations as great as 30° C across the hydraulic barrier separating the two systems. Discharge temperatures in the wells sampled are listed in Table 2.

Borehole temperature logs indicate ground-water temperatures associated with individual stratigraphic horizons vary and the temperatures do not increase linearly with depth. Instead, the temperature profiles show an overall temperature increase with depth. The rate of temperature increase varies with depth, and temperature decreases over short depth intervals are not uncommon. Zones of colder water may be sandwiched between zones of warmer water. Variations of ground-water temperatures found in the deep ground-water regime may be attributed to three factors:

1) Differences in the thermal conductivities of the stratigraphic horizons encountered in the boreholes. Smith (1981) reports calculated mean "in situ" thermal conductivity values for the rocks in the area to be:

Rock Type	Thermal Conductivity (cm/sec °C)
Basalt	3.62 ± 0.85
Granite	6.01 ± 0.50
Silicic Volcanics	4.54 ± 0.24
Sand & Clay	3.49 ± 0.90
Clay	2.79 ± 0.51

2) Differences in ground-water flow rates and volumes of the aquifers encountered.

3) The possible mixing of waters from different aquifers along the many faults in the area.

Artesian Conditions and Hydraulic Communication

The top of the deep ground-water regime is typically 150 to 300 meters below land surface. Wells penetrating this regime commonly free flow at the land surface. Free-flow discharge rates range from a few to more than 7,000 liters per second. The effect of long-term well discharges from the system are undocumented. Burnham (1980) suggests these discharges have lowered the pressure head of the deep regime. Reliable piezometric maps may not be constructed because correlation of pressure-head data with the associated hydrostratigraphic units cannot be made for most wells with the data available. Burnham (1980) also suggests the deep ground-water regime flows toward the southwest under a small gradient. It appears reasonable to assume that most ground-water movement is to the southwest, parallel to the bedding surface, although some movement along the fault trace also appears to be occurring. Vertical distribution of pressure heads between the hydrostratigraphic units has not been documented.

Pumping tests, including free-flow aquifer tests, have been conducted on many of the newer thermal wells in the State Capitol area (Anderson, 1981; Kelly, 1981; Nelson and others, 1980). Aquifer characteristics have been calculated from the test data and possible vertical hydraulic boundaries (faults) have been identified. The aquifer characteristics T (transmissivity) and S (storativity) were calculated. Because of the faulted nature of the aquifers, the test data should be viewed with some caution. Transmissivity is a measure of the ability of an aquifer to transmit water and storativity is a measure of the volume of water that an aquifer releases from storage per unit surface area of aquifer per unit decline in hydraulic head. Transmissivity is a function of the hydraulic conductivity of the strata and the saturated thickness. Hydraulic conductivity, like thermal conductivity may vary greatly from one stratigraphic horizon to another.

Most calculated values of T and S cannot be correlated with the hydrostratigraphic units suggested in this investigation because most of the wells tested are open to, and therefore have the potential to draw water from more than one unit. Capitol Mall No. 2 is open for approximately 525 meters (Kelly, 1981) and two INEL test holes in the State Capitol area have well screens opposite portions of several of the hydrostratigraphic units (Nelson and others, 1980). Capitol Mall No. 1 is only open to the entire thickness of Siliceous Volcanics (1) and a small portion of Interbed (2) of the Idavada Volcanics. A T value of 7.2×10^{-4} m/sec and a S value of 5.0×10^{-5} were calculated for Capitol Mall No. 1 (Anderson, 1981). T values ranging from 7.2×10^{-3} to 1.4×10^{-2} and S values ranging from 10^{-4} to 10^{-3} have been calculated from other tests. The highest T values are from wells located in the highly fractured Foothills Fault zone (Nelson and others, 1980), suggesting the faults may provide significant avenues for ground-water movement between hydrostratigraphic units. Test results from the four Boise Geothermal Ltd. wells, also located in the Foothills Fault zone, are proprietary.

Well tests have also yielded valuable information concerning the hydraulic connection between wells. Many of the wells are separated by faults which offset the strata between them. INEL test data (Nelson and others, 1980) suggest the existence of recharge boundaries (faults ?) and a test of Capitol Mall No. 2 demonstrated hydraulic communication between wells in the Boise Valley and wells in the Foothills Fault zone (Kelly, 1981). In the Capitol Mall No. 2 test, drawdowns of 2.25 meters in Capitol Mall No. 1, and 0.67 and 0.45 meters in the Boise Geothermal Ltd. wells were recorded at the end of three days. The Capitol Mall No. 2 test is particularly significant because it demonstrates hydraulic communication between hydrostratigraphic units offset by faulting, further suggesting the faults act as avenues for ground-water movement.

Geochemistry

Solutes

The results of the sixteen ionic analyses appearing in Table 2 have been plotted as Stiff (1951) diagrams, Figure 7, and as a trilinear diagram, Figure 8, in the manner of Piper (1944). Stiff diagrams facilitate the comparison of total solute concentration and ionic composition by the utilization of graphical shapes. The shape of the diagram represents composition, while the size reflects concentration. Two distinct water types, a sodium bicarbonate and calcium-sodium bicarbonate with, in some cases, sulfate, are evident from the Stiff diagrams. There is a strong correlation between discharge temperatures and the Stiff diagram form. Waters having discharge temperatures of 40° C or

TABLE 2. WATER CHEMISTRY

Well Number	Solute Concentrations meq/l (mg/l)									
	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	F^-	HCO_3^-	SiO_2(ppm)	pH
1. 5N 1E 35ACA1	0.24 (4.8)	0.01 (0.10)	2.47 (56.8)	0.08 (3.28)	0.45 (21.6)	0.12 (4.25)	0.55 (10.45)	1.94 (118.4)	41.0	8.10
2. 4N 1E 24DCC1	0.82 (16.4)	0.16 (1.95)	1.80 (41.4)	0.13 (5.08)	0.09 (4.5)	0.04 (1.31)	0.03 (0.65)	3.24 (197.7)	64.8	7.60
3. 4N 2E 22BCD2	1.92 (38.5)	0.18 (2.19)	0.55 (12.6)	0.04 (1.60)	0.69 (33.1)	0.06 (1.99)	0.03 (0.61)	1.07 (65.3)	32.0	6.75
4. 4N 2E 22BCD1	0.16 (3.2)	0.01 (0.10)	2.61 (60.0)	0.02 (0.90)	0.45 (21.6)	0.06 (2.20)	0.44 (8.36)	1.64 (100.1)	41.7	8.17
5. 3N 2E 12CDD1	0.16 (3.2)	0.01 (0.10)	3.60 (82.8)	0.04 (1.41)	0.45 (21.6)	0.17 (6.03)	1.01 (19.19)	1.80 (109.8)	73.5	8.15
6. 3N 2E 11BAA1	0.08 (1.6)	0.01 (0.10)	3.77 (86.7)	0.03 (1.29)	0.54 (25.9)	0.22 (7.80)	0.89 (16.91)	1.82 (111.1)	31.7	8.35
7. 3N 2E 10AAD1	0.08 (1.6)	0.01 (0.10)	3.87 (89.0)	0.02 (0.70)	0.34 (16.3)	0.03 (0.89)	0.96 (18.24)	2.07 (126.3)	56.5	8.47
8. 3N 2E 10AAB1	0.06 (1.3)	0.01 (0.10)	3.45 (79.3)	0.02 (0.59)	0.40 (19.2)	0.23 (10.64)	0.84 (15.96)	1.87 (114.1)	55.6	7.55
9. 4N 2E 29ACD2	0.20 (4.0)	0.01 (0.10)	2.98 (68.5)	0.02 (0.70)	0.42 (20.2)	0.09 (3.08)	0.56 (10.64)	2.20 (33.6)	26.0	8.35
10. 4N 2E 29ACD1	2.83 (56.7)	0.36 (4.38)	1.82 (41.8)	0.04 (1.64)	1.26 (60.5)	0.20 (7.09)	0.02 (0.36)	4.08 (249.0)	44.7	6.67

PUBLISHED DATA FROM MITCHELL AND OTHERS, 1980

| Well Number										
11. 3N 2E 11ABC1	0.22 (4.4)	0.01 (0.12)	3.87 (89.0)	0.04 (1.56)	0.44 (51.9)	0.04 (1.42)	0.89 (16.91)	2.60 (158.7)	80.0	8.5
12. 3N 2E 13ACB1	0.08 (1.6)	0.01 (0.12)	3.35 (77.0)	0.02 (0.78)	0.01 (1.2)	0.25 (8.86)	0.95 (18.05)	2.29 (139.7)	42.0	8.7
13. 3N 2E 36ABC1	0.95 (19.0)	0.07 (0.85)	0.95 (21.8)	0.03 (1.17)	0.29 (34.2)	0.17 (6.03)	0.03 (0.57)	1.59 (97.0)	23.0	7.3
14. 4N 2E 04BDC1	1.70 (34.1)	0.26 (3.16)	1.31 (30.1)	0.03 (1.20)	0.75 (88.5)	0.11 (3.90)	0.11 (2.09)	2.46 (150.1)	27.0	7.3
15. 5N 1E 25BCC1	1.90 (38.1)	0.35 (4.26)	1.22 (28.0)	0.09 (3.52)	1.12 (132.2)	0.12 (4.25)	0.09 (1.71)	2.46 (150.1)	38.0	8.6
16. 5N 1E 26DCD1	1.10 (22.0)	0.16 (1.95)	1.61 (37.0)	0.09 (3.52)	0.98 (115.7)	0.14 (4.96)	0.18 (3.42)	1.80 (109.8)	32.0	7.9
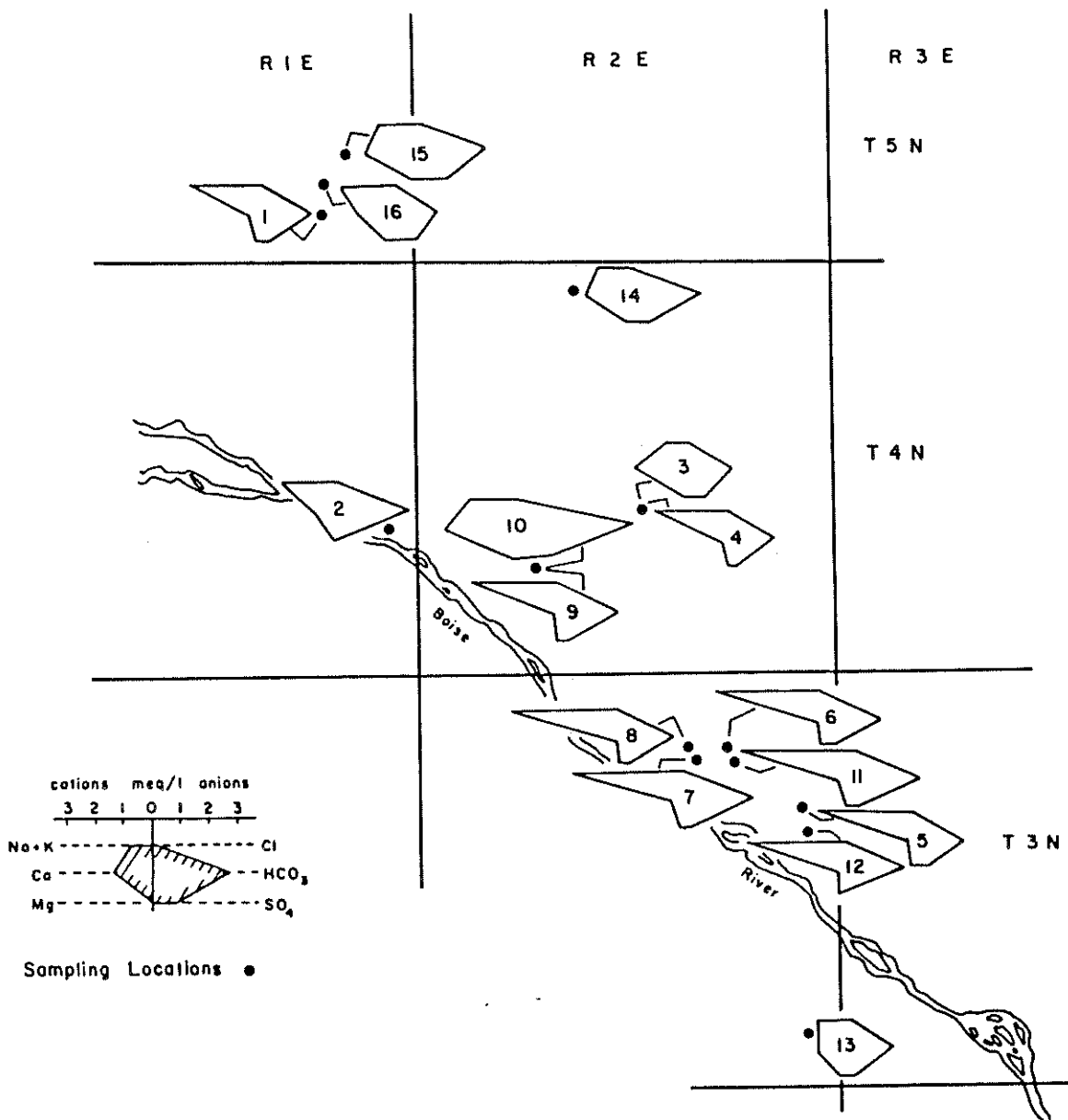
FIGURE 7. Stiff diagrams
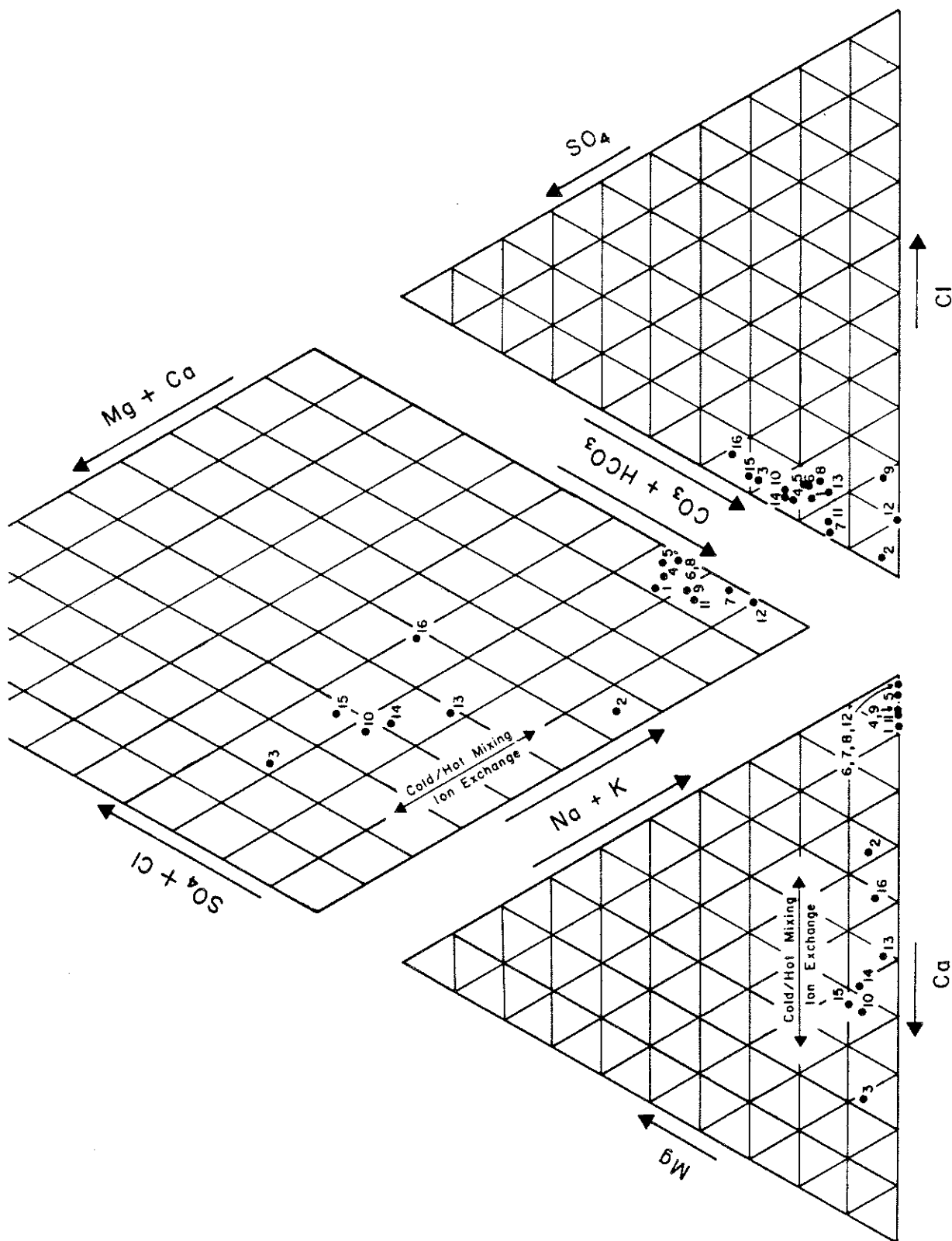
FIGURE 8. Trilinear diagram
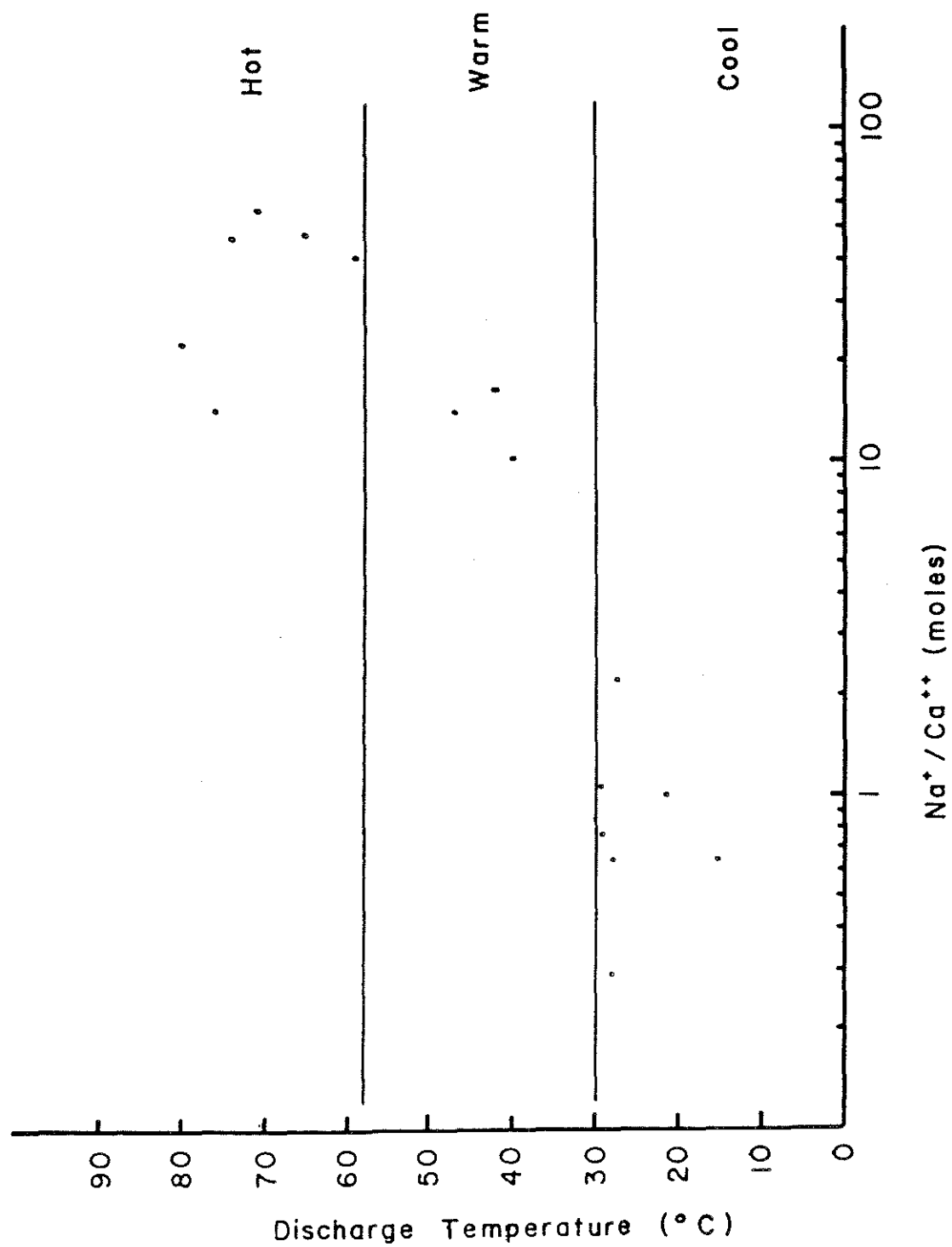
FIGURE 9. Plot of Na^+/Ca^{2+} versus discharge temperature

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greater are of the sodium bicarbonate type, whereas waters with cooler discharge temperatures are of the calcium-sodium bicarbonate type. Similar forms of Stiff diagrams are observed from analyses of the solute concentrations in thermal and non-thermal discharge waters in the batholithic rocks of the Boise River basin (Lewis and Young, 1982) and in the Idavada volcanic sequence in the Nampa-Caldwell area (Mitchell, 1981). Possible hydraulic continuity of thermal ground waters from the batholithic terrains in the Boise Foothills across the Foothills Fault zone (this investigation) and into the Idavada Volcanics in the Snake River Plain is currently being investigated by the authors.

The trilinear diagram (Figure 8) shows the relative contribution of major anions and cations making up the total solute concentration, independent of the actual ionic strength (salinity) of the water. The cationic triangle (lower left) shows the CA^{2+}/Mg^{2+} of the waters to be about constant, whereas $Na^+ + K^+$ content increases linearly with decreasing Ca^{2+} content. Additionally, there appears to be a nearly linear relationship between increasing discharge temperatures and an increase in Na^+/CA^{2+} (Figure 9). Ionic exchange or ground water mixing could be responsible for these relationships.

Groundwater may exchange Ca^{2+} for Na^+ due to ionic exchange with zeolites, clays, or other minerals. Such exchange could result from ground water contact with zeolites observed in interbeds in Idavada volcanic cuttings from near the Foothills Fault or from batholithic clay minerals in buried weathered zones or along deep fractures. The waters most exhibiting this apparent exchange are the warmest of the samples, and except for sample #4, are closely associated with the Foothills Fault zone. Depletion of Ca^{2+} from solution would cause additional dissolution of calcium minerals such as calcite ($CaCO_3$) and fluorite CaF_2). The calcium from this dissolution would continue to be exchanged while F^- and the total anion concentration would increase. There is a general increase in F^- concentration with increasing discharge temperatures and increasing Na^+/Ca^{2+}, which suggest ionic exchange. Discharge waters having a F^- concentration of 0.2 meq/l or less have Na^+/Ca^{2+} of less than 10 and discharge temperatures of 30° C or less. F^- concentrations of 0.4 to 0.6 meq/l are generally associated with discharge waters having Na^+/Ca^{2+} of 20 to 50 and discharge temperatures of 40 to 50° C. F^- concentrations of 0.8 to 1.0 meq/l are generally associated with discharge temperatures of 59° C or greater.

The sample pairs 3 and 4, and 9 and 10 are of particular interest in that they represent cold (shallow) and warm (deep) discharges from the same location. Samples 3 and 4 are cold and warm discharges, respectively, from a doubly constructed well in the Boise foothills. The cold discharge is of the calicum-bicarbonate type, whereas the warm discharge is of the sodium bicarbonate type (Figure 8). Sample 4 has a slightly increased

total solute concentration and a substantial increase in F^- concentration, which supports the idea of ionic exchange in the deeper, warmer aquifer system. Sample 3 may be typical of the solute chemistry of recharge water of the shallow and deeper aquifer systems. This chemistry is consistent with dissolution of carbonate minerals in the soil zone and is similar to cold ground waters in the crystalline terrain of the Boise River basin (Lewis and Young, 1982).

Samples 9 and 10 are warm and cold discharges, respectively, from closely spaced wells in the Boise Valley near the Foothills Fault. The solute chemistry of sample 9 is typical of the warm and hot water discharges. Sample 10, however, has the greatest solute concentration of all water samples and contains substantial amounts of both Ca^{2+} and Na^+. The high Ca^{2+} and SO_4^{2-} concentrations are attributed to dissolution of carbonate minerals and possibly gypsum in alluvial covered volcanoclastics of the Boise Valley. The high Na^+ content may represent mixing of deeper and warm Na^+ rich ground water with the shallow alluvial aquifer.

Stable Isotopes

About 104 elements have been identified, most of which occur in nature. By definition, the number of protons in the nucleus of an atom of a given element determines which element it is. One proton is found in the nucleus of hydrogen, two in lithium, three in berylium, four in boron, and so on. Not only protons, but also neutrons can exist in the nucleus of an atom. The number of neutrons in the nucleus of an atom has no influence on the element, but rather, determines the isotopic number of a nuclide.

Water is made up of the elements hydrogen and oxygen in an atomic proportion of two to one. The most common nuclide of hydrogen in nature has an isotopic number of one (one proton and no neutrons) while common oxygen has 16 (eight protons and eight neutrons). [This relationship of equal numbers of neutrons and of protons in the nucleus of the most common isotope of an element is common in elements of lower atomic numbers (atomic number equals the number of protons) but the number of neutrons tends to exceed the number of protons at higher masses.] These isotopes make up more than 99.8 percent of their respective elements. Thus, most water molecules have the isotopic configuration of $^1H_2^{16}O$. But one hydrogen in about 6500 has one neutron. This nuclide, with an isotopic number of two is called deuterium. Also, about one oxygen atom in 500 has ten neutrons rather than eight. Although other rare isotopes of hydrogen and oxygen exist, ^2H and ^{18}O make up practically all of the respective elements which do not occur as the common isotope. Thus, some water also occurs as $^1H_2^{18}O$, $^1H^2H^{16}O$, $^1H^2H^{18}O$, $^2H_2^{16}O$, and $^2H_2^{18}O$. Of these, only $^1H_2^{18}O$ and $^1H^2H^{16}O$ occur in amounts sufficient to be useful in hydrology. These represent about 0.20

percent and 0.02 percent of all waters respectively, while $^1H_2^{16}O$ makes up virtually all the remaining 99.78 percent.

The determination of absolute isotopic concentrations in a sample of water is extremely difficult. In hydrology it is conventional, and just as useful, to determine the relative isotopic composition of a sample with respect to a standard of known composition. Concentrations are therefore not expressed as absolute abundance ratios, R (where R = number of heavy rare nuclide/ number of light common nuclides) but rather as relative δ units defined

$$\delta = \left(\frac{R \text{ sample}}{R \text{ standard}} - 1 \right) \times 10^3 .$$

This unit expresses the difference in isotopic composition in parts per thousand between the sample and a standard. The standard for both ^2H and ^{18}O is Standard Mean Ocean Water (SMOW) defined by Craig (1961a). A sample having $\delta^{18}O$ = -5 ^{o}/oo SMOW contains five parts per thousand less ^{18}O than does the standard. These isotopic differences are readily measurable by dual trace mass spectrometry.

In the case of hydrogen isotopes, the sample is quantitatively converted to hydrogen gas, since water vapor is corrosive to the hot tantalum filament in the source of the mass spectrometer. This is done by reducing H_2O on hot depleted uranium or zinc metal, producing metal oxides and hydrogen gas. Such gas produced from the sample is run alternately with hydrogen of standard composition in the mass spectrometer, yielding the relative difference in the isotopic ratios of the two gases.

Similarly, ^{18}O can also not be analyzed mass spectrometrically as H_2O. It must first be equilibrated with a volume of CO_2 with a known isotopic composition according to the method of Epstein and Mayeda (1953). The mass 44/46 ratio ($^{12}C^{16}O_2/^{12}C^{16}O^{18}O$) of this gas is compared to that of the standard to obtain the $\delta^{18}O$ of the sample.

These analyses are useful since the three isotopic forms of water are not distributed in constant proportions throughout the water cycle. Some reservoirs have larger fractions of the rarer isotopic forms than do other reservoirs. This would not be the case if the isotopic forms behaved absolutely identically. They do not. In some changes of phase, when some fraction of mass is transferred from one reservoir to another, some of the forms have a greater propensity to complete the transfer than do others. This process is called isotopic fractionation. Clearly, if one gram of water having the proportions $^1H_2^{16}O:^1H_2^{18}O:^1H^2H^{16}O$ of x:y:z is evaporated to form one gram of water vapor, the proportions in that vapor must also be x:y:z because of conservation of mass. But consider the case where one gram of water from a well

mixed relatively infinite reservoir of that same composition is evaporated. Because of isotopic fractionation, the lighter and more volatile isotopic form $^1H_2^{16}O$ tends to evaporate preferentially. The resulting vapor will have composition x+ x:y- y:z- z which is isotopically lighter than the residual parent liquid phase. This phase is infinitesimally enriched in heavy isotopes during this process. This enrichment can be defined in terms of an equilibrium fractionation factor α. For the isotopic equilibrium

$$(H_2^{16}O + H_2^{18}O)_{liquid} = (H_2^{16}O + H_2^{18}O)_{vapor}$$

the fractionation factor is defined as

$$\alpha^{18}O = \frac{R\ liquid\ phase}{R\ vapor\ phase}$$

Bottinga and Craig (1969) have shown this factor to vary as a function of temperature according to the relationship

$$10^3 ln\,\alpha^{18}O = 2.644 -3.206 \times 10^3 T^{-1} + 1.534 \times 10^6 T^{-2}$$

In practice, this leads to a variation in the isotopic content of natural waters, as a function of the temperature at which they were "formed." Evaporation occurs at a wide variety of temperatures. In this case, it is the rate or flux which is temperature dependent. In the case of precipitation, condensation occurs at the single, dew-point temperature of the air mass. The isotopic composition of precipitation is also a function of the initial isotopic composition of the water in the air mass, but it can be used to get an idea of temperature (or related parameters) when source composition is about constant. Dansgaard (1964) has obtained precipitation samples from stations near the oceans from 90°S to above 80°N latitude and has correlated this data with mean annual surface temperature to obtain the following empirical relationships:

$$\delta^{18}O = 0.695t -13.6\ (^o/oo)$$
$$\delta^{2}H = 5.6t -100\ (^o/oo)$$

where t is temperature in degrees centigrade. Solving for t in the second equation and replacing into the first yields the following relationship between ^{18}O and ^{2}H for these waters:

$$\delta^{2}H = 8.1\delta^{18}O + 9.6\ (^o/oo)$$

This is remarkably similar to the relationship obtained by Craig (1961a) for over 1000 samples of precipitation from continental stations:

$$\delta^{2}H = 8\,\delta^{18}O + 10\ (^o/oo)$$

This relationship is represented in Figure 10 as the "Meteoric Line." The relationships from Dansgaard (1964) have been used to place a general temperature scale on the line. The scatter of Craig's data falls approximately within the bounds drawn about the line in the figure. It is important to realize that the meteoric line represents a global average. Precipitation at a given point tends rather to be described by a short stroke across the line, as illustrated by the dashed line in the figure. Further, if the source area of the water vapor is not typically marine, the regional meteoric line may be offset but parallel to Craig's line, as shown by Nir (1967) for precipitation from the eastern Mediterranean region:

$$\delta^2 H = 8\delta^{18}O + 22 \ (^o/oo)$$

The intercept of this equation, which varies with source composition, is called the deuterium excess.

The stable isotopic composition of ground waters may also be tailored by interactions subsequent to evaporation. Since the temperature dependence of oxygen-18 and of deuterium fractionation is not the same, the equilibrium evaporation of a fraction of rain water (before infiltration) enriches the residual water by different amounts for the two elements. This results in a diagonal translation of the composition of the water in a $\delta^2 H$ versus $\delta^{18}O$ diagram, as shown in Figure 10.

Another mechanism by which the isotopic composition of ground waters may be altered is by interaction with aquifer materials. At low (below 50 to 80° C) temperatures, the kinetics of the isotopic equilibrium are too slow to show any appreciable shift in composition, even when the water is exposed to these materials for very long times. At higher temperatures, an isotopic exchange does take place. Since rocks generally contain no hydrogen, it is only the oxygen isotopic composition which becomes altered. This exchange with the heavier isotopic reservoir (generally with silicates) causes a translation in composition parallel to the $\delta^{18}O$ axis, shown in Figure 10.

The deuterium and oxygen-18 content of nine of the waters sampled (Table 3) are also plotted in the figure. All the data plot within the zone of scatter for the Craig (1961a) data. Eight of the data correspond to a mean annual surface air temperature of approximately -6° C, which is consistent with the probable recharge area. None of the samples, except perhaps that from well T4N R2E 22BCD2, show any isotopic shift due to evaporation. Although the sample from T4N R2E 22BCD2 lies appreciably away from the other data points in the figure, it is also within the scatter interval and therefore no unequivocal conclusion can be made about its history. Nevertheless, it maps well along an evaporation line to join the remaining points, it corresponds with an unrealistically high (approximately -3° C)
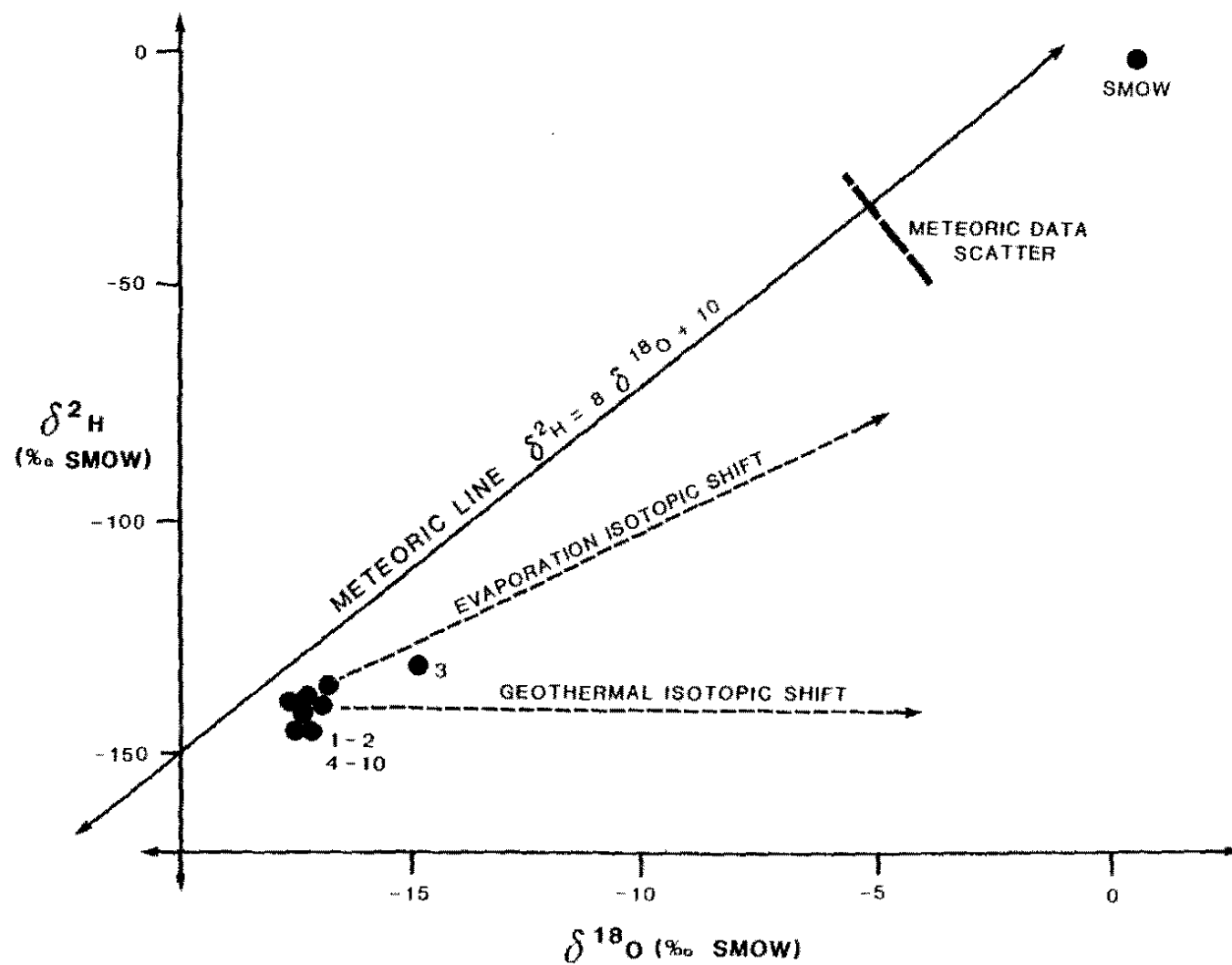
FIGURE 10. Plots of δ^2H versus $\delta^{18}O$

TABLE 3. — ISOTOPIC DATA OF WELLS SAMPLED

Well Number	$\delta^2 H$ ($^o/oo$ SMOW)	$\delta^{18} O$ ($^o/oo$ SMOW)	$^{13} C$ ($^o/oo$ PDB)	$^3 H$ (T U)	$A^{14} C$ (pmc)	Estimated mean subsurface residence times (years)
5N 1E 35ACA1	−141 ± 1	−17.2 ± 0.2	− 9.5 ± 0.1	---	17.5 ± 0.1	8,900 ± 700
4N 1E 24DCC1	−143 ± 1	−18.2 ± 0.2	− 2.6 ± 0.1	---	13.6 ± 0.1	11,700 ±
4N 2E 22BCD1	−136 ± 1	−16.6 ± 0.2 16.8	−10.8 ± 0.1	---	31.6 ± 0.1	4,100 ± 300
4N 2E 22BCD2	−130 ± 1	−14.9 ± 0.2	−10.9 ± 0.1	---	60.0 ± 0.1	500 ± 50
4N 2E 29ACD1	−139 ± 1	−17.1 ± 0.2	−16.2 ± 0.1	---	104.6 ± 0.1	Modern
4N 2E 29ACD2	−138 ± 1	−17.1 ± 0.2	− 9.5 ± 0.1	---	13.1 ± 0.1	11,200 ± 1,000
3N 2E 11BAA1	−142 ± 1	−17.3 ± 0.2	− 9.8 ± 0.1	---	11.1 ± 0.1	12,600 ± 1,200
3N 2E 12CDD1	---	---	− 9.3 ± 0.1	---	6.6 ± 0.1	17,000 ± 1,200
3N 2E 10AAD1	−139 ± 1	−17.4 ± 0.2	−11.8 ± 0.1 −11.9	1.6 ± 1.4	21.5 ± 0.1 20.9	7,100 ± 600
3N 2E 10AAB1	−140 ± 1	−17.1 ± 0.2	−10.5 ± 0.1	3.7 ± 1.4	23.7 ± 0.1	6,700 ± 600

mean annual surface air temperature and it comes from a cool (compare to T4N R2E 22BCD1 in Table 1), rapid [See the discussion of the 500 $\pm$ 50 year ground-water age of this sample in the section below.] flow system. Thus, the possibility of some surface ponding before recharge is not inconsistent with the information available about the system from which this sample was taken.

None of the samples show any shift in oxygen-18 composition due to geothermal interaction with aquifer materials. There is no reason to think that any of the waters have ever been above about 100° C for any appreciable time, based on their stable isotope data.

The offset of the points from the meteoric line many have several interpretations. First, it must be kept in mind that local precipitation may vary about the line, as shown by the dashed line in Figure 10. All the points fall within the scatter interval shown. Second, the waters may have precipitated from an air mass atypical of continental systems. The waters from such a system could have a smaller deuterium deficit than the meteoric line. This data would correspond to a deficit of about -11 °/oo. Third, there could be a systematic error in the experimental measurements. Attributing all the error to the oxygen-18 measurement would correspond to an offset of about +1.5 °/oo in $\delta^{18}O$, while attributing all the error to deuterium measurement would correspond to an offset of -12 °/oo in δ^2H. Combinations of errors of smaller magnitude could also cause the same result. Nevertheless, this would be a large error to go unnoticed, and no evidence exists that such a systematic error may have occurred. No control samples were analyzed for this study. There is no way to determine for which of these reasons, or combination of reasons, the data in Figure 10 do not fall on the meteoric line without further stable isotopic analysis of surface water, rain, snow, and water vapor.

In any case, the stable isotopic data is consistent with a meteoric origin for the ground waters, with no (or very minor) evaporation and no geothermal influence.

Radiocarbon

The principles behind radioactive dating are best illustrated with the example of dating vegetal material. Radiocarbon is produced in nature by neutrons coming from cosmic ray spallation reactions colliding with atmospheric nitrogen, resulting in the reaction

$$n + {}^{14}N \longrightarrow p + {}^{14}C$$
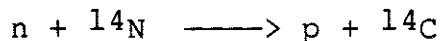
With time, a steady state has been approached between production by this reaction and depletion from the atmosphere due to radioactive decay and transfer to other reservoirs of carbon (such as
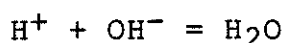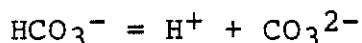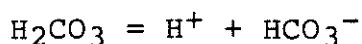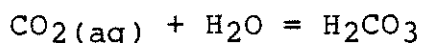
the oceans). This steady state value has been arbitrarily defined as 100 pmc (percent modern carbon). [100 pmc is defined to correspond to 13.56 decays per minute per gram of carbon.] Some fluctuations about this value have occurred due to variations in cosmic ray flux, but are negligible for most cases of dating. The burning of fossil fuels has diluted the atmospheric ^{14}C by the introduction of radiocarbon-free CO_2 since the industrial revolution, causing the atmospheric concentration to descend below 100 pmc. Anthropogenic radiocarbon has been injected into the atmosphere by thermonuclear bomb tests of the early 1960's, resulting in a northern hemisphere peak of about 200 pmc. Transfer to the oceanic reservoir has reduced this value until presently it is about 130 pmc. Those perturbations have occurred only since about 1880 and need be considered only when dating young materials. The significance of these perturbations within that context will be discussed as a special case, below, and a pre-1880 condition will be considered first.

Plants obtain all their carbon from atmospheric CO_2. Therefore, except for a minor enrichment due to fractionation on the order of two pmc, the ^{14}C content of a living plant tissue is identical with that of the atmosphere. When this tissue dies, it is no longer resupplied in ^{14}C and radioactive decay slowly reduces the amount of ^{14}C in the plant at the rate of about half in 5780 years. If the ^{14}C content of the plant material A_m is measured sometime later as, say 25 pmc (i.e. = 3.37 decays per minute per gram of carbon), the radioactive decay equation

$$-t = \frac{\tau}{\ln 2} \ln \left(\frac{A_m}{A_o} \right)$$

may be used to calculate the time it has taken (-t) to reduce the initial activity (A_o) to the measured level (A_m). Here   is the half life and in this case -t would be 11,560 years (since two complete half lives have elapsed to reduce this activity from 100 pmc to 25 pmc). Thus, to date a sample, not only its current ^{14}C activity must be known, but its initial activity must be estimated.

This is not as straight forward for ground water as it is for plant material. Precipitation also obtains some radiocarbons from the atmosphere, as do plants, but other reactions occur between the atmosphere and the sampling point. The actual amount of CO_2, and therefore of ^{14}C, taken up by a rain water droplet in the atmophere is quite small because of the buffering effect of the water. This is controlled by the following reaction series:

$$CO_{2(g)} = CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O = H_2CO_3$$

$$H_2CO_3 = H^+ + HCO_3^-$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

$$H^+ + OH^- = H_2O$$

The uptake of gaseous CO_2 is soon inhibited by the build up of H^+ from the disassociation reaction of H_2CO_3 and HCO_3^-, controlled by their respective equilibrium constants (Garrels and Christ, 1965). When water reaches the earth's surface and begins to infiltrate, the following reaction can consume H^+:

$$H^+ + M_eCO_{3(s)} = HCO_3^- + M_e^{2+}$$
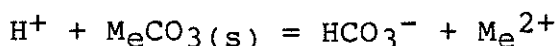
Here M_e represents some divalent cation and $M_eCO_{3(s)}$ is usually mineral $CaCO_{3(s)}$ (calcite) in the soil. This provides a second source of carbon to solution, that of the soil mineral carbonate phase. The reactions above can be combined and written:

$$CO_{2(g)} + M_eCO_{3(s)} + H_2O = 2HCO_3^-$$
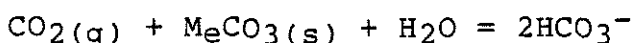
in the case where the pH of the water is less than 8.3 and HCO_3^- is the aqueous carbon preferred over CO_3^{2-}. Clearly, because of stoichiometry, for each two carbon atoms in solution as bicarbonate (HCO_3^-), one comes from the atmosphere (or soil atmosphere) and the other from mineral carbonate. Soil $CO_{2(g)}$ has the same ^{14}C concentration as the atmosphere (100 pmc) since it comes from the root respiration of plants, but here CO_2 may make up a larger total fraction of the gas than it does in the free atmosphere ($^PCO_2$ of 10^{-2} or even $10^{-1.5}$ atm compared to $10^{-3.5}$ atm in free air). If contributions from these two sources are considered, the initial activity (A_o) of the dissolved carbonate in groundwater can be expressed

$$A_o = FA_g + (1-F) A_m$$

here F is the fraction of carbon coming from the gaseous reservoir, A_g is the ^{14}C activity of that reservoir and A_m is the ^{14}C activity of the mineral phase. The activity of soil zone carbonates is usually zero pmc, suggesting they have existed long enough for any ^{14}C to decay away. The soil carbonates in some soils in desert regions may have appreciable ^{14}C activity, but this is not plausible in the region being considered. Thus, if $A_g = 100$ pmc, $A_m = 0$ pmc and $F = 1/2$, then $A_o = 50$ pmc. Had 100 pmc been used in the radioactive equation above rather than this value, the age of the water would have been over estimated by one half life.

The assumption that $F = 1/2$ is based on the pH of the infiltrating water as being the same as that of the rain. Since this is not necessarily the case, the value of F can be better calculated from actual experimental values for aqueous carbonate content. If half the HCO_3^- and all the $CO_{2(aq)}$ and $H_2CO_3^{\circ}$ are taken to come from the atmosphere, then (Ingerson and Pearson, 1964)

$$F = \frac{1/2\ m\ HCO_3^- + H_2CO_3^*}{_mHCO_3^- + {_m}H_2CO_3^*}$$

where $_m$ denotes molality and $_mH_2CO_3^*$ represents $_mCO_2^{2-}$ plus $_mH_2CO_3^{\circ}$ by convention. This gives a somewhat different value of A_0, but one which is usually quite near 50 pmc.

The equation for isotopic mixing for the two reservoirs is not completely rigorous, since A_g and A_m should be the activities of the contributions of two reservoirs rather than the activities of the reservoirs themselves. These differ because carbon, like oxygen, undergoes an isotopic fractionation as it transfers between phases. To the first approximation

$$A_1 = 0.2\,\varepsilon_{12}\ A_2$$

where ε is the ^{13}C enrichment factor defined $\varepsilon = \alpha - 1$ (Wrigley and Muller, 1981). Thus the ^{14}C activity of bicarbonate ion (A_b) in equilibrium with the two reservoirs would be written

$$A_b = 0.2\,\varepsilon_{bg} + A_g$$

and

$$A_b = 0.2\,\varepsilon_{bm} + A_m$$

respectively. Here ε_{bg} and ε_{bm} are the ^{13}C enrichment factors for the bicarbonate/carbon dioxide gas and the bicarbonate/mineral carbonate systems, respectively. Thus, the equation for isotopic mixing can be written more rigorously as

$$A_0 = F(0.2\varepsilon_{bg}) + (1-F)\ (0.2\varepsilon_{bm} + A_m).$$

This accounts for the fractionation between carbon reservoirs in the system.

An alternative approach to finding F is by using the fact that ^{13}C and ^{14}C behave chemically and isotopically identically except that (1) ^{14}C is subject to radioactive decay and that (2) a factor of 0.2 relates their fractionation factors. Thus, if this factor of 0.2 is accounted for, ^{13}C can be treated as analogous to a non-decaying ^{14}C, and the initial ^{14}C activity can be obtained. Carbon -13 content is also expressed in δ units,

as are the stable isotopes of hydrogen and oxygen (Figure 11). The accepted standard for this isotope is a sample of <u>Belemnitella americana</u> from the Pee Dee Formation in South Carolina (PDB).

Consider the simple linear isotopic mixing system in Figure 11. The ^{14}C activity of the carbonate mineral phase is plotted at zero pmc, while the ^{13}C content is shown as 0 °/oo PDB. The vast majority of continental mineral carbonates fall within this range. No carbonate samples were analyzed from this area, although a recent study in the Meade thrust area of southern Idaho (Muller and Mayo, 1982) shows the range to be reasonable there. The ^{13}C content of carbon dioxide in the soil zone approaches the ^{13}C composition of vegetative cover of the area. In temperate forest regions, this value is about -25 °/oo PDB, while under somewhat more arid conditions, the soil tends to be isotopically heavier. The range of -20 ± 3 °/oo PDB is plotted on Figure 11 for the composition of the soil carbon dioxide, which checks well with the results calculated by Muller and Mayo (1982) for their field area. Further support of these values is developed below. The line and the associated uncertainty interval in the figure represents an isotopic mixing between these reservoirs. If a value of -10 °/oo PDB is determined, and it is assumed that it represents both the initial and final ^{13}C content of the water, since it undergoes no decay, then the initial ^{14}C content may be projected. According to the similar triangles:

$$\frac{\delta_s - \delta_m}{\delta_g - \delta_m} = \frac{A_o - A_m}{A_g - A_m}$$

Here the subscript s indicates the sample. Solving for A_o yields (after Pearson and Hanshaw, 1970):

$$A_o = \left(\frac{\delta_s - \delta_m}{\delta_g - \delta_m}\right) A_g + \left(1 - \frac{\delta_s - \delta_m}{\delta_g - \delta_m}\right) A_m$$

so by this approach

$$F = \left(\frac{\delta_s - \delta_m}{\delta_g - \delta_m}\right) .$$

As in the treatment above, the expression can be made rigorous by mixing isotopic compositions of bicarbonate derived from the gaseous and mineral carbon reservoirs rather than by mixing the composition of the reservoirs themselves. In this case, the $\delta^{13}C$ must also be corrected for fractionation according to the expressions

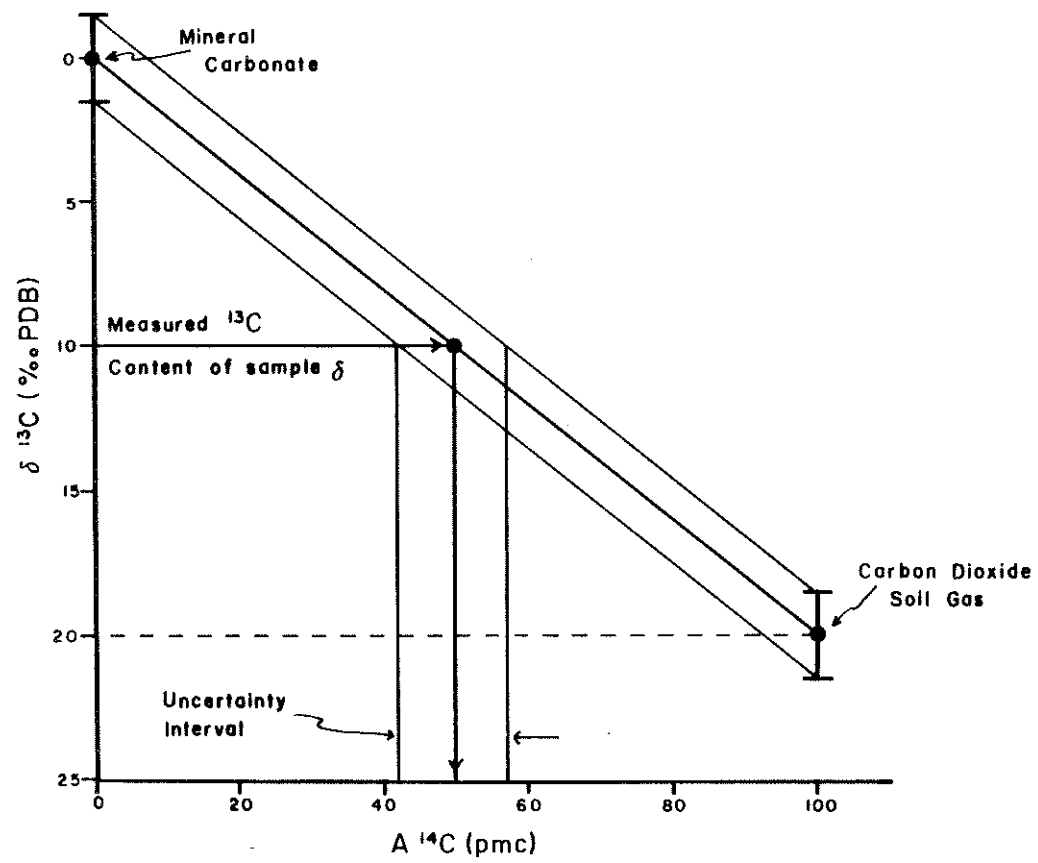$$\delta_b = \varepsilon_{bg} + \delta_g$$

and

FIGURE 11. Linear isotope mixing model for radiocarbon age dating

$$\delta_b = \varepsilon_{bm} + \delta_m$$

The expression for isotopic mixing is the same as that in the case above while the expression for the fraction derived from the gaseous reservoir becomes:

$$F = \frac{\delta_s - \varepsilon_{bm} - \delta_m}{\varepsilon_{bg} + \delta_g - \varepsilon_{bm} - \delta_m}$$

This represents a second and independent method of estimating F and, subsequently, A_o. Since the isotopic mixing expressions are identical and since the equations for F have no terms in common, these equations may be set equal to each other. Gaining this degree of freedom allows for the solution of one of the dependent variables of the resultant expression. All the variables, but δ_m and δ_g, may be determined experimentally. Since the ^{13}C composition of the carbonate minerals (δ_m) can be assumed to be the same now as it was when the water was infiltrating (at time zero), the ^{13}C composition of the soil gas (δ_g) is the variable known with least certainty. Solving the combined expression of δ_g gives:

$$\delta_g = (\delta_s - \varepsilon_{bm} - \delta_m) \frac{(mH_2CO_3^* + mHCO_3^-)}{(1/2\ mH_2CO_3^* + mHCO_3^-)} - \varepsilon_{bg} + \varepsilon_{bm} + \delta_m$$

If the value for δ_g obtained from this expression is reasonable for the field conditions observed, then two methods converge using a reasonable and consistent set of input parameters, independently determining and cross confirming the value obtained for F and A_o.

This treatment was applied to the data in Tables 2 and 3. With the exception of the samples from wells T4N R2E 29ACD1 and T4N R1E 24DCC1, the remaining water showed δ_g values in the range of $-19.5 \pm 1.5/2.5\ ^o/oo$ PDB. This is a remarkably small spread, considering the uncertainties involved in the method of analysis. This range is consistent with the dry, temperate highland vegetation in the region, and in the region during the geologic recent past. The range also falls within the interval used for δ_g in Figure 11. The resulting A_o values and the measured ^{14}C activities for these eight sites from Table 3 were used to obtain the "age" estimates in that table.

The water from well T4N R2E 29ACD1 has a remarkably high measured ^{14}C activity. A value of greater than 100 pmc can be reconciled with very young water, having an appreciable component from the thermonuclear testing era (i.e., from the last 20 years). This "age" is consistent with the low temperatures, low total dissolved solids, and geologic interpretation (see above) of this well.

The water from well T4N R1E 24DCC1 shows an anomalously high measured $\delta^{13}C$ (i.e., δ_s) value. This invalidates the approach using $\delta^{13}C$ and mixing, because of acute end effects (Figure 11). The reason for this unusually high ^{13}C content is unclear. The water may be taking up some ^{14}C-free $CO_{2(aq)}$ at depth, derived from the thermal decomposition of carbonate minerals deep in the aquifer. The discharge temperature, $^{2}H/^{18}O$ results (showing the water has never been very hot) and the measured ^{14}C activity (which would be far less if "dead" carbon were being absorbed) do not support this idea. The water could also be undergoing a degassing as it comes up from depth, liberating a lighter gaseous phase such as $CO_{2(g)}$ or $CH_{4(g)}$ and isotopically enriching the residual bicarbonate fraction. Such a mechanism could account for the increased ^{13}C measured, and would also increase the ^{14}C activity, causing the sample to appear too young. The water could be undergoing a more complicated, two-stage geochemical and isotopic evolution, first equilibrium in the soil zone and then in the aquifer. Two models for A_0 exist for such processes (Mook, 1976; Fontes and Garnier, 1979) but they are too complex to discuss here. The "age" of this sample, reported in Table 3, was calculated using the simple stoichiometric model first described above, but was confirmed by both the complex A_0 model calculations using a consistent input data set.

At this point, it is appropriate to discuss the meaning of ground-water "age" and significance of the numbers in the right-most column of Table 4. Like the rings in the heartwood of a tree, which fixed their ^{14}C content in different years, and which yields a composite age for a composite sample, the "age" of ground water is also a composite number. The pail full of water which flows from a spring during a minute clearly did not fall as a discrete pail of water at the recharge zone a specific number of years ago. Rather, it is an integration of many precipitation events, perhaps the melt of many snows, which has undergone further convective and dispersive mixing in the aquifer on its way to the discharge point. In an open, porous aquifer the "age" calculated here can be considered the mass-weighted mean subsurface residence time of the waters represented in the sample. In water controlled by flow in fractures, the "age" is an even more difficult concept which also incorporates the effect of flow paths of various flow rates. The waters from wells T3N R2E 10AAD and T3N R2E 10AAB were also sampled for tritium, the radioactive isotope of hydrogen having a half life of 12.36 years. These results are included in Table 3. Tritium is reported in Tritium Units (T.U.). One T.U. corresponds to an actual abundance of one ^{3}H atom for every 10^{18} atoms of ^{2}H. The results from the two Capitol Mall wells reported show very small, but measurable, amounts of tritium. Since precipitation contained on the order of 10 T.U. before the thermonuclear bomb test era, no ^{3}H should be detectable if all the water were on the order of 7000 years old. The small amount present shows that

even this water, coming up under considerable artesian pressure has had some small (probably less than two percent) contribution of mixed younger water, either in the aquifer or during sampling.

In conclusion, the mean subsurface residence times of the ground waters presented in this study are extremely valuable clues in the interpretation of the hydrologic system being studied, when used correctly, but should not be interpreted as hard and fast ages in an absolute sense.

Discharge and Estimated Aquifer Temperatures

Discharge temperatures fall into three general groups which are arbitrarily assigned as cool (0 to 30° C), warm (31 to 58° C) and hot (greater than 59° C). It should be noted that all measured discharge temperatures are more than 5° C above mean annual air temperature and therefore may be considered thermal.

Silica (Fournier and Rowe, 1966) and Na-K-Ca (Fournier and Truesdell, 1973; Fournier and Potter, 1979) geothermometers were used to estimate maximum aquifer temperatures (Table 4).

Temperatures estimated from geothermometers are valid only if several basic assumptions are met (Fournier and others, 1974): 1) the temperature-dependent reactions occur at depth, 2) an adequate supply of the temperature-dependent constituents are available, 3) water-rock equilibrium occurs at the reservoir temperature, 4) there is negligible reequilibration or change in composition of the water at lower temperatures near the surface, and 5) the water does not mix with hotter or colder water.

Fournier and others (1979) have shown that waters which plot on or near the equal temperature line (T °C SiO_2 = T °C Na-K-Ca) are probably waters which are unmixed or have reequilibrated with the aquifer skeleton after mixing. Calculated SiO^2 and Na-K-Ca are shown on Figure 12. For the most part, the discharge waters are undersaturated[1] with respect to amorphous silica, saturated to supersaturated with respect to chalcedony, and supersaturated

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[1] The degree of saturation is a measure of the thermodynamic tendency of a water to dissolve a particular mineral phase or species. Saturation is measured by the saturation index (SI). SI = log Ap/Kt. Saturation is defined as SI = 0.00 $\pm$ 0.1; undersaturation has negative values, and supersaturation has positive values.

TABLE 4. GEOTHERMOMETER TEMPERATURES AND SATURATION INDICES

Well Number	T_d	$T_{Na-K-Ca}$	T_{qt_3}	T_{silica}	T_{chalc}	SI_{qt_3}	SI_{silica}	SI_{chalc}
1. 5N 1E 35ACA1	40.0	87.4	92.8	−21.7	62.2	0.58	−0.33	0.20
2. 4N 1E 24DCC1	27.2	73.0	114.3	−3.3	85.4	0.98	0.03	0.56
3. 4N 2E 22BCD2	28.0	15.7	82.1	−30.7	50.9	0.66	−0.29	0.24
4. 4N 2E 22BCD1	42.5	55.8	93.5	−21.1	63.0	0.55	−0.35	0.18
5. 3N 2E 12CDD1	79.5	72.2	120.7	2.3	93.3	0.33	−0.45	−0.06
6. 3N 2E 11BAA1	74.0	85.4	81.7	31.0	50.5	0.00	−0.79	−0.28
7. 3N 2E 10AAD1	65.0	65.8	107.7	−9.0	78.2	0.35	−0.48	0.04
8. 3N 2E 10AAB1	70.5	64.2	106.8	−9.7	77.3	0.35	−0.46	0.06
9. 4N 2E 29ACD2	47.2	45.9	73.6	−37.7	42.0	0.27	−0.62	−0.09
10. 4N 2E 29ACD1	15.5	38.2	96.6	−18.4	66.3	1.00	0.00	0.54
11. 3N 2E 11ABC1	76.0	61.9	125.1	6.2	97.1	0.35	−0.44	0.07
12. 3N 2E 13ACB1	59.0	67.7	93.8	−20.8	63.4	0.25	−0.59	−0.07
13. 3N 2E 36ABC1	21.0	21.9	68.8	−41.7	36.9	0.62	−0.35	0.18
14. 4N 2E 04BDC1	29.0	176.0	75.1	−36.5	43.5	0.57	−0.37	0.16
15. 5N 1E 25BCC1	28.0	41.6	89.4	−24.5	58.6	0.69	−0.26	0.27
16. 5N 1E 26DCD1	29.0	53.3	82.1	−30.7	50.9	0.64	−0.31	0.22

T_d = measured discharge temperature

Geochemical thermometers: sodium−potassium−calcium, quartz, silica, chalcedony

SI = saturation index (logarithmic, 0 denotes equilibrium)

with respect to quartz. Temperature estimates for an under-
saturated water will tend to be low, and estimates for a super-
saturated water will tend to be high. Consequently, chalcedony
temperature estimates were plotted on Figure 12 unless SI_{chalc}
<-0.1, in which case quartz temperature estimates were used.

Many of the temperature values plot subtantially away from
the equal temperature line, suggesting mixed or non-thermally
equilibrated waters. Most of the data plots are above the equal
temperature line, which may result from mixed waters, a SiO_2
excess, gain in Na^+ or Ca^{2+}, or other factors.

Data points #1 and #14 plot substantially below the equal
temperature line. Because both of these waters are chalcedony
supersaturated and they do not exhibit an unusual K^+ concentration
which would shift their $Na^+ + K^+ + Ca^{2+}$ geothermometer temperature
below the equal temperature line, they may be mixed waters.

If Na^+ for Ca^{2+} cation exchange occurred at less than maximum
aquifer temperature, the resulting geothermometer disequilibrium
would tend to yield calculated Na-K-Ca temperatures which are too
high. Because most of the data plots are above the equal tem-
perature line, it would appear that this exchange has not
occurred after maximum aquifer temperatures were reached.
However, similar SiO_2 vs Na-K-Ca data plots can be obtained from
Na-Ca exchanged waters having a SiO_2 excess. At low temperatures,
such as found in the study area, metastable silica equilibrium
conditions are likely to exist. The extent of quartz and chalce-
dony supersaturation suggests the dissolved silica is controlled
by silicate phases other than quartz or chalcedony, possibly by
low temperature, near-surface, metastable equilibration with
amorphous silica. This condition would yield quartz and chalce-
dony predicted temperatures which are too high. Therefore,
silica temperatures are not considered reasonable predictors of
maximum aquifer temperatures.

Although the geothermometer aquifer temperatures do not
accurately predict maximum aquifer temperatures, they do provide
insight: 1) Maximum aquifer temperatures appear to be 100° C or
less. This estimate is consistent with measured discharge tem-
peratures, geothermometer predicted temperatures, and the absence
of an ^{18}O shift. 2) There is a general correlation between
high and low measured discharge temperatures and geothermometer
predicted high and low temperatures. This correlation suggests
the higher discharge temperatures are associated with aquifers
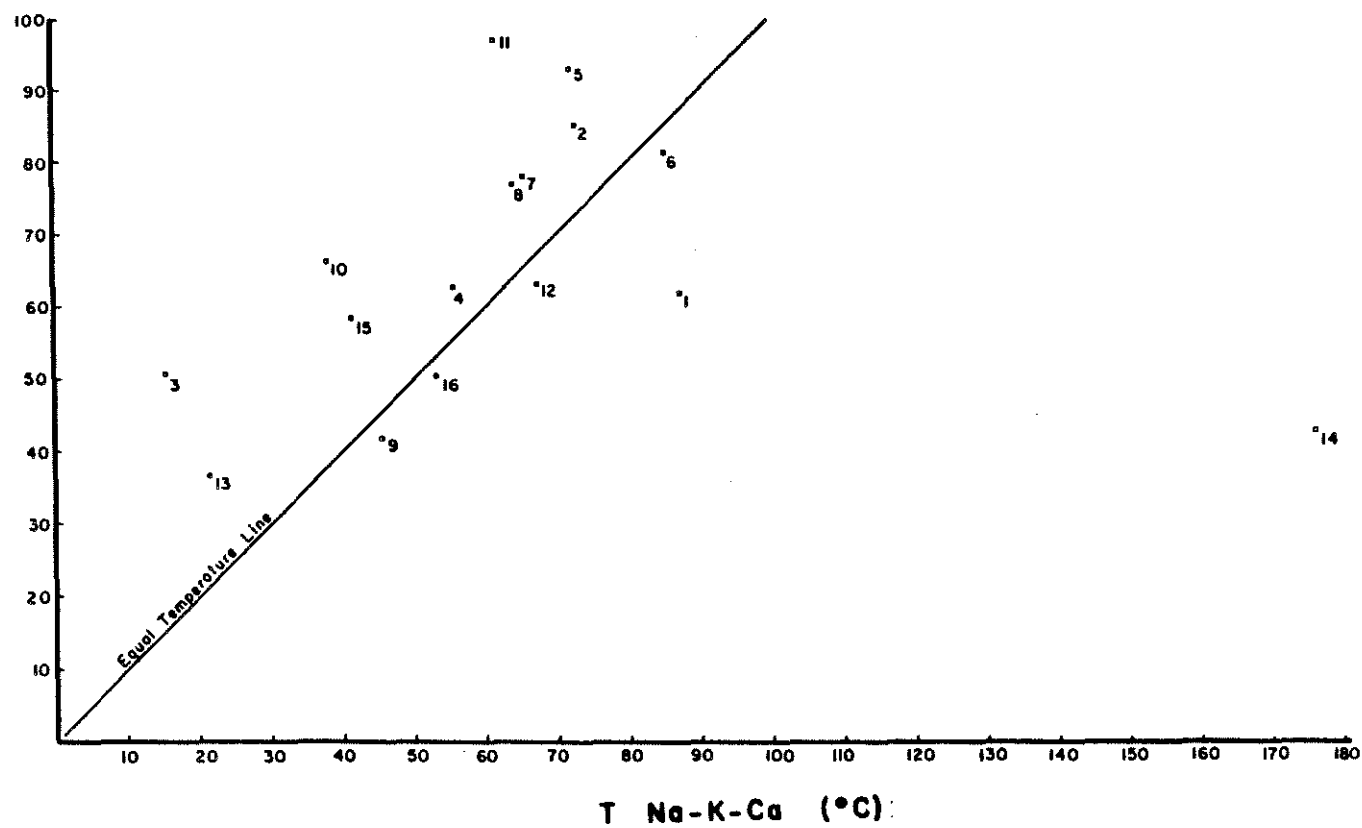having the highest subsurface temperatures.

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FIGURE 12. Geothermometer temperatures, Na-K-Ca versus chalcedony or quartz

V. DISCUSSION

Evaluation of the nature of the geothermal ground-water flow regime in the Boise area must encompass a wide range of geophysical, geological, hydrological, and geochemical data. Most of the information needed for a preliminary evaluation of the regime has been previously collected, although much of the details are incomplete. In this report we have attempted to bring together an overview of the existing data and to integrate this information with the chemical and isotopic data we have collected. In this section we will review the major parameters within which the geothermal regime is operating and we will discuss the implications these parameters have on the thermal flow patterns.

Shallow and deeper ground-water flow regimes coexist in the Boise area. These regimes are hydraulically isolated from each other by a thick sequence of low hydraulic conductivity strata commonly referred to, in most locations, as the "blue clay" horizon. This sequence is typically 100 to 200 meters below land surface. Shallow aquifers have low water temperatures, 12° to 15° C, are unconfined and have a water table below land surface. The deeper aquifers are thermal, 30° to 80° C, and are under considerable artesian pressure. Wells drawing water from the deeper aquifers commonly free flow at the surface. The difference in pressure heads between the two regimes effectively prevents the downward migration of colder water from the unconfined aquifers into the underlying thermal aquifers; thus, a local recharge source for the thermal aquifers is discounted. Radiocarbon ages support this conclusion, as the unconfined aquifers have modern or very young waters, whereas the deeper aquifers have much older water. The 500 year-old water found in well T4N R2E 22BCD1 has a temperature considerably greater than that typical of the upper aquifers, and it is thought the warm deeper water has mixed with the colder water in the well. The well is doubly constructed so as to tap the shallow and deep system.

Hydrostratigraphic units, having extensive areal continuity, have been designated on the basis of lithologic and hydrogeologic characteristics. From the limited data available, it appears that two hydrostratigraphic units, Siliceous Volcanics (1) and Siliceous Volcanics (2) of the Idavada Volcanics, are the most productive thermal aquifers, and therefore they seem to have greater hydraulic conductivities than do the other hydrostratigraphic units encountered below the "blue clay" horizon. Zones of greater hydraulic conductivity are capable of transmitting larger volumes of water at greater flow rates than comparable zones of less hydraulic conductivity.

Faults are of particular significance to the occurrence of thermal water in the Boise area. Warmer discharge temperatures

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are commonly clustered along or near fault traces, and the Foothills Fault zone, near the State Capitol area, has the hottest known discharge temperatures in this region of the western Snake River Plain (70° to 80° C). The Foothills Fault zone is also coincident with a linear region along which heat flow values are extremely high. Aquifer test data taken in the fault zone has demonstrated that the faults may be zones of increased hydraulic conductivities. Thus, highly faulted areas are believed to form avenues for vertical hydraulic communication between hydrostratigraphic units. Faulting often juxtaposes hydrostratigraphic units with differing hydraulic conductivities, which may tend to reduce lateral hydraulic communication. Aquifer tests conducted outside the fault zones also tend to confirm the faults as avenues of vertical hydraulic communication. In these tests, pumping from strata on one side of the fault commonly affects the water level in wells drawing water from the same strata on the other side of the fault even though the strata are no longer opposite each other.

Geochemical evidence also suggests the fault zones are the avenue of upward migration of thermal waters. The thermal waters are generally depleted in Ca^{2+} and enriched in Na^+ and F^-. An abundance of zeolites have been noted in cuttings taken from the Foothills Fault area. Zeolites are secondary minerals; hence their occurrence in fault zones is not unusual. Upward moving thermal waters in the fault zones may become depleted in Ca^{2+} and enriched in Na^+ by ionic exchange as the waters encounter the zeolites in the Idavada Volcanics. Dissolution of CaF_2 or a similar mineral would be possible and would result in the increased F^- concentration. Similar Ca^{2+}, Na^+ and F^- relationships could result from thermal ground waters encountering clay minerals in batholithic rocks.

The source of heat for the Boise geothermal system and its relationship to thermal flow patterns is the most difficult issue to resolve. Most researchers agree that radiogenic decay in the granitic rocks of the Idaho Batholith is the principal source of heat, and this heat is transferred to the surface and near surface by some mechanism associated with the deep seated faults along the Boise Foothills. Smith (1981) visualized the deep seated faults acting as near vertical conduits for a "forced convective system" along which, presumably, deeply circulating thermal water in the granitic rocks would arise. Burnham (1980) and Wood and Burnham (1983) also suggested the deep seated faults are the avenues along which deeply circulating thermal waters rise. In Burnham's model, the system is recharged in the granitic terrain at higher elevations to the north and east. The ground water then circulated to depth in the granitics along faults and fractures oriented obliquely to the deep seated frontal faults. However, $^2H/^1H$, $^{18}O/^{16}O$, and radiocarbon analyses raise questions about the possibility of the Boise thermal discharge waters having come from deep circulation in the granitic batholithic rocks.

The $2H/1H$ and $18O/16O$ analysis suggests the maximum aquifer temperatures of the discharge waters have not exceeded about 100° C. This is collaborated by the geochemical thermometers and the maximum discharge temperatures. Most thermal waters have discharge temperatures in the 40° to 50° C range, which may indicate they have not reached the elevated temperatures found in the State Capitol area. Mean ground-water ages and therefore mean residence times of water in the thermal aquifers range from about 4,000 to 17,000 radiocarbon years. Most of the thermal waters have a mean age of about 12,000 radiocarbon years, and there does not appear to be a relationship between aquifer temperature and radiocarbon age. Radiocarbon ages of about 12,000 years do not appear to be consistent with slow circulation patterns thought to be associated with deep circulation in fractured granites. Likewise, extremely deep circulation does not appear to be consistent with the maximum aquifer temperatures suggested by the $2H/1H$ and $18O/16O$ analyses and is even less consistent with maximum aquifer temperatures in the 40° to 50° C range. Shallow circulation in the granites could account for the radiocarbon dates; however, it probably would not elevate ground-water temperatures to 80° C and the linear heat flow anomaly would be difficult to explain.

The data on apparent water age and its lack of correlation with water temperature complicates any effort to describe the mechanics of the thermal-water system in the Boise area. These data do, however, suggest that water users and regulatory agencies should be concerned about the system's sustainable yield. Radiocarbon ages ranging from 4,000 to 17,000 years indicate that the pressures in the system have developed over many years.

Idaho water law will not necessarily protect artesian flow, but the economics of thermal-water use change significantly if pumping is required. Management strategies should seek to equilibrate withdrawals and recharge. Data should be collected on withdrawls from the system and their impact on aquifer pressures. Recharge can only be quantified when the dynamics of the system are known. The annual volume is likely to be small given precipitation patterns in the area and apparent fault control.

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