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WITH THE NAVAJO AQUIFER,
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**Paper for American Water Resources Association monograph on Mountain West U.S. Regional
Aquifers**

GEOCHEMISTRY OF WATER ASSOCIATED WITH THE NAVAJO SANDSTONE AQUIFER, SAN RAFAEL SWELL AREA, UTAH

by

Briant A. Kimball¹

ABSTRACT: Water samples collected from the Navajo aquifer in south-central Utah indicate that there are areas that have dissolved-solids concentrations larger than normal for the region. These larger concentrations result solely from chemical reactions between aquifer minerals and the ground water. Stable-isotope ratios of water samples collected from the aquifer indicate that, in some areas, water in the Navajo Aquifer may have acquired solutes from dissolving minerals in the Carmel Formation. Those ground-water samples with the greatest salinity have stable-isotope ratios characteristic of water in the Carmel Formation. After accounting for the sources of bicarbonate in these waters, the ages determined by ¹⁴C activity were corrected. The resulting ages ranged from 8,100 to 15,600 years in samples distant from recharge areas. This range corresponds to the high stand of late Pleistocene lakes, and may indicate that recharge occurred during wetter climatic conditions.

(KEY TERMS: Geochemistry, stable isotopes, ground-water dating.)

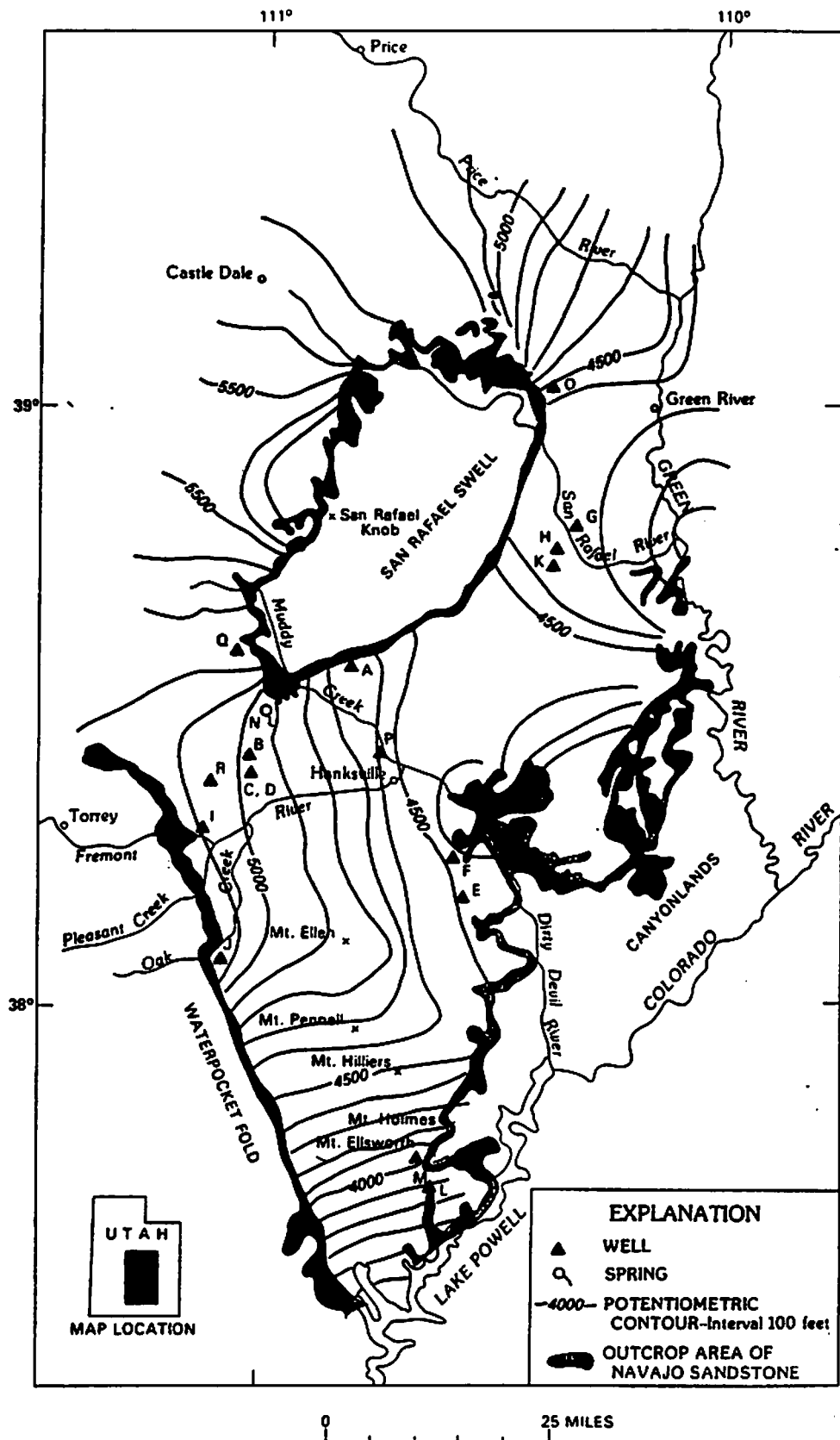
INTRODUCTION

Ground water has become an important resource in areas of the Western United States that are sometimes subject to drought. In a semi-arid climate, the use of ground water is analogous to mining a limited resource because there is relatively little potential recharge to keep pace with rates of pumping. In an effort to define the availability and quality of this resource in the Upper Colorado River Basin, a Regional Aquifer-System Analysis (RASA) study program was begun in 1981 (Taylor and others, 1983). The first study to tie local ground-water studies together into a regional perspective was by Price and Arnow (1974). One of the most important hydrogeologic units they describe is the Navajo-Nugget aquifer, or the Navajo aquifer, because it is near the land surface in much of south central Utah (fig. 1) and generally produces water that is suitable for most uses (Hood and Danielson, 1981). Hood and Danielson (1981) show a structure-contour map for the top of the Navajo Sandstone in this area. Based on their map, the Navjo Sandstone generally is less than 1,800 ft below the land surface, except in the Henry Moutain Basin east of the Waterpocket Fold, where the sandstone is as much as 5,900 ft deep.

Although most of the ground water associated with the Navajo Sandstone is fresh, with dissolved-solids concentrations less than 1,000 mg/L (milligrams per liter), saline water is found in some parts of the Navajo Sandstone as noted by Freethey and others (1984). Kimball (in press) has indicated that the source of saline water in the Navajo Sandstone in the Four Corners area of Utah (east of the area shown in fig. 1) is the underlying Paleozoic hydrogeologic units. The purpose of this paper is to describe the geochemistry of water in the Navajo Sandstone near the San Rafael Swell to help identify the source of saline water. To investigate the source of saline water in the Navajo Sandstone, samples of water were obtained from 17 artesian wells and 2 springs. Some of the wells were sampled more than once, and at site J two different, nearby wells were sampled. Standard methods were used to collect samples for determination of concentrations of major ions, stable isotopes, and radiocarbon (Rainwater and Thatcher, 1960; Brown and others, 1970; Wood, 1976). Alkalinity, which is principally bicarbonate alkalinity, was determined by titration on site and calculated by the Gran method (Stumm and Morgan 1981). Locations of wells and springs that were sampled for this study, contours of potentiometric head, and outcrop locations for the Navajo Sandstone are shown in figure 1. Letters are used to designate the sites for reference to tables and subsequent figures presented in this paper.

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Figure 1.--Location of sampling sites, physiographic features, outcrop area
of the Navajo Sandstone, and altitude of the potentiometric surface. --



The Navajo Sandstone of early Mesozoic age crops out around the edge of the San Rafael Swell, along the Waterpocket fold, and also where deep canyons are incised into the rocks near the Canyonlands area to the east. In the area bounded by these geologic and physiographic features, ground water commonly occurs under artesian head (Hood and Danielson, 1981). The general direction of ground-water movement is eastward from recharge areas along the San Rafael Swell and southward from recharge areas along the Waterpocket fold. Discharge areas are in the Canyonlands area, where the rocks of the Navajo Sandstone are cut by streams, and to the south in the vicinity of Lake Powell (Weiss, 1987).

The Carmel Formation overlies the Navajo Sandstone. It is principally siltstone and limestone and is a confining unit between the underlying Navajo Sandstone and the overlying Entrada Sandstone of Jurassic age. Most of the recharge to the Navajo Sandstone occurs in the mountainous areas to the west of the area shown in figure 1 (Hood and Danielson, 1981). Streams crossing the Navajo Sandstone outcrop, principally Muddy Creek and the San Rafael River, also provide some recharge. In areas affected by folding and faulting, water may move through the Carmel Formation into the Navajo Sandstone. Hood and Danielson (1981) specifically describe the possibility of this movement near the west flank of the San Rafael Swell, east of the Waterpocket Fold, and in the Red Desert (at wells B, C, and D; fig. 1). The Entrada Sandstone crops out over much of the area, where precipitation can directly recharge the aquifer. In some places, folding and faulting can increase hydraulic connection between the Entrada and Navajo Sandstones. Where there is movement of water through the Carmel Formation to the Navajo Sandstone, solutes are acquired by the water. Solute from minerals dissolved from the Carmel Formation provide an isotopic signature that is distinct from that of solutes from the Navajo Sandstone.

GEOCHEMISTRY OF THE AQUIFER WATER

Results of chemical determinations for samples collected during this study are listed in table 1. The data are grouped by hydrogeologic unit and then sorted on the basis of increasing dissolved-solids concentration within each unit. In addition, Hood and Danielson (1981) reported that samples of water collected from the Navajo Sandstone, southwest of the San Rafael Swell have dissolved-solids concentrations as much as 76,000 mg/L. Although the samples listed in table 1 have much smaller dissolved-solids concentrations, they do represent water from the Navajo Sandstone that has been affected by mixing with more saline water. The large concentrations of dissolved solids that are present in underlying Paleozoic hydrogeologic units should affect the salinity of water in the Navajo Sandstone if there is any upward leakage (Kimball, in press). However, water in the rocks in upper Paleozoic and the Navajo Sandstone does not reflect the salinity and sodium chloride character of underlying units in this area, indicating that upward movement does not occur (Lindner-Lunsford and others, in press). Weiss (1987) suggests that movement of water is downward, not upward, in the aquifers in Paleozoic rocks.

The sample collected from a spring that discharges from the Carmel Formation is the most saline of all the samples; its dissolved-solids concentration is very near the median of all the samples from the Carmel Formation that have been obtained during the RASA study. The major constituents are sodium, chloride, and sulfate. These solutes are acquired from dissolution of halite and gypsum in the Carmel Formation (Hood and Danielson, 1981). Much smaller concentrations of solutes were determined in samples collected from a spring discharging from the Entrada Sandstone and from wells in the Navajo Sandstone. Major constituents of the samples that have dissolved-solids concentrations less than about 500 mg/L are calcium, magnesium, and bicarbonate (reported as alkalinity). These also are the principal solutes in samples collected from wells A and O (table 1), both of which are near the recharge areas of the San Rafael Swell (fig. 1). If the dissolution of carbonate minerals is the principal source of these solutes, then the milliequivalent ratio of the alkaline-earth (calcium and magnesium) metals to alkalinity should be about 1, because an equal number of equivalents of cations and anions are produced by dissolving both calcite and dolomite (see equations under section "Ground-water ages"). This is true of those samples collected from wells near recharge areas that plot along the equal-equivalents line (fig.--2). Other samples,—particularly

Table 1.--Chemical determinations of samples from the San Rafael Swell area, Utah

[Site letter, identifier for locations in figure 1, (s) indicates spring rather than well; Lat, latitude, in decimal degrees; Long, longitude, in decimal degrees; pH, in log units; Temp, temperature in degrees Celsius; DS, dissolved solids; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Cl, chloride; SO₄, sulfate; Alk, field-titration alkalinity, as CaCO₃; SiO₂, silica; dashes, missing values.]

Site letter	Lat	Long	pH (units)	Temp	Major ions, in milligrams per liter								Alk	SiO ₂
					DS	Ca	Mg	Na	K	Cl	SO ₄			
												in milligrams per liter		
Entrada Sandstone														
V(s)	38.0625	111.0833	7.80	15.0	403	77	22	33.0	2.1	13.0	70	284	19.0	
Carmel Formation														
N(s)	38.4733	111.0122	7.60	23.0	4,710	250	65	1,400	6.9	1,900	1,000	185	10.0	
Navajo Sandstone														
J1	38.0733	111.0861	8.05	13.5	153	34	14	3.1	1.5	4.1	22	126	10.0	
J2	38.0650	111.0794	--	--	177	32	20	6.5	2.5	2.8	26	144	9.6	
E	--	--	7.80	--	259	28	37	7.8	2.5	2.6	61	181	11	
			6.20	24.5	262	30	37	8	2.4	2.6	62	180	12	
L	37.6628	110.6339	7.70	21.0	271	33	25	24	4.3	4.2	61	179	11	
M	37.6853	110.6964	7.70	22.0	272	30	20	35	5.9	3.7	53	182	14	
O	39.0339	110.3964	7.10	15.0	274	85	36	20	8.9	8.3	150	274	9.9	
F	38.2447	110.6078	--	--	368	59	31	26	7.5	15.0	110	196	11	
I	38.2850	111.1450	6.60	14.5	507	84	42	12	4.6	9.5	250	136	12	
H	38.7139	110.3808	7.40	15.0	508	75	48	15	7.4	4.6	230	174	8.6	
I	38.2850	111.1450	6.80	15.0	512	78	40	11	4.6	9.6	230	144	11	
A	38.5906	110.7031	7.10	18.5	513	71	66	11	6.9	3.8	180	273	9.5	
H	38.7139	110.3808	7.50	14.5	515	73	48	15	7.4	4.7	220	190	8.3	
A	38.5906	110.7031	6.90	18.5	523	72	66	10	6.9	3.9	190	273	9.2	
			7.40	18.0	540	68	67	11	6.6	3.7	200	290	9	
R	38.3414	111.1560	--	--	862	106	70	57	3.8	14.0	489	200	11	
D	38.3261	111.0564	7.60	16.0	931	110	54	120	4.8	130.0	380	203	10	
			6.20	16.0	946	110	52	120	4.6	140.0	390	194	10	
			7.60	16.0	960	120	55	120	4.7	140.0	390	202	10	
G	--	--	7.10	15.5	1,010	160	63	62	15.0	22.0	540	210	8.2	
K	38.6836	110.3994	7.20	15.0	1,500	240	95	66	18.0	30.0	830	228	8.4	
B	38.3400	111.0750	6.50	18.0	1,900	150	55	420	4.0	440.0	670	247	10	
			6.50	18.0	1,900	150	55	420	4.1	460.0	650	247	10	
			7.50	17.0	1,910	160	57	420	4.1	440.0	670	260	9.7	
Q	38.5856	111.0847	--	--	2,530	435	152	136	10.0	134.0	1,470	312	8.1	
C	38.3389	111.0628	--	--	2,560	86	30	821	4.9	846.0	627	236	9.5	
P	38.4131	110.6961	--	--	2,910	130	53	920	11.0	1,700.0	11	147	10	

those with larger dissolved-solids concentrations, have an alkaline-earth excess. Calcium continues to increase as dissolved solids increase, but not because of the dissolution of carbonate minerals.

The increase in dissolved-solids concentration among the samples mostly is from increases in sodium, calcium, chloride, and sulfate. The trend of calcium with sulfate (fig. 3) indicates a proportional increase of both solutes at concentrations greater than about 150 mg/L. Such a proportional increase indicates the dissolution of gypsum. Likewise, the trend of sodium with chloride (fig. 4) indicates a proportional increase at larger concentrations because of the dissolution of halite. However, these minerals are not present in the Navajo Sandstone; the dissolution must occur as water passes through a different hydrogeologic unit.

INDICATIONS OF SOLUTE ORIGIN

The source of particular solutes in ground water sometimes can be determined by ratios of stable isotopes that are characteristic of a particular source (Frape and others, 1984). Isotopic data are listed in table 2. These data also are grouped by hydrogeologic unit and then sorted based on increasing dissolved-solids concentration.

Isotopes of oxygen, hydrogen, carbon, and sulfur were determined only for samples from selected wells. The radioactive isotope ^{14}C (carbon 14) also was determined. These isotopes can provide an indication of the length of time ground water has been isolated from the atmosphere. Stable isotope ratios were determined for $\delta^{18}\text{O}$ (the ratio of ^{18}O to ^{16}O), δD (the ratio of ^2H to ^1H), $\delta^{13}\text{C}$ (the ratio of ^{13}C to ^{12}C), and $\delta^{34}\text{S}$ (the ratio of ^{34}S to ^{32}S in sulfate). These are reported in the delta notation that compares the ratio in the sample to that in a standard, and the difference is reported as parts per thousand (permil) greater than or less than the standard (Fritz and Fontes, 1980). Thus, a negative permil determination indicates that there is more depletion of the heavier isotope in the sample than in the standard; a positive permil determination means that there is more enrichment of the heavier isotope in the sample than in the standard.

The relation of δD to $\delta^{18}\text{O}$ (fig. 5) indicates that the water in the Navajo aquifer is derived from meteoric water. That is, recharge is from precipitation, and no other processes affect the ratio of these two stable isotopes. None of the samples seems to have undergone evaporation nor do they contain water associated with the brines of the Paradox basin (Kimball, in press). The ratio of δD with $\delta^{18}\text{O}$ is offset from the global meteoric water line by a small shift that results in a local meteoric water line.

There are systematic changes in $\delta^{13}\text{C}$ among the ground-water samples (fig. 6). In general, samples from wells located closest to the recharge areas have the most negative $\delta^{13}\text{C}$. The most negative $\delta^{13}\text{C}$ is from the Entrada Sandstone. A $\delta^{13}\text{C}$ of soil-gas carbon dioxide was not determined, but can be estimated from the ^{14}C activity in water from wells located nearest the recharge areas. Wells I and J2 (table 2) have activities of about 42 pmc (percent modern ^{14}C activity). Because these wells are near recharge areas and have the largest ^{14}C activities, they are assumed to yield "modern" water. A soil-gas $\delta^{13}\text{C}$ can then be calculated from the diluted ^{14}C activity and the $\delta^{13}\text{C}$ in the water sample as:

$$\delta^{13}\text{C}_s = \frac{\delta^{13}\text{C}_w}{A_s} \times 100$$

where

$$\begin{aligned} \delta^{13}\text{C} &= \text{soil-gas } \delta^{13}\text{C}; \\ \delta^{13}\text{C}^s &= \delta^{13}\text{C} \text{ of the sample; and} \\ A_s &= ^{14}\text{C} \text{ activity in the sample.} \end{aligned}$$

The calculation for wells I and J2 gives $\delta^{13}\text{C}$ of -17.8 permil. Each of the other samples represents a mixture of the active ^{14}C in soil carbon dioxide and dead, or inactive, carbon from mineral dissolution.

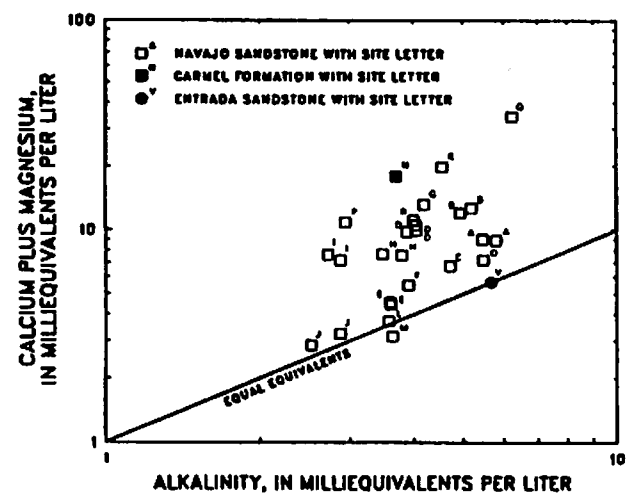
Table 2.--Isotopic determinations and age corrections

[Site letter, identifier for locations in figure 1, (s) indicates spring sample; DS, dissolved solids, in milligrams per liter; $\delta^{18}\text{O}$, oxygen 18/16 ratio, in permil; δD , hydrogen 2/1 ratio, in permil; $\delta^{13}\text{C}$, carbon 13/12 ratio, in permil; $\delta^{34}\text{S}$, sulfur 34/32 ratio, in permil; A_s , carbon 14 activity, in percent modern ^{14}C activity; dashes indicate that value was not determined]

Site	DS	$\delta^{18}\text{O}$	δD	$\delta^{13}\text{C}$	$\delta^{34}\text{S}$	A_s	A_o	Age	
								Apparent	Corrected
Entrada Sandstone									
V(s)	403	-11.6	-96.0	-10.6	17.1	--	58.9	--	--
Carmel Formation									
N(s)	4,710	-15.2	-114.0	-4.1	6.0	--	22.8	--	--
Navajo Sandstone									
J1	153	-12.2	-95.0	-5.7	12.2	29.6	31.7	10,100	560
J2	177	-12.3	-95.0	-7.5	--	42.1	41.7	7,150	modern
E	259	-13.9	-100.0	-8.2	--	--	45.6	--	--
	262	-14.0	-100.0	-7.6	--	--	42.2	--	--
L	271	--	--	--	--	13.0	--	16,900	--
M	272	-15.8	-121.0	--	12.0	8.0	--	20,900	--
O	274	-13.8	-109.0	-5.8	-5.9	7.0	32.2	22,000	12,600
F	368	-15.2	-118.0	-6.0	--	8.9	33.1	20,000	10,900
I	507	-14.3	-109.0	-6.5	--	--	36.1	--	--
H	508	-12.8	-98.5	-6.4	--	--	35.6	--	--
I	512	-14.3	-113.0	-7.4	5.1	41.6	41.1	7,250	modern
A	513	-11.1	-85.0	-5.9	--	--	32.8	--	--
H	515	-12.8	-102.0	-6.5	-0.9	5.5	36.1	24,000	15,600
A	523	-11.2	-82.5	-5.6	--	--	31.1	--	--
	540	-11.3	-92.0	-6.4	-21.9	6.0	35.6	23,300	14,700
R	862	-10.6	-90.0	-5.6	11.2	6.2	31.3	23,000	13,400
D	931	--	--	--	--	--	--	--	--
	946	-12.0	-88.0	-4.0	--	--	22.2	--	--
	960	-12.0	-91.5	-4.5	7.8	--	25.0	--	--
G	1,010	-13.8	-105.0	-5.8	--	--	32.2	--	--
K	1,500	-13.9	-112.0	-6.9	6.2	--	38.3	--	--
B	1,900	-13.0	-97.5	-3.5	--	--	19.4	--	--
	1,900	-12.7	-97.0	-2.2	--	--	12.2	--	--
	1,910	-13.1	-104.0	-2.9	0.9	3.9	16.1	26,800	11,700
Q	2,530	-12.8	-100.0	0.4	4.8	2.1	5.6	31,900	8,100
C	2,560	-13.3	-102.0	-4.1	9.6	5.6	22.8	23,800	11,600
P	2,910	-14.0	-110.0	-5.4	6.9	5.0	30.2	24,800	14,900

Figure 2.--Relation of alkaline-earth metals to alkalinity.

Figure 3.--Relation of calcium to sulfate.



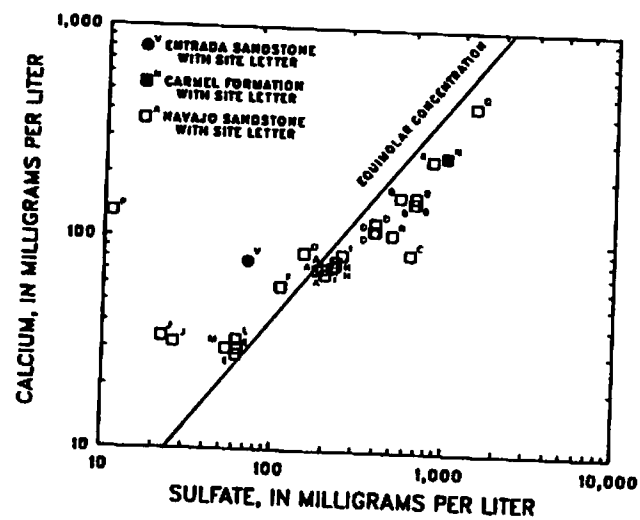
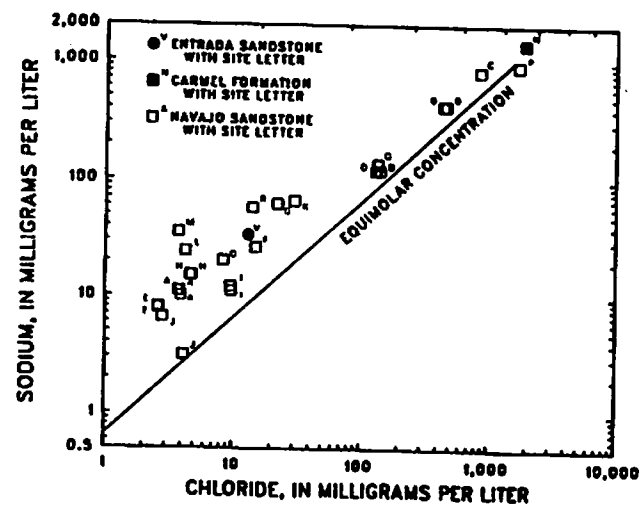


Figure 4.--Relation of sodium to chloride.



The extent of the mixture is reflected by the changes in $\delta^{13}\text{C}$. From the lightest value of $\delta^{13}\text{C}$, there is a general trend to heavier values with the increase of sulfate concentration (fig. 6). This may indicate that the formation containing dissolving sulfate minerals may also contain dissolving carbonates with a heavier $\delta^{13}\text{C}$. Marine carbonates, as suggested by Keith and Weber (1964), typically are near 0 permil. This agrees with the trend observed in these data. Dissolution of carbonate minerals in the marine Carmel Formation should produce water that has a heavier $\delta^{13}\text{C}$. If the addition of sulfate represents solutes from the Carmel Formation, then the $\delta^{13}\text{C}$ dilution comes from marine $\delta^{13}\text{C}$ of the Carmel Formation.

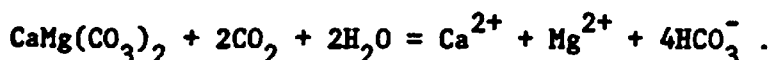
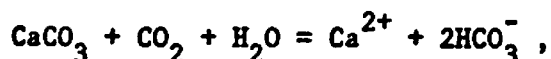
The value of $\delta^{34}\text{S}$ also should reflect the acquisition of solutes from the Carmel Formation. Values of $\delta^{34}\text{S}$ at small sulfate concentrations range from -21 to +18 permil (fig. 7). In samples that have larger sulfate concentrations the range becomes more restricted, from about 0 to +10 permil. In those three samples K, N, and Q that have the largest sulfate concentrations, the value of $\delta^{34}\text{S}$ is restricted to about 6 permil. Sample N is from the Carmel Formation and represents dissolution of gypsum in the water from the Carmel Formation. This convergence of $\delta^{34}\text{S}$ values as sulfate concentration increases indicates that the source of sulfate is gypsum that occurs in the Carmel Formation.

Spatial trends in the concentrations of major solutes and stable isotopes in water samples from wells in the Navajo aquifer indicate that the increase of dissolved solids may be related to local structural features. Those samples collected closest to recharge areas, principally from wells near the Waterpocket fold and the San Rafael Swell, have the smallest concentrations of dissolved solids and the lightest $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$. Samples from wells in the Red Desert, centered on the Caineville anticline, have larger concentrations of dissolved solids, calcium, sodium, sulfate, and chloride. The same samples have the heaviest $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$. The Caineville anticline, because of fracturing, may allow water from the Entrada Sandstone to move downward through the Carmel Formation to the Navajo Sandstone. Although the quantity of water movement may be small, the effect on solutes seems to be important.

GROUND-WATER AGES

Activities of ^{14}C listed in table 2 represent apparent ages of the ground water. To correct the apparent age of the ground water, an accounting needs to be made of each source of carbon in the ground water that would dilute the ^{14}C in recharge carbon dioxide and not the composite carbon in the sample (Wigley and others, 1978, 1979; Plummer and others, 1983; Kimball, 1984). The calculations can be complex since there may be several sources of carbon; some sources may contribute "active" ^{14}C , and others that may contribute "dead" carbon, or carbon with no measurable ^{14}C . It is beyond the scope of this paper to present the detailed calculations, but some general calculations will be made.

Bicarbonate is almost exactly balanced by the calcium and magnesium concentrations in these water samples indicating that calcite and dolomite are the principal sources of bicarbonate along with soil-gas carbon dioxide. This is shown in the following reactions.



One can account for the bicarbonate in solution by the change in $\delta^{13}\text{C}$ and then use this mass balance to correct for ^{14}C also. The equation for this calculation comes from Ingerson and Pierson (1964). The equation is:

$$A_o = \frac{\delta^{13}\text{C}}{-18} \times 100 \text{ pmc.}$$

A soil-gas carbon dioxide of -18 permil is the rounded value of soil-gas carbon dioxide calculated above. From this dilution activity, A_o , and the sample activity, A_s , a corrected age is calculated from the general age equation:

$$t = \frac{\tau}{\ln(2)} \times \ln \frac{A_o}{A_s},$$

where

t = the age of the ground water;
 τ = the half-life in time units; and
 A_o = the dilution activity, and
 A_s = the activity of the sample.

For ^{14}C , τ is equal to 5730 +/- 30 years. The values of A_o and the corrected ages calculated for these waters are listed in table 2.

Even this simple correction suggests a large change to the apparent ages. Well J1 has an age of about 600 years. This means that ground water from the nearby Waterpocket fold is traveling at a rate of about 12 feet per year. Wells at J2 and I were used for the calculation of soil-gas carbon dioxide and so they are assumed to be modern water. The most noticeable point about the other calculated ages is that they only range from about 8,100 to 15,600 years. The uncorrected or apparent ages range from 7,150 to 31,900 years. The corrected range bridges the proposed time period of the last major stand of Lake Bonneville and Lake Lahontan, or a time of wetter climatic conditions (Spencer and others, 1984; Currey and Oviatt, 1985; Benson and Thompson, 1987). This implies that most of the recharge to the aquifer occurred during different climatic conditions than those of the present time. Thus, increased recharge rates may have prevailed at that time.

CONCLUSIONS

Isotopic data have helped to identify sources of water and sources of solutes in the Navajo aquifer, part of the Navajo aquifer. The main conclusions of this isotopic study are:

1. Water in the Navajo Sandstone is from recharge of meteoric water. Isotopic signatures do not indicate upward leakage from underlying units.

2. Solutes in the Navajo Sandstone are acquired from water-rock reactions within the aquifer but also are acquired from dissolution reactions in the Carmel Formation as water moves through the formation. This is supported by the trends in stable isotopes as the concentration of sulfate increases in the aquifer.

3. Ground-water ages, determined from ^{14}C measurements, can be refined by considering the geochemical reactions that affect the total inorganic carbon of the water. The ages of the water correspond to a time of wetter climatic conditions in the range of 8,100 to 15,600 years ago.

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