Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri*

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Abstract—Na-Ca-Cl groundwaters with salinities of 1 to 30‰ discharge from natural springs and artesian wells in Mississippian carbonates and Ordovician sandstones and carbonates in central Missouri. Carbonate saturation and quartz supersaturation are maintained throughout the salinity range. Major and trace element and isotopic variations in the waters are used to place constraints on models for rock-water interaction and regional hydrology.

The groundwaters have δD values that range from -108 to -45‰ and $\delta^{18}O$ values that range from -14.7 to -6.5‰ (SMOW). These data lie approximately along the meteoric water line, ranging from values similar to local recharge in Missouri, to significantly lower values that are similar to $\delta^{18}O$ and δD for meteoric recharge in high altitude and high latitude regions of North America. The more saline samples have the lowest ^{18}O and D contents, a trend that is opposite to that observed in most other studies of saline waters. The H-O isotopic correlation and the range in salinity and several major and trace element concentrations in central Missouri groundwaters are readily explained by a saline-dilute water mixing model. $^{87}Sr/^{86}Sr$ ratios for the groundwaters range from 0.7155 to 0.7161. These values are significantly higher than previously published values for: 1) estimates of $^{87}Sr/^{86}Sr$ in Phanerozoic seawater (0.7068–0.7092); and 2) carbonates of the Mississippian Burlington-Keokuk Fm. (0.7075–0.7105), through which some of the waters migrate as they pass to the surface. $\epsilon_{Nd}(0)$ values in the groundwaters range from -10.9 to -8.1, and $^{147}Sm/^{144}Nd$ ratios range from 0.108 to 0.128. These values are similar to or lower than previously published analyses of carbonates and other authigenic phases from the Burlington-Keokuk Fm. (mean $\epsilon_{Nd}(0) = -7.8 \pm 0.8$ (1σ); mean $^{147}Sm/^{144}Nd = 0.141$).

The H, O, Sr and Nd isotopic data and the results of model calculations preclude: 1) models involving the modification of ancient seawater for the origin of the saline waters, and 2) extensive interaction between the groundwaters and their host carbonates. The waters apparently acquired their $\delta^{18}O$ and δD values as meteoric recharge and their $^{87}Sr/^{86}Sr$ and rare earth element signatures from extraformational crustal sources (high $^{87}Sr/^{86}Sr$; low $\epsilon_{Nd}(0)$; low $^{147}Sm/^{144}Nd$) and largely preserved these isotopic signatures during subsequent migration through the carbonates. Chemical exchange *via* rock-water interaction is required for isotopic exchange to occur. Therefore, the present state of chemical equilibrium between the groundwaters and carbonate aquifer minerals may serve to limit rock-water interaction, and hence preserve the extraformational isotopic signatures in the waters.

The integration of geochemical, isotopic and hydrologic data on a local and regional scale suggests a history for the central Missouri groundwaters involving: 1) meteoric recharge in the Front Range of Colorado; 2) dissolution of Permian halite in the subsurface of Kansas; 3) interaction with predominantly silicate mineral assemblages in Paleozoic strata (and possibly Precambrian basement), with aquisition of crustal Sr and REE signatures; 4) dilution and migration to shallow aquifer levels in central Missouri; and 5) mixing with local meteoric recharge and discharge through Mississippian carbonates with no significant change of the isotopic signatures acquired in stage (3).

INTRODUCTION

THE ORIGIN OF SALINE water in sedimentary aquifers has variously been ascribed to processes of seawater evaporation, dissolution of evaporite deposits and shale-membrane filtration of meteoric water (GRAF *et al.*, 1966; CARPENTER, 1978; HANOR, 1979). The effects of mineral-solution equilibria and ion exchange during the residence of fluids in sedimentary basins play crucial roles in the subsequent chemical evolution of such saline fluids (LAND, 1987). These same processes have mutually important effects on sediment diagenesis and ore deposition (SVERJENSKY, 1986). Therefore, in order to understand the genesis of any formation water, it is essential to evaluate the extent to which rock-water interaction has modified the water during its migration history. Our understanding of these processes has been improved through the use of major and trace element concentrations, organic speciation and the

isotopic distributions of H, O and C (*e.g.*, CLAYTON *et al.*, 1966; CARPENTER *et al.*, 1974; KHARAKA *et al.*, 1986). Radiogenic isotopes of Sr, Pb and Nd have not been as widely applied, but several studies of the isotopic composition of Sr in subsurface brines have demonstrated the utility of this technique as a hydrologic tracer (SUNWALL and PUSHKAR, 1979; STARINSKY *et al.*, 1983; STUEBER *et al.*, 1984, 1987; McNUTT *et al.*, 1984; CHAUDHURI *et al.*, 1987).

The distribution of Nd isotopes and the rare earth elements (REE) in sedimentary environments has several potential applications to understanding the rock-water interaction history of sedimentary pore fluids. Sediments, having different ages and depositional and diagenetic histories, can have diagnostic Nd isotope ratios and REE patterns due to variations in provenance and fractionation in aqueous environments (McCULLOCH and WASSERBURG, 1978; SHAW and WASSERBURG, 1985; BANNER *et al.*, 1988a). These differences may be imposed on formation waters during rock-water interaction. As a consequence of the large enrichment of REE in most sediments (1–100 ppm Nd; PIPER, 1974) relative to

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seawater and riverwater (10^{-6}–10^{-3} ppm Nd; PIEPGRAS and WASSERBURG, 1980; GOLDSTEIN and JACOBSEN, 1987), a diagenetic fluid with such low REE contents will acquire the REE signature of its host rock at extremely low rock:water ratios during rock-water interaction. Therefore, it would be expected that the Nd isotope and REE systematics in a subsurface fluid would reflect the most recent stages of rock-water interaction that the fluid had experienced.

Groundwaters with salinities ranging from 1 to 30‰ discharge from Mississippian carbonates and Ordovician sandstones and carbonates *via* natural springs and artesian wells in the Saline County area of central Missouri (Figs. 1 and 2). In their study of the major and trace element geochemistry of saline groundwater from 21 localities in this region, CARPENTER and MILLER (1969) concluded that water compositions are controlled to a large extent by reactions with carbonate and silicate minerals in central Missouri aquifer rocks. Previous studies have been made on the Nd, Sr and O isotopic compositions and REE abundances of sediments from the Mississippian Burlington-Keokuk Fm. in Missouri, Iowa and Illinois (BANNER *et al.*, 1988a, 1989), which is a principal aquifer in this region that some of the groundwaters pass through during their migration to the surface. In this study, we present H, O, Nd and Sr isotopic and major and trace element data for saline groundwaters from several localities in the Saline County area. The isotopic data for both the

FIG. 2. (a) Distribution of Mississippian and Pennsylvanian rocks in Missouri. These rocks are not present in central and southeastern Missouri. Study area indicates outline of Saline County. (b) Groundwater salinities in Mississippian rocks in Missouri. Salinities expressed as total dissolved solids (TDS), in permil. The trend of increasing salinity extends westward into Kansas (data from JORGENSEN *et al.*, 1986, and MILLER, 1971). The contact between saline (>1‰ TDS) and fresh groundwater approximates the lithologic contact between Mississippian and Pennsylvanian rocks. Arrows show generalized groundwater flow directions, based on equivalent freshwater head contours in IMES (1985), JORGENSEN *et al.* (1986), YOUNG *et al.* (1986) and IMES and EMMETT (1989). Similar salinity distributions and flow directions are obtained for Cambrian-Ordovician rocks in Missouri.
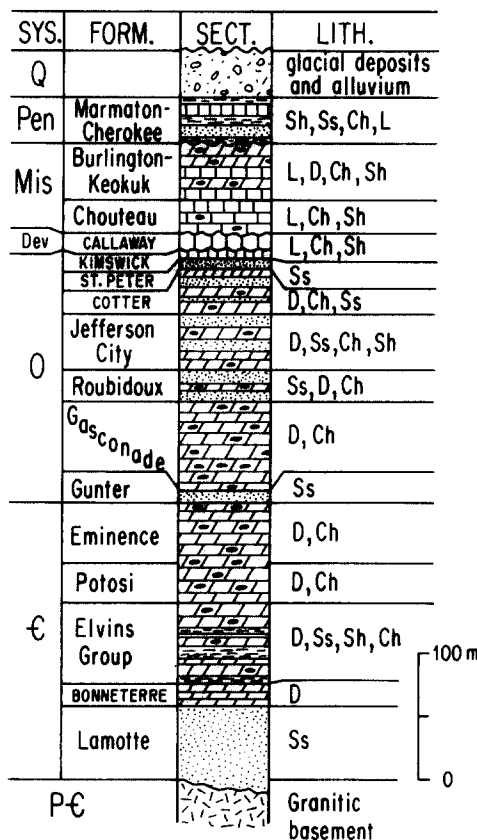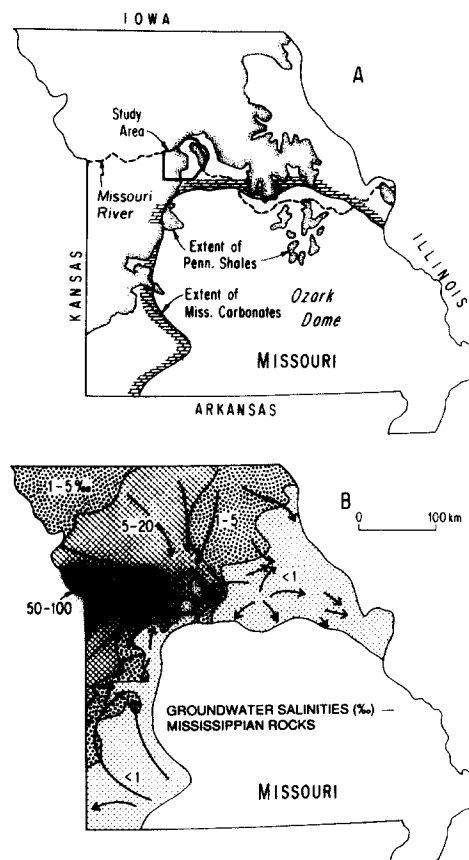

FIG. 1. Generalized lithostratigraphic section in central Missouri after MILLER (1971). L = limestone, D = dolostone, Ch = chert, Ss = sandstone, Sh = shale.

groundwaters and their present aquifer rocks provide a basis for constructing quantitative models of isotopic exchange during rock-water interaction. Considering the low REE concentrations of most seawater and river water samples measured to date, the springs offer an opportunity to measure the isotopic composition of small amounts of Nd in saline subsurface waters that have not been exposed to potential sources of anthropogenic contamination such as well casings and drilling fluids. In order to assess the degree to which various elements are associated with particulate matter in the waters, we have made measurements on both filtered (0.4, 0.1, 0.025 μ pore sizes) and unfiltered aliquots of individual samples. The calculation of mineral saturation states and isotopic exchange during rock-water interaction and an integration of geochemical data with regional hydrogeology are used to test hypotheses for the origin and evolution of the chemical characteristics of the waters.

HYDROGEOLOGIC SETTING

In central Missouri, approximately 600 m of nearly horizontal Paleozoic sediments lie on Precambrian crystalline basement (Fig. 1). Cambrian-Ordovician rocks are predominantly dolostone and sandstone, with chert, argillaceous carbonates and shale occurring in smaller amounts. Devonian and Mississippian rocks are primarily limestone, dolostone and chert, with minor amounts of shale. Pennsylvanian rocks comprise thin-bedded shales and limestones, micaceous sandstones, and thin coal seams. Quaternary sediments consist of Pleistocene glacial deposits and Holocene alluvium. Mississippian carbonates and Pennsylvanian shales are the predominant bedrock lithologies exposed in the Saline County area, with Mississippian carbonates extending up to 100 m into the subsurface (MILLER, 1971). A regional NE-SW contact between the two extends through Saline County (Fig. 2a). Carbonates and sandstones of Cambrian-Ordovician through Mississippian age constitute the principal aquifers in this region, while Pennsylvanian shales serve to confine underlying Mississippian aquifers.

The regional hydrology of the central midwestern United States comprises several major aquifer systems. To the west and southwest of central Missouri, subsurface waters become increasingly saline (Fig. 2b) and reach salinities in excess of 200‰ in both Mississippian and Cambrian-Ordovician rocks in northern Oklahoma (JORGENSEN et al., 1986). Regional flow of this saline groundwater in Kansas, northern Oklahoma and western Missouri is primarily eastward (CHRISTENSON and ADAMS, 1988; JORGENSEN et al., 1989; SIGNOR, 1988). In southern and central Missouri, regional flow in this system encounters a freshwater system that recharges locally and from the Ozarks (Fig. 2b). North of the Missouri River, groundwater in Cambrian-Ordovician rocks flows to this region from the northwest (YOUNG et al., 1986).

The saline springs of Saline and Howard Counties have been investigated by WOODWARD (1890), SCHWEITZER (1892), SHEPARD (1907), CARPENTER and MILLER (1969) and MILLER (1971). In this region, eastward-flowing saline water and infiltration of local meteoric water appear to be the major sources to aquifers in the Mississippian and Cambrian-Ordovician section (Fig. 2b). The principal transmissive unit in Mississippian strata in this region is the Burlington-Keokuk Fm., which commonly contains karstic solution channels (IMES, 1985). The petrography and geochemistry of limestones, dolostones, cherts and argillaceous carbonates in the Burlington-Keokuk Fm. document a diagenetic history that is correlative on a scale of 100,000 km² in Iowa, Illinois and Missouri (BANNER et al., 1988b, 1989; KAUFMAN et al., 1988; CANDER et al., 1989). Although Burlington-Keokuk rocks from Saline and Howard Counties were not part of these studies, the lack of any significant petrographic or geochemical gradients over this wide region allows us to estimate the mineralogy and the isotope and trace element geochemistry of this aquifer through which some of the saline groundwaters migrate to the surface.

SAMPLING AND ANALYTICAL METHODS

Water samples with a salinity range of 4.7 to 26‰ were obtained from three natural springs from the Mississippian Burlington-Keokuk Fm. and Chouteau Group (localities 2, 3 and 5) and two artesian wells (localities 1 and 4) during the period 10/31/86 to 11/4/86 (Table 1). The well at locality 1 was cased to the Burlington-Keokuk Fm. (9 m) and open to the Ordovician Gunter Fm. (326 m). The well at locality 4 was cased to the Ordovician (122 m) and open to 305 m in the Ordovician (SHEPARD, 1907). Samples were taken from the central portions of the springs where flow rates were the highest in order to minimize the incorporation of entrained particles in the water samples. The predominant particulate observed in the waters was iron sulfide, with lesser amounts of native sulfur. Samples were withdrawn by bailing or pumping with pre-cleaned polyethylene bottles or handpumps. Filtration and preservation were conducted either on site (localities 1 and 4) or in the laboratory of Dr. P. I. Nabelek at the University of Missouri, Columbia, starting within two hours of sample collection. For each locality, 0.4, 0.1 and 0.025 μ filtrates were collected by passing up to 10 l of water through Millepore filter membranes using an automated filtration apparatus. Filtration parts were pre-cleaned with HNO_3, HCl and distilled water, and the system was purged with ~200 ml of sample water prior to collection. Samples were acidified to pH <2 with purified 10 N HCl immediately after

filtration. Unfiltered samples, both acidified and unacidified, were also collected at each site.

Alkalinity was measured by titration with 0.1 N HCl of filtered sample aliquots while samples were being filtered and again several months later in the laboratory. Alkalinities determined at these different times show no systematic differences and indicate a reproducibility of ±5%. Na, Ca, K, Mg, Sr, Si, Li and B concentrations were measured at Chevron Oil Field Research Company using a Bausch and Lomb inductively coupled plasma source emission spectrometer (ICP). All samples were run in replicate. Replicate analyses of samples and gravimetric standard solutions indicate a precision of better than ±2% for these cations. Good agreement is observed between Sr concentration determinations by ICP (Table 1) and isotope dilution (Table 2). Chlorinities were determined by $AgNO_3$ titration with a precision of ±1%. Br, SO_4, NO_3 and organic species concentrations were measured by ion chromatography (±5%).

Hydrogen isotopic measurements were made at Caltech in the laboratory of Dr. S. Epstein. For determination of deuterium concentrations, 200 to 400 μmole water samples were loaded into capillaries and quantitatively converted to H_2 for isotopic analysis by reaction with uranium at 700°C (BIGELEISEN et al., 1952). The oxygen isotopic compositions of these waters were determined in the U.S.G.S. laboratory of Dr. J. R. O'Neil in Menlo Park, using a modified procedure of ROETHER (1970). Five ml water samples were loaded into vessels and evacuated, and then filled with ~1 atm. tank CO_2. The vessels were immersed in a 25°C water bath for 24 to 72 hours. The equilibrated CO_2 gas was extracted and analyzed. Analytical reproducibility for δD and δ¹⁸O values, based upon replicates of standards and unknowns, is ±1.0 and ±0.1‰, respectively.

Rb and Sr concentrations and Sr isotope compositions were determined on sample aliquots of <0.5 ml, following chemical and mass spectrometric procedures described in PAPANASTASSIOU and WASSERBURG (1973). The Caltech seawater standard gave a ⁸⁷Sr/⁸⁶Sr value of 0.70912, which corresponds to a value of ⁸⁷Sr/⁸⁶Sr = 0.71023 for the NBS SRM 987 standard (VON DRACH et al., 1986). Quoted ⁸⁷Sr/⁸⁶Sr data from other studies have been adjusted to this value for the NBS standard.

Sample aliquots of 25 to 30 ml were used to determine Sm and Nd concentrations by isotope dilution to ±10%. These concentration data were then used to spike samples of 0.5 to 3 l size with ¹⁴⁷Sm and ¹⁵⁰Nd. The REE were co-precipitated with Fe(OH)₃ (PIEPGRAS and WASSERBURG, 1980). Sm and Nd were extracted from the precipitate using cation exchange procedures. Elemental yields for the co-precipitation and chemical separation processes were typically greater than 85%. Mass spectrometry was used to determine precise Sm and Nd concentrations and Nd isotopic compositions on sample sizes of 10 to 30 ng Nd. Corrections for mass discrimination and oxygen isotope composition were applied following WASSERBURG et al. (1981). The nNdβ standard gave the following mean values: ϵ_{142} = -0.05; ϵ_{143} = -14.69; ϵ_{145} = -0.95; ϵ_{146} = -0.08; ϵ_{148} = -0.64. These values were obtained using a new Keithley amplifier and Fluke digital voltmeter. In order to facilitate comparisons with data from other studies, data in this study have been adjusted to a value of ϵ_{143} = -13.86 for the nNdβ standard (WASSERBURG et al., 1981) by increasing measured ¹⁴³Nd/¹⁴⁴Nd ratios by 0.0000425. Replicate ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd analyses on samples indicate a precision similar to that given by the two-sigma of the mean for in-run statistics of individual analyses.

Blanks were determined for Rb, Sr, Sm, Nd and the other cations for the sampling, filtration, preservation, chemical extraction and mass spectrometry procedures described above. The blank determinations were made on ultrapure distilled water that was processed in the field and laboratory in an identical manner to samples. Blank values are given in Table 3. Sr blanks were negligible for the samples analyzed. Filtration of samples in the field yielded an order of magnitude higher blank for Nd compared to laboratory filtration. For the Boone's Lick samples (locality 4), which were filtered on site and have the lowest REE concentrations, the Nd blank comprised less than 1.5% of the total Nd processed. For all other samples, sample to blank ratios for Nd were greater than 300. Filtration and procedural blanks for Na were less than 7 ppm, and for Ca, K, Mg, Sr, Si, Li and B these blanks were below the ICP detection limits, which range from 0.0001 ppm for Ca to 0.2 ppm for K.

Table 1.   Central Missouri Groundwaters - Geochemical Analyses (mg/ℓ).

Locality,[a] Size Fraction	Na	K	Ca	Mg	Sr	Li	Si	B	Br	Cl	SO₄	Alk.[b]	NO₃	pH	Density	TDS	T°C
1. Sweet Springs																	
Untreated	1220	16.9	333	145	7.90	0.42	3.97	0.76	–	–	–	–	–	7.30	1.0014	–	14.5
Unfiltered	1250	17.3	338	148	8.09	0.43	4.07	0.74	–	–	–	–	–	–	–	–	–
< 0.4 μ	1240	17.3	337	148	8.06	0.42	4.07	0.76	5.3	2510	148	259	< 1	–	–	4680	–
< 0.1 μ	1240	17.2	335	148	8.07	0.42	4.04	0.76	–	–	–	–	–	–	–	–	–
< 0.25 μ	1220	16.9	332	146	7.97	0.42	3.98	0.72	–	–	–	–	–	–	–	–	–
C & M (1969)	1488	24.1	374	162	10.8	0.78	3.89	0.58	6.5	3122	188	267	–	7.13	1.0030	5660	12.5
2. McCallister Springs																	
Untreated	1840	26.0	306	141	9.78	0.65	4.05	1.30	6.7	3420	249	284	5.1	6.90	1.0024	6300	13.8
C & M (1969)	2542	40.8	480	189	15.0	1.36	4.04	1.39	8.8	5012	318	317	–	6.93	1.0047	8960	15.0
Schw (1892)	4290	–	742	279	–	–	2.06	–	–	7920	457	-	–	–	1.0064	13700	14.3
3. Salt Branch Springs																	
Unfiltered	2270	33.1	404	135	11.4	0.77	9.07	2.26	–	–	–	–	–	7.44	1.0028	–	–
< 0.1 μ	2300	33.4	408	136	11.5	0.78	8.47	2.35	8.0	4300[c]	408	293	< 1	–	–	7920	–
C & M (1969)	4044	67.1	705	251	16.0	2.09	5.37	3.70	27	7699	717	309	–	6.70	1.0079	13800	14.5
4. Boone's Lick																	
Untreated	6550	106	1120	417	36.4	2.80	6.18	6.96	–	–	–	–	–	6.80	1.0132	–	13.5
Unfiltered	6530	107	1130	420	36.7	2.83	6.34	6.98	–	–	–	–	–	–	–	–	–
< 0.4 μ	6550	107	1120	418	36.4	2.82	6.25	6.96	–	–	–	225	–	–	–	–	–
< 0.1 μ	6590	108	1120	422	36.8	2.85	6.24	6.89	27	11700	1380	–	< 1	–	–	21600	–
< 0.025 μ	6570	109	1130	422	36.8	2.86	6.32	7.00	–	–	–	–	–	–	–	–	–
C & M (1969)	5980	115	1091	410	59.5	3.08	3.51	5.80	28.4	11600	1320	266	–	6.73	1.0129	20900	15.5
Schw (1892)	6580	–	967	420	–	–	8.42	–	–	12100	1310	–	–	–	1.0168	21400	–
5. Blue Lick																	
Untreated	7680	113	1330	474	40.4	3.65	5.94	6.21	–	–	–	–	–	–	1.0154	–	15.3
Unfiltered	7620	112	1320	472	40.9	3.62	6.30	6.10	–	–	–	–	–	–	–	–	–
< 0.4 μ	7680	113	1330	475	41.0	3.67	6.07	6.14	–	–	–	287	–	6.99	–	–	–
< 0.1 μ	7750	114	1350	479	41.4	3.71	5.96	6.21	30	14200	1240	–	26	–	–	25500	–
< 0.025 μ	7620	115	1340	480	41.6	3.72	6.03	6.20	–	–	–	–	–	–	–	–	–
C & M (1969)	8693	134	1432	528	36.1	4.34	9.5	6.12	50	17020	1362	303	–	6.74	1.0188	29600	16.3
Schw (1892)	8620	106	1370	505	–	–	7.01	–	–	15900	1280	–	–	–	1.0214	27800	17.0
Seawater	11030	408	425	1310	8.3	0.19	2.1	4.5	69	19800	2770	144	0.3	7.89	1.023	36000	25

a. Sample localities: 1. Sweet Springs, Saline County. Well completed in 1902, reported as cased to Mississippian Burlington-Keokuk Fm. bedrock (9 m), open to Ordovician Gunter Fm. (326 m). 2. McCallister Springs, Saline County. Burlington-Keokuk Fm. bedrock; spring sample. 3. Salt Branch Springs, Saline County. Burlington-Keokuk Fm. bedrock; spring sample. 4. Boone's Lick State Historic Site, Howard County. Well completed in 1872, reported as cased to Ordovician (122 m), open to 305 m in Ordovician. Carpenter and Miller (1969) sample from surface spring in Pennsylvanian Des Moines Fm. at same locality. Schweitzer (1892) sample from well. 5. Blue Lick, Saline County; Mississippian Chouteau Group bedrock; spring sample. Additional locality information and chemical analyses given in Schweitzer (1892), Shepard (1907), Carpenter and Miller (1969) and Miller (1971). b. Alk = total alkalinity determined in field on filtered, unacidified sample aliquots, except for sample 4, which was analyzed several months later in the laboratory. c. Cl not measured for this HCl-preserved sample. Stated Cl concentration calculated assuming electrical neutrality. TDS = calculated total dissolved solids ≡ salinity. (-) = not determined. Temperatures were measured *in situ*. pH was measured *in situ* for samples 1, 2 and 4, and within two hours of collection for samples 3 and 5. "Unfiltered" and "filtered" size fractions were acidified with 1ON HCl, except for aliquots for Cl, Br and SO₄ determinations, which were acidified with citric acid for samples 1, 4 and 5. Br, SO₄, NO₃ analyzed by N. Thompson. C & M = Carpenter and Miller; Schw = Schweitzer. Mean seawater concentration data from Quinby-Hunt and Turekian (1983).

Table 2.   Central Missouri Groundwaters - Isotopic Data.

Locality/ Size Fraction	Rb (mg/ℓ)	Sr (mg/ℓ)	$^{87}Sr/^{86}Sr$	Sm (ng/ℓ)	Nd (ng/ℓ)	$^{143}Nd/^{144}Nd$	$^{147}Sm/^{144}Nd$	$\varepsilon_{Nd}(0)$	δD (°/oo SMOW)	$\delta^{18}O$ (°/oo SMOW)
1. Sweet Springs										
Untreated	–	–	–	–	--	–	–	–	-44.6	-6.5
Unfiltered	–	--	–	–	31[a]	–	–	–	–	–
< 0.1 μ	0.0352	8.15	0.71607±3	5.45	30.5	0.511382±21	0.1078	-9.1±0.4	–	–
2. McCallister Springs										
Untreated	–	10.23	0.71606±5	–	–	–	–	–	-50.3	-7.0
3. Salt Branch Springs										
Unfiltered	--	–	–	–	--	–	–	–	-57.0	-7.8
< 0.1 μ	–	11.6	0.71578±3	9.36	52.5	0.511381±22	0.1078	-9.1±0.4	–	–
4. Boone's Lick										
Untreated	–	–	--	–	–	–	–	–	-108	–
Unfiltered	–	–	–	2.82	13.3	0.511290±16	0.1283	-10.9±0.3	–	-14.6
< 0.4 μ	0.243	36.8	0.71551±6	2.5[a]	14[a]	–	–	–	–	–
< 0.1 μ	0.226	36.8	0.71555±4	2.62	12.6	0.511297±20	0.1268	-10.8±0.4	–	-14.6
< 0.1 μ R	0.229	36.5	0.71559±3	–	–	–	–	–	–	–
< 0.25 μ	–	–	–	–	–	–	–	–	–	-14.7
5. Blue Lick										
Untreated	–	–	–	–	–	–	–	–	-85.2	-11.0
< 0.1 μ	–	41.4	0.71596±3	21.2	112.1	0.511432±26	0.1148	-8.1±0.5	–	–
< 0.1 μ R	–	–	–	–	111.9	0.511419±20	–	-8.4±0.4	–	–

Localities and size fraction designations as in Table 1. [a] Aliquot run (±10%). Concentration data by isotope dilution. Reported uncertainties are for the last digits shown and represent $\pm 2\sigma_{mean}$. $^{143}Nd/^{144}Nd$ normalized to $^{146}Nd/^{142}Nd$ = 0.636151. $^{87}Sr/^{86}Sr$ normalized to $^{86}Sr/^{88}Sr$ = 0.1194. "R" designates replicate analysis.

Table 3. Blank Determinations for Water Sample Handling Procedures.

Procedure	Rb	Sr	Nd	Sm
Distilled water, untreated (pg/ℓ)	9	90	3	-
Distilled water, filtered in lab (pg/ℓ)	90	6.2×10³	20	-
Distilled water, filtered in field (pg/ℓ)	110	2.3×10³	170	-
Chemical separation + mass spectrometry (pg/analysis)	120	140	30	5

RESULTS

Sample information and major and trace element concentrations are presented in Table 1 and isotopic data for the samples are presented in Table 2. For each sample, the different size fractions (0.4, 0.1 and 0.025 μ), the acidified unfiltered aliquot and the untreated aliquot all have the same concentrations of Na, Ca, K, Mg, Li, Si and B within the analytical uncertainty. Sr concentrations and $^{87}Sr/^{86}Sr$ ratios of the waters also do not vary as a function of filter pore size or acid treatment. This indicates that all of these elements occur almost exclusively as dissolved species in the groundwaters. The oxygen isotope data indicate that these isotopic compositions are not affected by the filtration and preservation procedures.

A comparison of the Nd and Sm concentration data for the unfiltered and filtered (0.4, 0.1 μ) samples from localities 1 and 4 (Table 2) indicates that approximately 90% of the REE are in solution in these water samples. The unfiltered and filtered samples have essentially identical $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios. These results suggest that the REE associated with any particulates in these groundwaters affect neither the isotopic composition of the dissolved Nd nor the relative abundances of the dissolved REE.

The sample from locality 4 has had a notably constant chemical composition through time, with no substantial differences in either relative or absolute elemental concentrations between the results of the present study and the studies conducted 20 and 97 years ago. Samples from the other four localities have significantly lower concentrations of nearly all constituents compared with the data of CARPENTER and MILLER (1969). However, alkalinity and SiO₂ levels are not proportionally lower in these samples. Similar to this temporal trend, each study shows a narrow range of alkalinity and SiO₂ concentrations over the wide salinity range observed between localities.

The predominant dissolved constituents in the central Missouri groundwaters are Na, Cl and Ca. The most saline of the samples have abundances of Na, Cl and total dissolved solids that are about 70% as concentrated as seawater. Na and Cl concentrations are well-correlated in the groundwaters (Fig. 3a). CARPENTER and MILLER (1969) concluded that mixing between a saline fluid (high Na, Cl) and a dilute fluid can account for the concentration ranges of several constituents observed in these groundwaters. The Na and Cl concentrations in the groundwaters lie on a mixing line between dilute meteoric water, with essentially no Na or Cl, and a saline groundwater (e.g., no. 5). Oilfield waters sampled from Mississippian carbonates in west central Kansas and modern seawater also lie along this mixing line (Fig. 3a; Table 4). Na-Cl brines derived from Permian evaporites in central Kansas are far more saline than both the groundwaters and the oilfield waters and have equal molar concentrations of Na and Cl (Table 4), indicative of halite dissolution. A mixing line be-

tween a Na-Cl brine and dilute meteoric water has a similar trend to the other mixing lines but it can be seen that the Na-Cl brines have higher Na concentrations at equivalent Cl concentrations compared with the oilfield waters, seawater and most of the groundwaters (Fig. 3a; Table 4).
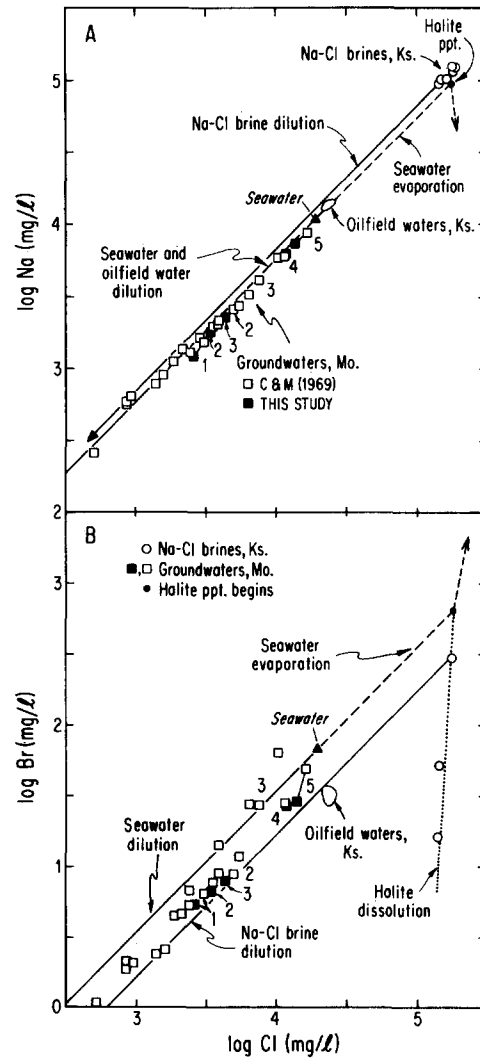

FIG. 3. (a) Na-Cl relationships in central Missouri groundwaters. Data from this study and CARPENTER and MILLER (C&M, 1969). Numbered points are localities in Table 1 of this study. Lines between numbered points connect analyses from the same locality. Also shown are data for oilfield waters from Mississippian carbonates in Kansas (CHAUDHURI et al., 1987) and Na-Cl brines from Permian evaporites in Kansas (GOGEL, 1981). Dilution trends for Na-Cl brines, oilfield waters and seawater illustrate effects of mixing pure water with each fluid. Dashed line shows seawater evaporation trajectory through the beginning of halite precipitation (solid circle). Seawater evaporation trajectories are detailed in CARPENTER (1978). Groundwater data lie on a mixing line between an oilfield water and a dilute meteoric water. Seawater (solid triangle) also lies on this line. The oilfield waters, seawater and the groundwaters have slightly lower Na/Cl ratios than the Na-Cl brines. Representative analyses given in Table 4. (b) Br-Cl relationships for the same samples shown in (a). Na-Cl brines from Permian halite, oilfield waters from Kansas and groundwaters from this study all have lower Br/Cl ratios than seawater and evaporated seawater. Saline-dilute water mixing processes can produce low Br/Cl ratios in less saline fluids. Symbols as in (a).

Table 4. Geochemical comparison (mg/ℓ) of saline groundwater from central Missouri with oilfield water from Mississippian carbonates in central Kansas, Na-Cl brine from Permian evaporites in central Kansas and modern seawater.

	Saline Groundwater[a]	Oilfield Water[b]	Na-Cl Brine[c]	Seawater[d]
Na	7,750	12,980	100,000	11,030
K	114	330	63	408
Li	3.7	12.1	-	0.19
Mg	479	460	73	1,310
Ca	1,350	1,450	750	425
Sr	41	41	-	8.3
Cl	14,200	22,500	150,000	19,800
Alk.	287	56	2	144
Br	30	32	17	69
SO$_4$	1240	2380	1900	2770
m_{Na}/m_{Cl}	0.841	0.888	1.03	0.859
m_{Sr}/m_{Ca}	0.0138	0.0129	-	0.0088
$^{87}Sr/^{86}Sr$	0.71596±3	0.72285±5	-	0.7092

a. Locality 5 (Blue Lick) of this study. b. Oilfield water from Mississippian carbonates, 1.55 km depth, Bindley Field, Hodgeman County, Kansas (Chaudhuri et al., 1987). c. Brine from Wellington aquifer (< 0.5 km depth), Permian, McPherson County, Kansas (Gogel, 1981). d. Seawater from Quinby-Hunt and Turekian (1983). m_{Sr}/m_{Ca}, m_{Na}/m_{Cl} refer to molar ratios.

Br-Cl concentration relationships for the same water samples and the mixing and evaporation trends are shown in Fig. 3b. The central Missouri groundwater samples analyzed in this study and the oilfield waters from Mississippian carbonates and Permian evaporites in central Kansas lie to the right of the seawater dilution and evaporation trajectories. The high Br/Cl ratios of some groundwaters measured by CARPENTER and MILLER (1969) may be attributable to analytical inaccuracies. Dissolution or recrystallization of halite by meteoric water can produce brines with relatively high Cl and variable Br concentrations (LAND and PREZBINDOWSKI, 1981), similar to the Na-Cl brines from Permian evaporites (Fig. 3b). Mixing between such a halite-derived brine and dilute meteoric water may account in part for the relatively low Br/Cl ratios in the central Missouri groundwaters and oilfield waters from Kansas. Dilution of seawater or seawater evaporated to halite precipitation would produce waters with higher Br/Cl ratios than the groundwaters.

CARPENTER and MILLER (1969) attributed the narrow range of alkalinity and SiO$_2$ concentrations over the large salinity range in the groundwaters to dilution followed by reaction between the groundwaters and small amounts of calcite, dolomite and quartz in central Missouri aquifer rocks. The extent to which a water sample has equilibrated with various mineral phases can be estimated by the calculation of saturation indices, based on the chemical activities of dissolved species in the sample. For example, thermodynamic equilibrium between calcite and water may be expressed by the reaction

$$CaCO_3 \text{ (s)} = Ca^{++} \text{ (aq.)} + CO_3^- \text{ (aq.)}.$$
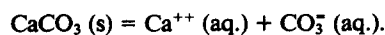
The saturation index is expressed as S.I. = log([Ca^{++}][CO$_3^-$]/ K_T), where brackets denote ion activities, calcite has an activity of unity, and K_T is the temperature-dependent equilibrium constant for the above reaction. Saturation indices are calculated here using the more recent thermochemical data and species distribution computations of the chemical equilibrium model WATEQF (PLUMMER et al., 1976; NORDSTROM et al., 1984). Using the chemical analyses and sampling

temperatures of the present study (Fig. 4), we obtain a larger range in calcite and dolomite saturation indices compared with 1) values for quartz and 2) values obtained for calcite and dolomite using analyses from CARPENTER and MILLER (1969). The calculated saturation states for calcite and dolomite are strongly pH-dependent, and thus fluctuations in pH prior to and during sampling (as discussed in CARPENTER and MILLER, 1969) may produce uncertainties in the calculated indices. The results for quartz give more uniform values of supersaturation, whereas the waters may be inferred to be approximately saturated with respect to calcite and dolomite. These mineral-solution equilibria results obtained using the chemical equilibrium model (Fig. 4) are generally consistent with the conclusions of CARPENTER and MILLER (1969).

The groundwaters are enriched relative to seawater in several constituents, including Sr, Ca, Sr/Ca, Li and the REE. They have a range of Nd concentrations of 13 to 112 ng/l compared with a range of 2 to 9 ng/l Nd for most modern seawater samples (ELDERFIELD and GREAVES, 1982). The Sr, Ca and Sr/Ca enrichments are typical of more saline waters from many oilfields and have been attributed to extensive reaction between the oilfield waters and either marine carbonate minerals or detrital feldspar (CARPENTER, 1978; LAND, 1987). The concentrations of acetate, butyrate and propionate in the groundwater samples are all less than 1 mg/l. Nitrate concentrations range from less than 1 mg/l in three samples to 26 mg/l in sample 5. These concentrations of organic species and nitrate are below levels that would significantly contribute to alkalinity or trace element distributions in the water samples. Iron concentrations in all samples were determined to be less than 0.2 mg/l by ICP analysis.

The central Missouri groundwaters show a general trend of decreasing δD and $\delta^{18}O$ with increasing salinity (Fig. 5a,b; Table 2). This trend is opposite to that observed for more saline subsurface fluids from several sedimentary basins and Precambrian granitic basement (Fig. 5c). The positive correlations between the salinities of the waters and their ^{18}O and D contents in these other studies have been attributed to mixing between meteoric waters and saline brines that
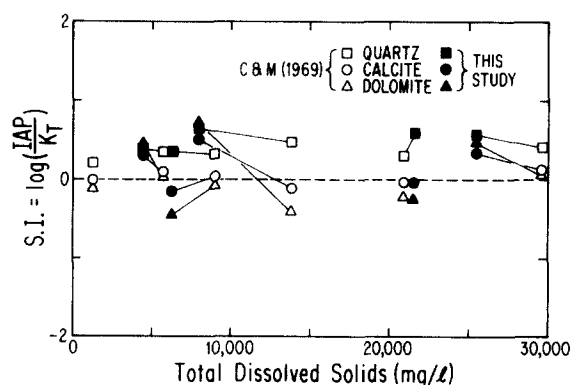

FIG. 4. Saturation index (S.I.) vs. total dissolved solids for quartz, calcite and dolomite in central Missouri groundwaters from five localities in this study and the least saline sample of CARPENTER and MILLER (C&M, 1969). Indices calculated using water analyses from this study and C&M (1969). Lines connect analyses from the same locality.
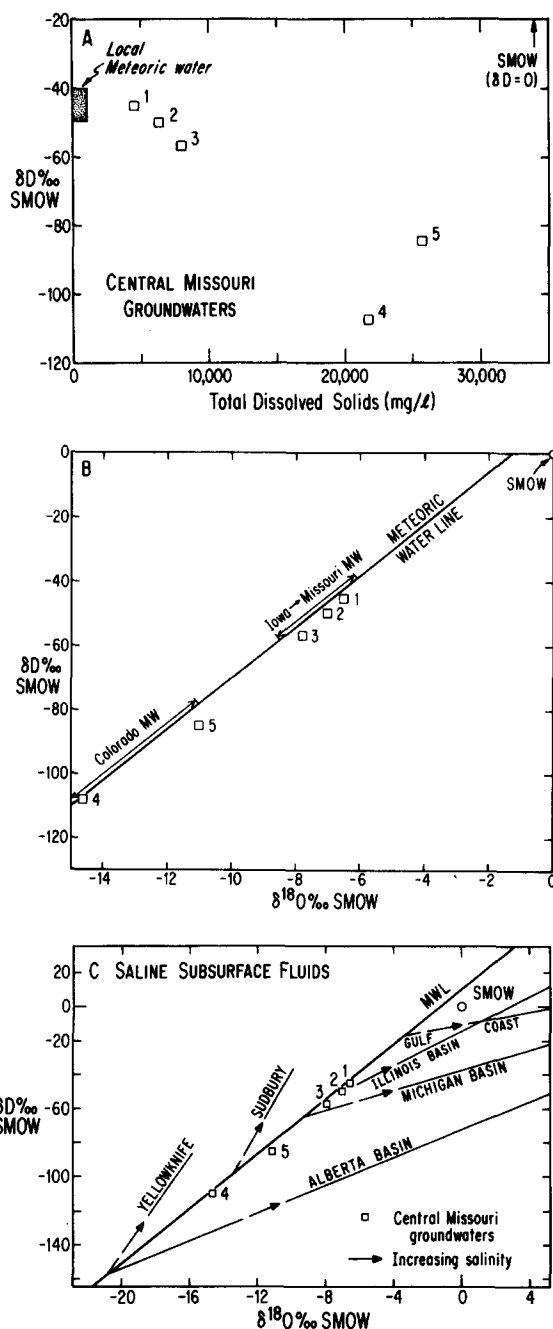
of five samples lie within the statistical limits of the line, the data are systematically shifted by <0.8‰ in $\delta^{18}O$ to the right of (or <8‰ in δD below) the meteoric water line (Fig. 5b). The groundwater data more closely approximate the meteoric water line of TAYLOR (1974), which is given by the relationship $\delta D = 8\delta^{18}O + 5$. The less saline samples have similar δD and $\delta^{18}O$ values to meteoric precipitation in central Missouri, while the δD and $\delta^{18}O$ values of the saline samples (4, 5) are much lower and similar to values for meteoric precipitation in high altitude and high latitude regions of North America (see compilation in TAYLOR, 1974).

The $^{87}Sr/^{86}Sr$ ratios of the water samples range from 0.71551 to 0.71607. Figure 6a illustrates that these values
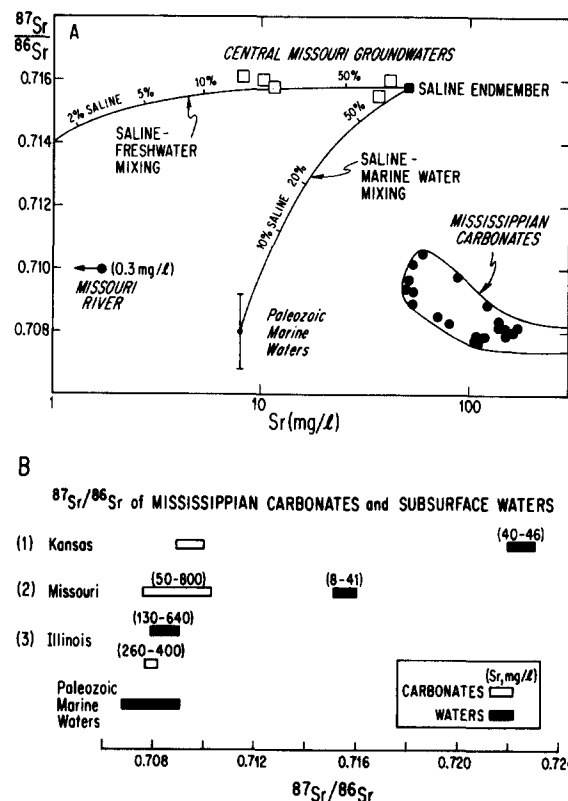
FIG. 6. (a) $^{87}Sr/^{86}Sr$ vs. Sr concentration for central Missouri groundwaters (open squares). Sr and Nd data presented in this and subsequent figures are for <0.1 μ size fraction, except for locality 2 (untreated fraction). Also shown are analyses of whole-rock and dolomite and calcite mineral separates from Mississippian carbonates of the Burlington-Keokuk Fm. of Iowa, Illinois and Missouri (KAUFMAN, 1985; BANNER et al., 1988b; CHYI, unpub. data), estimates of Paleozoic marine waters based on carbonate, phosphate and evaporite analyses (BURKE et al., 1982), and Missouri riverwater from Washington, MO (GOLDSTEIN and JACOBSEN, 1987). Two curves show variations in these parameters during mixing of 1) a hypothetical saline endmember groundwater and a dilute water represented by Missouri riverwater, and 2) the saline endmember and a subsurface fluid of marine origin (e.g., ancient seawater, evaporative brine). (b) Comparison of $^{87}Sr/^{86}Sr$ values and Sr concentrations for subsurface waters and their host Mississippian carbonate rocks from three mid-continent localities: 1) oilfield waters from carbonates at 1.5 km depth, central Kansas (CHAUDHURI et al., 1987), representative chemical analysis given in Table 4; 2) groundwaters from this study; and 3) oilfield brines from 1 km depth, Illinois Basin (STUEBER et al., 1987). Data for carbonates in (a) and (b) are for acid-soluble portions of samples, Sr concentrations in ppm.

FIG. 5. (a) δD vs. total dissolved solids for central Missouri groundwaters. Numbered points in all figures refer to samples in Tables 1 and 2. (b) δD vs. $\delta^{18}O$ for groundwaters compared with meteoric water line (MWL). Values for meteoric waters are from CRAIG (1961), LAWRENCE and TAYLOR (1972), and HARMON et al. (1979). (c) δD vs. $\delta^{18}O$ for saline subsurface fluids from studies of several other localities, showing positive correlations between salinity and both δD and $\delta^{18}O$. In contrast, the central Missouri groundwaters display an inverse relationship between salinity and δD or $\delta^{18}O$. Trends based on data from CLAYTON et al. (1966) and FRAPE et al. (1984).

have evolved through seawater modification or rock-water interaction. δD and $\delta^{18}O$ values in the groundwaters of this study are positively correlated and lie approximately along the meteoric water line of CRAIG (1961), which is given by the relationship $\delta D = 8\delta^{18}O + 10$ (Fig. 5b). Although four

are significantly more radiogenic than 1) estimates of [87]Sr/[86]Sr for seawater throughout Phanerozoic time, which range from 0.7068 to 0.7092 (BURKE *et al.*, 1982); and, 2) [87]Sr/[86]Sr ratios for carbonate rocks and minerals of the Mississippian Burlington-Keokuk Fm. of Iowa, Illinois and Missouri, which have a range of 0.7075 to 0.7105 (BANNER *et al.*, 1988b). Minor, argillaceous carbonates within the formation range to higher [87]Sr/[86]Sr values (CHYI *et al.*, 1985) than the waters. The *in-situ* growth of [87]Sr in the waters is negligible due to their low Rb/Sr ratios. It can be seen that the [87]Sr/[86]Sr values of most mixtures between saline and dilute groundwaters would be dominated by the value of the saline endmember (Fig. 6a). The [87]Sr/[86]Sr ratios of the water samples are intermediate between Sr isotopic compositions that have recently been determined (Fig. 6b) on oilfield formation waters from Mississippian carbonates in Kansas (0.7220–0.7231) and Illinois (0.7080–0.7090; CHAUDHURI *et al.*, 1987; STUEBER *et al.*, 1987). The oilfield waters from Kansas have major and trace element concentrations that are similar to the most saline samples of this study (Table 4).

[143]Nd/[144]Nd ratios of the water samples are expressed as deviations relative to a chondritic uniform reservoir (CHUR), having a present-day value of [143]Nd/[144]Nd = 0.511847 (JACOBSEN and WASSERBURG, 1981), using the epsilon notation of DePAOLO and WASSERBURG (1976):

$$\epsilon_{Nd}(T) = \left(\frac{^{143}Nd/^{144}Nd_{sample} \text{ at } T}{^{143}Nd/^{144}Nd_{CHUR} \text{ at } T} - 1 \right) \cdot 10^4.$$

The water samples have a range of $\epsilon_{Nd}(0)$ values from −10.9 to −8.1, and [147]Sm/[144]Nd values from 0.108 to 0.128. Carbonates and other authigenic sediments from the Burlington-Keokuk Fm. have generally higher $\epsilon_{Nd}(0)$ and [147]Sm/[144]Nd values compared with the groundwaters (Fig. 7). Clastic sediments of Mississippian age from Illinois and Indiana (BANNER *et al.*, 1988a) have similar $\epsilon_{Nd}(0)$ and [147]Sm/[144]Nd values to the water samples, with the exception of water sample 4.
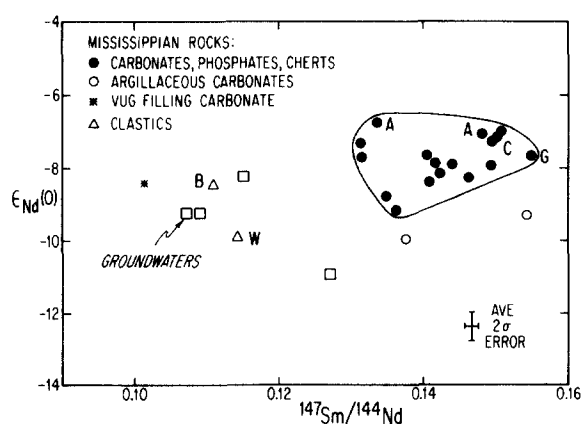

FIG. 7. $\epsilon_{Nd}(0)$ vs. [147]Sm/[144]Nd for central Missouri groundwaters (open squares; this study) and Mississippian carbonates, authigenic phases and clastic sediments from the Burlington-Keokuk and associated formations in Iowa, Illinois and Indiana (BANNER *et al.*, 1988a, and CHYI, unpub. data). Symbols as follows: unlabeled solid circles = dolostones; A = fish apatite; G = glauconite; C = chert; V = vug-filling calcite; B = Borden Siltstone (central Indiana); W = Warsaw Shale (western Illinois). The Borden and Warsaw clastics do not extend into central Missouri.

DISCUSSION

Subsurface fluids may acquire their chemical characteristics through a variety of processes, including 1) dissolution, recrystallization and ion exchange involving any number of inorganic and organic phases, 2) evaporation, 3) shale membrane filtration, 4) mixing of waters, and 5) ion diffusion. In this section, we evaluate these processes with respect to the origin and evolution of the central Missouri groundwaters. First we discuss the limits that can be placed on these processes from major and trace element abundances and isotopic variations. Then we consider a quantitative evaluation of rock-water interaction between the Mississippian carbonates and the groundwaters. Finally, the multiple constraints that may be placed on the system through the combined use of geochemical data, geologic relationships and regional hydrologic studies are used to consider the extent to which the waters have been modified by interaction with rocks along possible flow paths, and to test models for the origin of the waters and their salinity.

Major and trace element constraints

Key features of the central Missouri groundwaters are: 1) the predominance of Ca, Na and Cl as major constituents, 2) the salinity range of 1 to 30‰, 3) the low Na/Cl and high Ca/Cl ratios relative to Na-Cl brines that are derived from halite dissolution (Fig. 3a; Table 4), and 4) the high Sr/Ca ratios relative to seawater. The variation in Na and Cl concentrations for 21 groundwater samples from the Saline County area are readily explained by a mixing model involving a water of near-seawater salinity and a dilute meteoric water (CARPENTER and MILLER, 1969). For other elements that do not follow a simple dilution trend, more complex rock-water interaction processes are evaluated. The near-constancy of carbonate and quartz saturation indices over the wide range in salinity (Fig. 4) suggests that either 1) mineral-solution equilibria proceed during or subsequent to the mixing/dilution process, thereby controlling HCO_3^- and SiO_2 concentrations (CARPENTER and MILLER, 1969), or 2) both the saline and dilute endmember water compositions are governed by similar mineral-solution equilibria and have essentially the same concentrations of HCO_3^- and SiO_2 prior to mixing. Dissolution of small amounts of calcite, dolomite and quartz or clay minerals may control the HCO_3^- and SiO_2 levels in the waters. Several samples in this study are measurably diluted relative to samples from the same localities (1–3, 5) studied by CARPENTER and MILLER (1969), yet they have similar HCO_3^- and SiO_2 concentrations and mineral saturation indices (Table 1, Fig. 4). This suggests that mixing and rock-water interaction are ongoing processes in this system. Isotopic data are used below to place limits on the extent to which these processes may occur.

The relatively low Na/Cl ratios of the groundwaters are similar to modern seawater, but isotopic evidence discussed later precludes models involving ancient marine waters for the origin of the salinity in the groundwaters. A Na-Cl brine derived from halite dissolution (Fig. 3a) may become deficient in Na relative to Cl through either ion exchange with clay minerals or albitization of plagioclase or K-feldspar, as discussed by several authors (LAND and PREZBINDOWSKI, 1981; STOESSELL and MOORE, 1983; CHAUDHURI *et al.*, 1987).

These reactions may also enrich the waters in Ca and Sr. Although subsurface equilibration of saline water with calcite and dolomite has also been proposed to account for the Ca and Sr enrichments and the Ca/Mg ratios of many subsurface waters (e.g., CARPENTER, 1978; LAND and PREZBINDOWSKI, 1985), Sr isotope data discussed below indicate that marine carbonates cannot be the predominant source of Sr for the groundwaters. In addition, the low Sr/Ca ratios of most Paleozoic carbonates are inappropriate for producing high Sr/Ca waters (Table 4) during rock-water interaction (BANNER et al., 1989). Thus, interaction with silicate minerals may account for the relative Na depletion and Ca and Sr enrichments that are characteristic of the groundwaters.

Isotopic constraints

The correlation of δD and $\delta^{18}O$ values in the central Missouri groundwaters and the near coincidence of this correlation line with the meteoric water line (Fig. 5b) suggests a meteoric origin for these waters. Evaporation at the Earth's surface and shale membrane filtration of meteoric water in the subsurface can produce increasingly saline fluids. These processes typically concentrate the heavier isotopes D and ^{18}O with increasing salinity (EPSTEIN, 1959; GRAF et al., 1966), although more complex reversals in evaporation trends have been shown (KNAUTH and BEEUNAS, 1986). δD and $\delta^{18}O$ values for the central Missouri groundwaters are inversely correlated with salinity (Fig. 5a), indicating that evaporation and membrane filtration of meteoric water are not likely mechanisms for the origin of the salinity-isotope relationships in the groundwaters. The progressive deviation along the meteoric water line of δD and $\delta^{18}O$ values from the value for SMOW with increasing salinity in the groundwaters demonstrates the inability of models involving ancient seawater or marine porewaters to account for the origin of the salinity in the groundwaters.

The inverse correlation between salinity and δD or $\delta^{18}O$ values (Fig. 5a) indicates that the salinity in the suite of samples is derived from an endmember fluid with low D and ^{18}O contents. A correlation between salinity and either δ value is not a strict function of mixing processes involving two waters because solids such as NaCl may be added to or removed from the system by mineral dissolution or crystallization without affecting H or O isotopic compositions. However, δD vs. $\delta^{18}O$ correlations among a suite of water samples are readily explained by mixing between two endmember waters. The H-O isotopic data therefore are broadly consistent with the saline-dilute water mixing model of CARPENTER and MILLER (1969) that was constructed on the basis of elemental concentrations. In such a mixing model, one endmember is a dilute water with H and O isotopic compositions similar to present-day recharge in central Missouri (e.g., sample 1 in Fig. 5b). The other endmember is saline and has lower δD and $\delta^{18}O$, similar to sample 4 or even some lighter isotopic composition. This endmember has H and O isotopic compositions that are similar to present-day recharge in high altitude and high latitude regions of North America. The Front Range in Colorado is the closest region to the study area that has precipitation with such low δD and $\delta^{18}O$ values (Fig. 5b), and thus the low D and ^{18}O contents of the more saline groundwaters may reflect far-travelled meteoric recharge.

Several other factors can affect the H and O isotopic compositions of meteoric waters. The systematic displacement of the central Missouri groundwater trend slightly to the right of the CRAIG (1961) meteoric water line can be ascribed to either 1) small extents of interaction and isotopic exchange between the waters and carbonates or silicates, or 2) the age of the waters. Limits on the amount of oxygen isotope exchange that may occur during rock-water interaction are evaluated using model calculations below. Relevant to the second hypothesis, if the low δ values for the saline samples indeed reflect recharge from a distant source, then the waters may be part of a relatively old flow system. The waters could have originated as recharge during periods of different climatic conditions (e.g., temperature, humidity) in the past, for which shifts in the deuterium excess, relative to SMOW, of meteoric precipitation have been proposed (GONFIANTINI et al., 1974; YAPP and EPSTEIN, 1977; SONNTAG et al., 1979). Precipitation during periods of cold paleoclimatic conditions can also account for low δD and $\delta^{18}O$ values of groundwaters relative to local recharge (CLAYTON et al., 1966; LONG et al., 1988). Although paleoclimatic effects on the H-O isotopic compositions of the central Missouri groundwaters cannot be excluded, in many instances altitude effects are proposed to be predominant over paleoclimatic effects in depleting the D and ^{18}O contents of ancient meteoric recharge (FONTES, 1981; WHITE and CHUMA, 1987). Glacial meltwaters will also have much lower δD and $\delta^{18}O$ values compared with local precipitation (EPSTEIN et al., 1970), and a Pleistocene meltwater source is inferred for low δD and $\delta^{18}O$ values in groundwaters from Cambrian-Ordovician strata in the north-central United States extending into northern Missouri (SIEGEL and MANDLE, 1984). However, a northern glacial meltwater source for the central Missouri groundwaters with low δD and low $\delta^{18}O$ is not consistent with the isotope-salinity relationships (SIEGEL and MANDLE, 1984; this study). The H-O isotopic data for the central Missouri groundwaters, when interpreted in the context of regional hydrogeologic and geochemical data discussed in a later section, are most consistent with an origin involving ancient, far-travelled recharge, most likely from the Front Range of Colorado.

The $^{87}Sr/^{86}Sr$ ratios (0.7155–0.7161) of the central Missouri groundwaters are significantly higher than values estimated for ancient seawater and values measured on marine carbonates, phosphates and evaporites from the Phanerozoic (Fig. 6). Therefore, a simple model involving ancient seawater or evaporite dissolution cannot account for the Sr isotopic signature of the groundwaters. High $^{87}Sr/^{86}Sr$ values in subsurface fluids similar to the values observed in the central Missouri groundwaters have been ascribed to 1) albitization or dissolution of K-feldspar in either granitic basement rocks or detrital clastic components (CHAUDHURI et al., 1987; LAND, 1987; McNUTT, 1987), or 2) cation exchange with clay minerals (STUEBER et al., 1984; CHAUDHURI et al., 1987). Low $^{87}Sr/^{86}Sr$ ratios may be obtained through reaction with marine carbonates or calcium evaporite minerals. These mineral-solution reactions were discussed earlier for the case of a Na-Cl brine or a diluted Na-Cl brine in accounting for several major and trace element variations in the central Missouri groundwaters.

The lower average $\epsilon_{Nd}(0)$ and $^{147}Sm/^{144}Nd$ values in the groundwaters relative to the carbonates are indicative of a crustal source of REE for the waters. Sm-Nd isotope data can be used to calculate Nd model ages, which can be used to estimate the average crustal residence time for the sources of the REE in the waters. Using an $\epsilon_{Nd}(0)$ value of -9 and a $^{147}Sm/^{144}Nd$ value of 0.11, an average crustal residence time of 0.9 AE is calculated assuming chondritic mantle parameters (DePaolo and Wasserburg, 1976). The same calculation using a depleted mantle composition yields a model age of 1.4 AE. A $^{87}Sr/^{86}Sr$ value of 0.716 is a reasonable average signature for continental crust in this age range (Faure, 1986). Since crystalline rocks and clastic sediments derived from such rocks will have similar Sr and Nd isotope and REE signatures, it is difficult to distinguish between the two as sources for dissolved Sr and REE in subsurface waters.

In summary, the H and O isotope data for the central Missouri groundwaters are most readily explained by a mixing model involving two meteoric water endmembers. One endmember is saline and preserves a depleted D and ^{18}O signature. The other endmember has H and O isotopic compositions similar to present-day recharge in Missouri. In accord with the H-O isotope relationships, Sr isotopic data provide evidence against models involving ancient seawater or marine porewaters for the origin of the salinity in the waters. Mineral-solution equilibria with predominantly silicate assemblages can account for the high $^{87}Sr/^{86}Sr$ values of the groundwaters.

Quantitative models for isotopic exchange during carbonate-groundwater interaction

The H and O isotope data suggest that the saline waters have migrated through a long flow path, along which interaction with a variety of lithologic units may have occurred. We first consider the effects of rock-water interaction between the groundwaters and carbonate aquifer rocks in central Missouri on the isotopic and trace element compositions of the waters. Subsequently, we can evaluate the prior rock-water interaction history and origin of the fluids. The limestones and dolostones of the Burlington-Keokuk Fm. are the principal aquifer in Mississippian rocks in central Missouri and some of the groundwaters sampled for this study and by Carpenter and Miller (1969) are derived from these strata. Based on modal and chemical analyses and measured sections of Burlington-Keokuk and associated Mississippian units in Missouri, Illinois and Iowa (Carpenter and Miller, 1969; Kaufman et al., 1988; Cander et al., 1989; Banner et al., 1988a,b), the carbonates comprise the predominant reservoir of Sr and REE in these strata. Owing to uncertainties in 1) determining subsurface flow paths in this region, and 2) specifying the sampled aquifer for the two artesian well waters (localities 1 and 4), older Mississippian and Ordovician carbonates in this region may also have an important role in rock-water interaction processes. Although there are no isotopic data for these rocks, they are likely to have Sr and O isotopic compositions that are similar to the Burlington-Keokuk carbonates and markedly different from the groundwaters. Therefore, rock-water interaction models involving the Burlington-Keokuk carbonates are likely to be representative of these processes in the other carbonate aquifers in this area.

Variations in the relative rates at which different isotopic systems are changed during rock-water interaction can provide useful information on the nature of the processes involved. The results of model calculations that simulate isotopic and trace element exchange during rock-water interaction are presented in Fig. 8. In this model, an initial fluid with the trace element and isotopic compositions of sample 4 (Tables 1, 2) infiltrates the Burlington-Keokuk Fm., repeatedly dissolving and recrystallizing calcite. Changes in the isotopic compositions of O, Sr and Nd in the fluid are determined using an iterative calculation procedure, mass balance relationships, fractionation factors and distribution coefficients, as detailed in Banner (1986) and Banner and Hanson (in preparation).

It can be seen from the exchange pathways in Fig. 8 that the oxygen isotopic composition of the fluid is changed towards equilibrium with the rock composition at relatively high rock:water ratios. Owing to the low Sr concentration in the fluid relative to the rock (compared with oxygen concentrations in the same phases), the Sr isotopic composition of the water is reset at an order of magnitude lower rock-water ratio compared with its O isotopic composition. In the same model, the fluid acquires the $\epsilon_{Nd}(0)$ value of the rock at extremely low rock:water ratios as a consequence of the low REE concentrations in the fluid $(13 \cdot 10^{-6}$ ppm) relative to the carbonates (10 ppm, Fig. 8). While this model uses sample 4 as a starting composition, similar relative differences be-
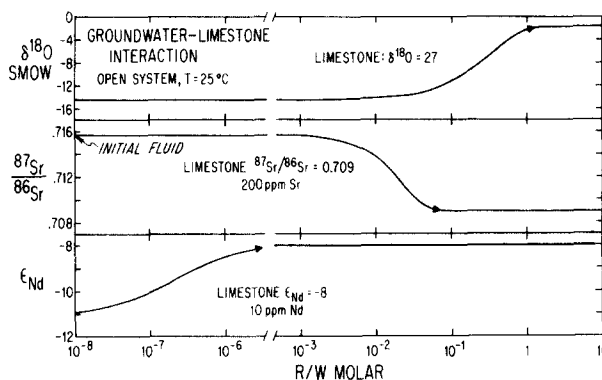

FIG. 8. Theoretical simultaneous variations in the O, Sr and Nd isotopic composition of a groundwater as a function of progressively increasing rock-water interaction. In this model, a groundwater with the composition of sample 4 (Tables 1 and 2) infiltrates a limestone aquifer comprised of calcite with the isotopic compositions and trace element abundances shown. The water repeatedly dissolves and recrystallizes calcite. An iterative calculation is used to simulate isotopic and trace element exchange during dissolution-recrystallization of the limestone using mass balance, distribution coefficients and fractionation factors following Banner (1986) and Banner and Hanson (in preparation). In the open system model shown, R/W MOLAR = (moles of rock):(moles of water); the calcite-water exchange $K_D(Sr/Ca) = (m_{Sr}/m_{Ca})_{calcite}/(m_{Sr}/m_{Ca})_{water} = 0.05$, where m_{Sr} and m_{Ca} are molar concentrations; $K_D(Nd/Ca) = 100$ (Palmer, 1985); and $\Delta_{calcite-water} = 2.78 \cdot 10^6 T^{-2} (°K) - 2.89$ (Friedman and O'Neil, 1977). Arrows denote R/W value at which the fluid has attained isotopic equilibrium with the host rock. Note the order of magnitude difference in the rock:water ratios at which O and Sr isotopes in the fluid are equilibrated with the rock composition, and the extremely low rock:water ratio required to completely reset the fluid's $\epsilon_{Nd}(0)$ value. Similar results are obtained using either dolomite or calcite-dolomite mixtures as the aquifer, or other groundwater sample compositions.

tween the isotopic systems are obtained using the other samples as starting compositions.

Sr vs. O isotopic variations in the groundwaters show an invariance in $^{87}Sr/^{86}Sr$ values over a wide range of $\delta^{18}O$ values (Fig. 9). Also shown in Fig. 9 are the relatively high $\delta^{18}O$ and low $^{87}Sr/^{86}Sr$ values of both Mississippian carbonates and local meteoric recharge in central Missouri. Two calculated model curves in Fig. 9 illustrate the simultaneous variations in Sr and O isotopes during 1) rock-water interaction between a saline endmember groundwater and the carbonates, and 2) mixing between the same endmember groundwater and local meteoric recharge. Rock-water interaction cannot explain the isotopic variations within the suite of waters because the isotopic compositions of the dissolved Sr will be reset to the $^{87}Sr/^{86}Sr$ value of the carbonate before the $\delta^{18}O$ value of the water will change significantly (Figs. 8, 9). Mixing between saline and dilute endmembers can readily account for the Sr-O isotopic relationships, and it is a model that is consistent with the major and trace element and H-O isotopic correlations discussed earlier.

While the Sr-O isotopic variations and model calculations indicate that interaction between the central Missouri groundwaters and Mississippian carbonates has been limited, Sm-Nd isotopes in the samples can potentially place even stricter limits on the extent of such interaction. The results of the model calculations show that Nd isotopic differences between water and rock can only be maintained in a system
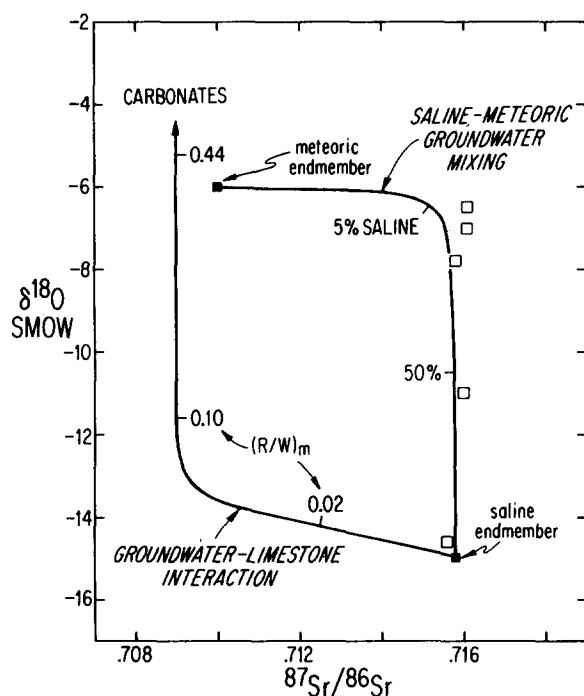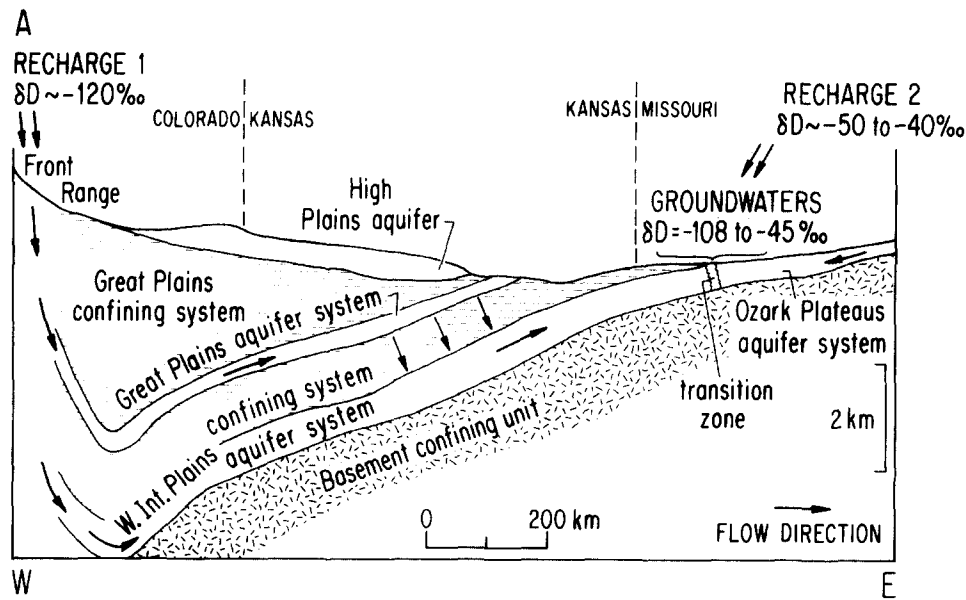

FIG. 9. $\delta^{18}O$ vs. $^{87}Sr/^{86}Sr$ for central Missouri groundwaters. Model curves are shown for 1) rock-water interaction between Mississippian carbonates and hypothetical saline endmember groundwater and 2) mixing between saline and dilute meteoric water endmembers. Range of carbonate data, saline and meteoric endmember values, and method of curve calculation as in previous figures. Owing to differences in relative concentrations of O and Sr in fluid and solid phases, these two processes are readily distinguished. The groundwater data are consistent with the mixing model.

with effectively low rock:water ratios (Fig. 8). Such a system can be envisioned as one in which the fluid migrates through an aquifer and experiences extremely limited interaction with the aquifer rocks. The groundwaters range to lower $\epsilon_{Nd}(0)$ values compared to the Burlington-Keokuk carbonates, chert, apatite and glauconite (Fig. 7), suggesting that at least some of the water samples have not reacted with Mississippian carbonate rocks to any significant extent.

An alternative model to the dissolution-recrystallization calculations presented above is a model involving a fluid that ceases to interact with the wall rock once carbonate saturation has been attained. The initial calcite and fluid isotopic compositions and trace element abundances are the same as those used in the earlier model (Fig. 8). In the present model, the greatest isotopic change in the fluid will occur under the conditions that produce the maximum dissolution of calcite. This maximum dissolution case involves a dilute fluid achieving calcite saturation under a relatively high CO_2 partial pressure and low temperature. The chemical equilibrium model discussed earlier was used to determine a range of P_{CO_2} values of 0.01 to 0.04 bar for the central Missouri groundwaters. FREEZE and CHERRY (1979, p. 256) demonstrate that at a higher P_{CO_2} of 0.10 bar, dissolution of 0.63 g of $CaCO_3$ per liter of water is required to produce saturation at 25°C. From mass balance calculations, it can be seen that dissolution of this small amount of calcite with significantly different $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ values relative to the fluid will not affect the isotopic composition of Sr or O of the fluid. The amount of Sr added to the water from the dissolution of calcite comprises <2% of the dissolved Sr budget over the concentration range of the water samples (8–41 mg/l Sr; Fig. 6). This same amount of calcite dissolution represents a factor of 500 times the amount of Nd originally in solution, and will result in Nd isotopic equilibration between water and rock.

Thus, a groundwater that has achieved both carbonate saturation and a Nd isotopic signature that is distinct from its carbonate aquifer rock most likely attained this saturation state prior to its entrance into the present carbonate aquifer. On the other hand, saline groundwaters can maintain an earlier acquired Sr isotope signature, even during dilution and subsequent dissolution of calcite to saturation. The equilibration of the central Missouri groundwaters with calcite and dolomite prior to their entrance into the present aquifer may inhibit further rock-water interaction and therefore serve to limit the extent of isotopic exchange. Additional factors that may limit this exchange include: 1) flow rates through the carbonate aquifer may be too high to permit reactions to progress; and 2) flow through the carbonates may be controlled by fractures or karstic channels that are lined with carbonates that have previously been recrystallized by, and chemically and isotopically equilibrated with, similar flow regimes. Similar chemical equilibrium controls on fluid-rock isotopic exchange may also play an important role in other aqueous systems and in magmatic systems. If an aqueous solution or silicate melt is at or near chemical equilibrium with the wall rock that constitutes the conduits or pore network through which the fluid migrates, then the thermodynamic limits imposed on chemical exchange in such a system may enable the preservation of gross isotopic differences between fluid and rock.

The small resolvable differences in Nd isotopic composi-

A

B

Fig. 10. (a) Generalized hydrologic model for the Central Great Plains area of the United States, modified from JORGENSEN *et al.* (1989). The gravity-flow system is sustained by meteoric recharge in the Front Range. Structural relationships are simplified here. The Western Interior Plains aquifer system principally comprises Cambrian-Ordovician and Mississippian carbonates and sandstones. The Western Interior Plains confining system comprises Pennsylvanian shales and limestones and Permian evaporites. Transition zone marks region where eastward-migrating saline groundwater in Western Interior Plains aquifer system encounters fresh groundwater in Ozark Plateaus aquifer system. The stable isotope data for the central Missouri groundwaters range from values measured for meteoric waters of local origin (Recharge 2) to values for meteoric waters found in the Front Range (Recharge 1). Significant cross-formational flow shown through Pennsylvanian shales in the Western Interior Plains confining system is a requirement for models that invoke a Permian evaporite source of high groundwater salinities (see Figs. 10b and 11). (b) Lithostratigraphic sequence and principal geologic and hydrologic units in central Kansas (Rice and Ellsworth County), from WALTERS (1978), BAYNE *et al.* (1971) and JORGENSEN *et al.* (1989). D = dolostone, L = limestone, Sh = shale, An = anhydrite, St = halite, Ss = sandstone, Ck = chalk. Vertical scale pertains to thickness of systems and Hutchinson Salt Member only.

tions between the groundwaters and the carbonates create uncertainties for quantitative models. In addition, the limited number of studies to date on Nd isotopes in ancient marine sediments (SHAW and WASSERBURG, 1985; KETO and JACOBSEN, 1987) make it difficult to assess the extent to which pre-Mississippian marine deposits may have influenced the Nd isotopic composition of the groundwaters. An examination of the relative abundances of the REE may help constrain the rock-water interaction history of the groundwaters. For example, $^{147}Sm/^{144}Nd$ ratios in authigenic marine sediments are typically higher than those determined for clastic sediments or granitic crust (Fig. 7; BANNER *et al.*, 1988a). Although the argillaceous carbonates that constitute approximately 5% of the Burlington-Keokuk Fm. have $\epsilon_{Nd}(0)$ values

that are similar to the groundwaters, the significantly higher $^{147}Sm/^{144}Nd$ ratios in the argillaceous carbonates suggest that they were not the principal source of REE for the waters. This reasoning assumes that no Sm-Nd fractionation occurs during dissolution-recrystallization processes, such that the water acquires the $^{147}Sm/^{144}Nd$ ratio of the host rock. The determination of Ce/Nd ratios in the groundwaters would provide a discrimination between a Burlington-Keokuk or older marine authigenic sediment signature (*i.e.*, anomalously low Ce/Nd) and an extraformational clastic or granitic signature (*i.e.*, normal Ce/Nd, similar to North American Shale Composite; see BANNER *et al.*, 1988a). Under reducing conditions in the subsurface, this parameter may be less sensitive to fractionation processes compared with $^{147}Sm/^{144}Nd$.

GROUNDWATER SALINITIES-
CAMBRIAN and ORDOVICIAN ROCKS
Jorgensen et al. (1986)

■ >200 ‰
▦ 100-200
▨ 50-100
▩ 20-50
▢ 5-20
□ <5 ‰

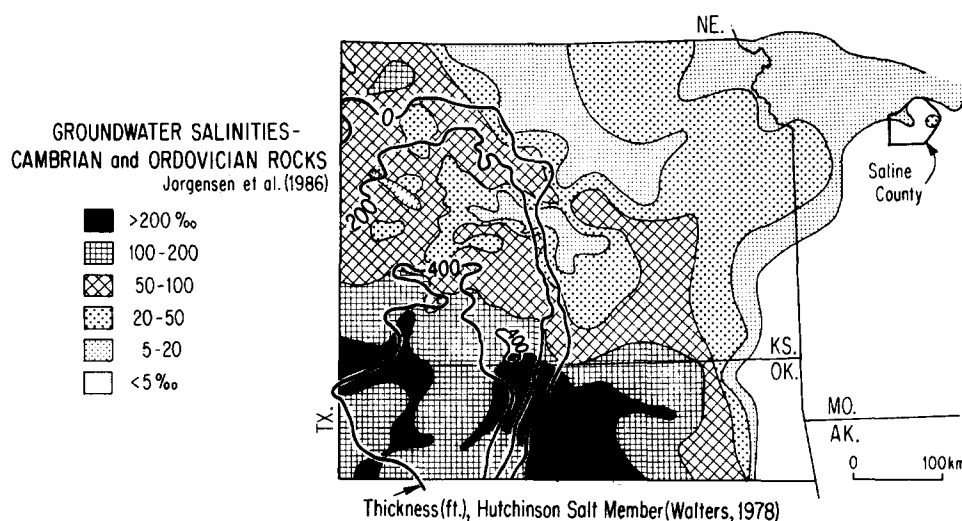Thickness(ft.), Hutchinson Salt Member(Walters,1978)

FIG. 11. Juxtaposition of groundwater salinities in Cambrian-Ordovician rocks in Kansas and parts of Missouri and Oklahoma, and areal extent and thickness of the Hutchinson Salt Member of the Permian Wellington Fm. Similar groundwater salinity distributions are obtained for Mississippian rocks in this region (JORGENSEN et al., 1986).

Hydrologic models and origin of the saline endmember

The approximation of the H-O isotopic data for the central Missouri groundwaters to the meteoric water line and the low $\delta^{18}O$ and δD values of the more saline samples indicate that the groundwaters could have originated in part as meteoric water from a distant, high altitude source. This interpretation appears to be consistent with the conceptual hydrologic model of JORGENSEN et al. (1989). In this model shown in Fig. 10, which is based on regional variations in groundwater compositions and potentiometric data, recharge from high elevations in the Front Range in Colorado is transmitted eastward through Paleozoic carbonates and sandstones (Western Interior Plains aquifer system) in the subsurface. Mixing between such waters of meteoric origin having low $\delta^{18}O$ and δD values and local meteoric recharge having higher $\delta^{18}O$ and δD values will produce the observed H-O isotopic correlation in the central Missouri groundwaters (Figs. 5b, 10a). From this model, it would be expected that other saline groundwaters in the Western Interior Plains aquifer system in Kansas and Missouri would have similarly low ^{18}O and D contents and a meteoric signature. The few isotopic studies that have been made to date on such waters give $\delta^{18}O$ and δD values that are lower than values for local meteoric recharge and lie on or parallel to the meteoric water line (CHAUDHURI et al., 1983; SIEGEL and MANDLE, 1984; COVENEY et al., 1987).

A comparison of the salinities of groundwaters in Mississippian and Cambrian-Ordovician rocks in Missouri, Kansas and Oklahoma with the distribution of bedded Permian halite in this region shows a close spatial coincidence between salt thickness and high groundwater salinities (Fig. 11). These Permian halite deposits are presently undergoing dissolution (GOGEL, 1981) and have been proposed as sources of salinity in subsurface water in the overlying Cretaceous Dakota Aquifer of Kansas and Nebraska (LEONARD et al., 1984) and in an underlying Mississippian oilfield in Kansas (CHAUDHURI et al., 1987). The spatial relationships shown in Fig. 11 strongly suggest a Permian halite source for the elevated Na

and Cl concentrations in groundwaters from Cambrian through Mississippian strata. This hypothesis requires significant vertical cross-formational flow of Na-Cl brines or diffusion of Na and Cl in response to density or concentration gradients. Either process would had to have been operable across a thick section of Pennsylvanian shales (Figs. 10a, b). The presence of highly saline fluids throughout the Paleozoic section in central Kansas (DINGMAN and ANGINO, 1969) suggests that this hypothesis is plausible. The groundwater salinity distributions in lower Paleozoic carbonates and sandstones in Kansas, Oklahoma and Missouri (Fig. 11) may reflect mixing between downward-migrating Na-Cl brines and dilute meteoric recharge from the west (Fig. 10). If the salinities of groundwaters from the region shown in Fig. 11 have originated in part from the halite in south-central Kansas, then saline groundwaters in central Missouri are indeed far-travelled, having migrated at least 400 km in the Western Interior Plains aquifer system.

In order for meteoric recharge from the Front Range to have been transmitted over a distance of 1000 km to the central lowlands of Missouri (Fig. 10) in the 65 Ma since the Front Range has been uplifted, flow rates in excess of 0.015 m/y are required. These rates are intermediate between: 1) model rates of up to several m/y determined for ancient gravity-driven brine migration through carbonates and sandstones in the Western Canada and Illinois basins (GARVEN, 1985; BETHKE, 1986), and 2) model rates as low as 10^{-5} m/y determined for present-day eastward flow of saline groundwater in the Western Interior Plains aquifer system in Kansas (CHRISTENSON and ADAMS, 1988; SIGNOR, 1988). Clearly, further geochemical, isotopic and hydrologic studies will lead to a more thorough understanding of the origin, age and flow patterns of saline groundwater in this large-scale system, which in turn may have important bearing on generalized models of element and hydrocarbon transport and sediment diagenesis.

The implication of a meteoric origin for the waters uniquely constrains the $\delta^{18}O$ values for the waters prior to any isotopic exchange during their evolution. The H-O isotopic data (Fig.

5b) indicate that no significant oxygen isotope shifts occurred during the migration history of the groundwaters. In contrast, the waters probably acquired their salinities and Sr and Nd isotopic signatures during this migration history. There are several scenarios in which a groundwater may aquire significant salinity and dissolved Sr and REE concentrations and radiogenic $^{87}Sr/^{86}Sr$ ratios with negligible changes in the water's H or O isotopic composition: 1) NaCl dissolution by meteoric water followed by rock-water interaction with silicates at sufficiently low rock:water ratios such that only Nd and Sr isotopic signatures in the water are reset toward the value of the rock; 2) NaCl dissolution by meteoric water followed by predominantly ion-exchange reactions between the saline water and interlayer cation sites in phyllosilicate minerals; 3) mixing on the order of 10:1 between a dilute meteoric water and a Na-Ca-Cl brine. If this brine had an extensive geochemical evolution in which high salinities (>300‰), high $^{87}Sr/^{86}Sr$ ratios (0.716) and marked positive $\delta^{18}O$ shifts (5–10‰) were attained, then such fluid-fluid mixtures would produce saline groundwaters with salinities of >30‰, $^{87}Sr/$ $^{86}Sr \simeq 0.716$, and $\delta^{18}O$ shifts of <1‰ from the meteoric water line.

The relatively high $^{87}Sr/^{86}Sr$ values of 0.7155–0.7161 for the groundwaters may reflect an integration of Sr that was incorporated during a long migration history, predominantly from reactions with clays and feldspars in argillaceous Paleozoic strata or Precambrian basement, and subordinately from carbonates. Higher subsurface temperatures of pore fluids in the Paleozoic section of Kansas (~50°C) relative to the present temperatures of the central Missouri groundwaters (13–16°C) may have promoted these reactions. The slow migration of a Na-Cl brine across a thick shale sequence may provide a setting for extensive ionic exchange between the brine and clays and feldspars in the shales, thereby enriching the brine in Ca, Sr, ^{87}Sr and REE and depleting it in Na. This evolved brine may then mix with dilute meteoric waters in underlying Paleozoic carbonates and sandstones in Kansas.

In summary, the central Missouri groundwaters may have acquired their chemical and isotopic characteristics as a result of a history that included far-travelled meteoric recharge, halite dissolution, interaction with Paleozoic shales, carbonates and sandstones, migration to shallow aquifer levels in Missouri and mixing with meteoric recharge of local origin and discharge in central Missouri through Mississippian carbonates, with minimal interaction between the groundwaters and the local carbonates. Several factors may act to inhibit reactions between the groundwaters and Mississippian carbonates during migration to the surface: 1) calcite and dolomite saturation in the groundwaters; 2) rapid flow rates through the carbonates; 3) flow pathways controlled by fractures or karstic channels that are lined with carbonates that have previously been equilibrated with similar groundwater compositions.

CONCLUSIONS

1) Na-Ca-Cl groundwaters discharge from Mississippian carbonates and Ordovician sandstones and carbonates in central Missouri and have salinities of 1 to 30‰, and severalfold enrichments relative to seawater in Ca, Sr and REE. Each element analyzed (Sm, Nd, Rb, Sr, Na, Ca, Mg, K, B,

Li, Si) occurs almost entirely as a dissolved species and different filtrate size fractions of individual water samples have essentially the same $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{147}Sm/^{144}Nd$ and $^{18}O/^{16}O$ ratios. Mixing between saline and dilute endmember waters and reaction with carbonate and silicate minerals can account for the compositional variation in this suite of groundwaters that maintain calcite and dolomite saturation and quartz supersaturation over the wide salinity range.

2) The groundwaters have a wide range of δD (−108 to −45‰) and $\delta^{18}O$ (−14.7 to −6.5‰) values that form a trend similar to that for modern meteoric waters ranging from central Missouri to high altitude and high latitude regions of North America. Both δD and $\delta^{18}O$ values are inversely correlated with salinity. The H-O isotopic correlation is consistent with the saline-dilute water mixing model that is based on elemental variations.

3) The groundwaters have $^{87}Sr/^{86}Sr$ ratios ranging from 0.7155 to 0.7161. These values are considerably more radiogenic than the estimated range of Paleozoic seawater and previously published data for Mississippian (Burlington-Keokuk Fm.) carbonates in central Missouri. Models involving the derivation of the saline groundwaters from ancient seawater or marine brines are precluded by the H, O and Sr isotopic data. The waters have $\epsilon_{Nd}(0)$ values that range from −10.9 to −8.1, and $^{147}Sm/^{144}Nd$ values of 0.108 to 0.128, which are generally lower than values for carbonates, chert, apatite and glauconite from Burlington-Keokuk strata.

4) The results of model calculations that simulate isotopic exchange between the waters and Mississippian carbonate host rocks in central Missouri indicate that interaction between the groundwaters and the carbonates has been extremely limited. The groundwaters apparently acquired their $\delta^{18}O$ and δD values as meteoric recharge and their Sr and Nd isotopic characteristics *via* interaction with extraformational crustal sources, and to a large extent preserved these signatures during subsequent migration through the carbonates in central Missouri. The present state of chemical equilibrium between the groundwaters and aquifer minerals may serve to limit rock-water interaction, thereby maintaining the earlier acquired isotopic signatures in the waters.

5) The geochemical characteristics of the saline groundwaters in central Missouri can be accounted for by a multistage history involving 1) meteoric recharge in the Front Range of Colorado, 2) derivation of Na and Cl *via* halite dissolution in the subsurface of Kansas, 3) mineral-solution equilibria during subsurface migration through Paleozoic strata (and possibly Precambrian basement) and acquisition of crustal Sr and REE signatures, 4) dilution and migration to shallow aquifer levels in central Missouri, and 5) mixing with dilute meteoric water of local derivation, discharge through Mississippian carbonates, and preservation of the pronounced isotopic disequilibrium between the waters and the carbonates.

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