

Regional Ground-Water Mixing and the Origin of Saline Fluids: Midcontinent, United States

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Ground waters in three adjacent regional flow systems in the midcontinent exhibit extreme chemical and isotopic variations that delineate large-scale fluid flow and mixing processes and two distinct mechanisms for the generation of saline fluids. Systematic spatial variations of major ion concentrations, H, O, and Sr isotopic compositions, and ground-water migration pathways indicate that each flow system contains water of markedly different origin. Mixing of the three separate ground waters exerts a fundamental control on ground-water composition. The three ground waters are: (i) dilute meteoric water recharged in southern Missouri; (ii) saline Na-Ca-Cl water in southeastern Kansas of far-traveled meteoric origin that acquired its salinity by halite dissolution; and (iii) Na-Ca-Cl brines in north-central Oklahoma that may have originated as Paleozoic seawater.

Saline ground waters are a common but poorly understood component of many sedimentary basins. The processes involved in the formation, evolution, and migration of saline ground waters are fundamental to an understanding of continental-scale hydrologic processes and have important implications for sedimentary basin evolution, hydrocarbon dynamics, ore formation, and water-use management. Three generalized processes have been invoked to account for the origin of saline fluids in sedimentary basins: (i) subsurface dissolution of evaporite deposits; (ii) subaerial evaporation and burial-modification of seawater; and (iii) shale membrane filtration (1). Shale membrane filtration, whereby water molecules pass through semipermeable, compacted clay layers and dissolved ions are retained to varying degrees, has not been documented in large-scale field examples (1). In addition to these processes, water-rock interaction and fluid mixing can significantly alter ground-water composition and thereby mask initial salinity-generating processes.

Ground waters in Cambrian-Ordovician and Mississippian sedimentary rocks in southwestern Missouri, southeastern Kansas, and northern Oklahoma exhibit extreme variations in chemical composition. In this article, we use elemental and isotopic results in conjunction with hydrogeologic data in order to characterize the chemical evolution and flow history of these ground waters. We then use these results to quantify the important role of fluid mixing processes in ground-water evolution and to identify the origins of two different saline ground waters in the same aquifer system. The operation of two distinct mechanisms for generating saline

ground waters in the same aquifer system has significant bearing on models for the origin of saline subsurface fluids.

Hydrogeologic setting. Regionally continuous Paleozoic carbonate rocks comprise large parts of two aquifer systems—the Ozark Plateaus and Western Interior Plains aquifer systems in Missouri, Kansas, and Oklahoma (2). Within these two aquifer systems, there are three regional patterns of ground-water flow (Fig. 1A). Ground water in southern Missouri migrates radially outward from the Ozark Dome through the Ozark Plateaus aquifer system; the resulting flow is westward in southwest Missouri into southeastern Kansas (3). In Kansas, ground water migrates to the southeast and east through the Western Interior Plains aquifer system (4–6). Discharge occurs from natural springs in Cambrian-Ordovician and Mississippian carbonate rocks in central and southern Missouri, and to the Missouri and Mississippi rivers (2). Ground-water salinity in the Western Interior Plains aquifer system increases to the west and southwest. In the southern part of this system, ground-water flow is out of the Anadarko Basin, which is overpressured, to the northeast (5, 6). These three regional flow components converge in the study area (Fig. 1A), a setting ideally suited to address large-scale ground-water mixing processes. The principal aquifers are Cambrian-Ordovician and Mississippian marine carbonate rocks (Fig. 1B). Underlying Precambrian crystalline basement rocks and overlying Pennsylvanian shale serve as confining units. Regional potentiometric gradients for both Cambrian-Ordovician and Mississippian aquifer rocks are similar (5), and the two units are hydraulically connected (7, 8). Thus, they are considered here as one regional hydrostratigraphic unit.

Paleozoic rocks were deposited in a broad epicontinental sea covering the greater Oklahoma Basin, which encompassed most of the southern midcontinent (9). Subsequent tectonic activity produced the Anadarko Basin, Nemaha Ridge, and Ozark Dome (Fig. 1), among other structures. Porosity and permeability vary considerably within the carbonate aquifer units because of the presence of abundant and spatially heterogeneous solution channels and fractures (7, 8). Aquifer porosity and permeability are presumed to be greater in uplifted areas, such as the Nemaha Ridge and Ozark Dome, where rocks have been subjected to greater solution weathering and fracturing, than in deeper basinal areas such as the Anadarko Basin (4).

Ground-water geochemistry. Thirty-nine sample localities were selected in order to assess regional variations in ground-water geochemistry. Ground-water samples from Cambrian-Ordovician and Mississippian aquifers were collected from municipal drinking water and industrial water supply wells, and oil and gas wells during November 1989 and June and July 1991 (10). Well depths range from approximately 270 m to 1340 m, increasing to the western and southwestern portions of the study area due to the regional dip of these units. We apply variations in major and trace element concentrations and H, O, and Sr isotopes to this flow system as tracers of hydrologic flow and water-rock interaction along ground-water migration pathways. Hydrogen isotope values and Cl concentrations are among the most conservative parameters in ground water during processes of water-rock interaction involving carbonates and many silicates, and are therefore particularly well suited to assess processes of fluid mixing.

The ground waters throughout the region exhibit a wide range in elemental and isotopic compositions (Table 1). Salinity ranges from 200 to 250,000 mg/liter total dissolved solids (TDS), and δD and $\delta^{18}O$ values (11) range from -108 to -5 per mil and -14.6 to 2.8 per mil, respectively. The $^{87}Sr/^{86}Sr$ values range from 0.7089 to 0.7167. Geochemical and isotopic variations over the study area allow the ground-water samples to be divided into three groups, each with a distinct endmember composition. Endmember 1 ground waters are dilute waters with small amounts of dissolved solids (200 to 800 mg/liter TDS), predominantly Ca, Mg, and HCO_3 ions. The δD and $\delta^{18}O$ values of this endmember vary from -44 to -36 per mil and -6.8 to -5.4 per mil, respectively, and reflect the composition of local meteoric water recharging to the Ozark Plateaus aquifer system (Fig. 2). The $^{87}Sr/^{86}Sr$ values (0.7099 to 0.7117) are intermediate between the

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other endmembers. Endmember 2 is a saline Na-Ca-Cl water with salinities of 22,000 to 35,000 mg/liter TDS, δD values of -108 to -98 per mil, and $\delta^{18}O$ values of -14.6 to -12.4 per mil. These low δD and $\delta^{18}O$ values are similar to those of modern meteoric precipitation to the west of the study area in the Front Range of Colorado [(12) Fig. 2]. The most saline samples of group 2 have the lowest δD and $\delta^{18}O$

values. The $^{87}Sr/^{86}Sr$ values (0.7121 to 0.7156) are higher than the values for the two other endmembers. Endmember 3 is a Na-Ca-Cl brine with salinities of 230,000 to 250,000 mg/liter TDS. This water has H and O isotope values that are not indicative of values for meteoric waters; rather they are close to values for modern ocean water, with slightly higher $\delta^{18}O$ values. H and O isotope data for group 3 ground waters are

consistent with trends observed for other saline basinal fluids where salinity increases with deviation from meteoric δD and $\delta^{18}O$ values (13). The $^{87}Sr/^{86}Sr$ values of these brines range from 0.7091 to 0.7099. These values are significantly lower than those for the other saline water (endmember 2), overlap with the estimated range of values for Paleozoic seawater (14), and are in the range of values for Paleozoic carbonate rocks in the midcontinent (15).

Endmember signatures and ground-water mixing models. The stable isotope data indicate that ground waters in groups 1 and 2 are meteoric in origin, but not those in group 3 (Fig. 2). The occurrence of saline ground waters with meteoric δD and $\delta^{18}O$ values (that is, endmember 2) is different from the trend commonly observed in saline ground waters from other localities where increasing salinity correlates with increasing deviation from the δD and $\delta^{18}O$ values of meteoric waters (13). This positive correlation is generally attributed to ground-water evolution by modification of seawater, extensive water-rock interaction, or mixing with evolved fluids. The position of endmember 2 ground waters along the meteoric water line indicates that these processes are not controlling their H and O isotopic composition.

An origin for endmember 2 ground waters involving meteoric precipitation in high altitude regions to the west of the study area (the Colorado Front Range) implies that eastward migrating waters in the central part of the Western Interior Plains aquifer system are far-traveled. Such an origin is consistent with the hydrologic model proposed by Jorgensen (4, 12). Other potential origins for ground waters with such low δD and $\delta^{18}O$ values include recharge during colder climatic periods and infiltration by glacial meltwater (16, 17). On the basis of geographic constraints, and rates and patterns of ground-water flow (2, 5, 12), a glacial meltwater origin is unlikely for endmember 2. A model involving far-traveled (~ 1000 km) water also necessitates that the water is old, and thus may reflect recharge during colder climatic periods. The calculated temperature difference (8° to $14^\circ C$ cooler) necessary to account for the observed $\delta^{18}O$ difference (6 to 9 per mil) between endmember 2 and present-day meteoric precipitation in central Kansas exceeds estimates of ice-age surface temperature changes of 4° to $5^\circ C$ for the North American midcontinent (18). Moreover, recharge during intermittent periods of colder climates is not a likely source for regional isotopic trends (12), and altitude effects are proposed to exert a dominant control on stable isotope values of meteoric precipitation relative to climatic effects (19). Halite dissolution can account for

Fig. 1. (A) Regional distribution of ground-water salinities in Cambrian-Ordovician rocks expressed as contours of total dissolved solids (TDS) in grams per liter. Regional ground water flow gradients in Cambrian-Ordovician rocks, based on equivalent freshwater potentiometric head values, are depicted with arrows and indicate three major flow systems converging in the study area [(2-6) NWIP = northern section of the Western Interior Plains aquifer system, SWIP = southern section of the Western Interior Plains aquifer system, OP = Ozark Plateaus aquifer system]. Ground waters in Mississippian rocks exhibit similar salinity and hydraulic gradients. Salinity and potentiometric data based on (5). Hydrologically important structural features are labeled. A-A' is line of cross section depicted in (B). Geochemical data for five ground-water samples from the Western Interior Plains and Ozark Plateaus aquifer systems in Saline County, Missouri, detailed in (12), are included in this study. (B) Representative west-east cross section through the study area from (44). Highs in Precambrian basement (for example, the Nemaha Ridge) exert local control over regionally continuous Cambrian-Ordovician and Mississippian carbonate aquifer units. (C) Close-up of study area from Fig. 1A showing ground-water sample localities. Symbols used in all figures correspond to geochemical sample groups as defined in Table 1. Open symbols represent group 1, half-filled symbols correspond to group 2, and filled symbols correspond to group 3. Circles denote endmember waters, and squares, triangles, and diamonds delineate waters of intermediate composition in each group. The geochemical variations of each endmember and group are shown in Fig. 3A and discussed in text. (D) Close-up of study area depicting relation between sample locality and ground-water composition. Sample group identifications (1A, 1B, 1C, and so forth) correspond to geochemical compositions identified in Fig. 3A. Position of boundary lines between groups, which are based on sample localities and geochemical characteristics, are less certain near edges of study area. Arrows represent regional ground-water flow patterns based on data in (2-6). Note correlation of geographic sample locations, ground-water flow patterns, and geochemical composition.

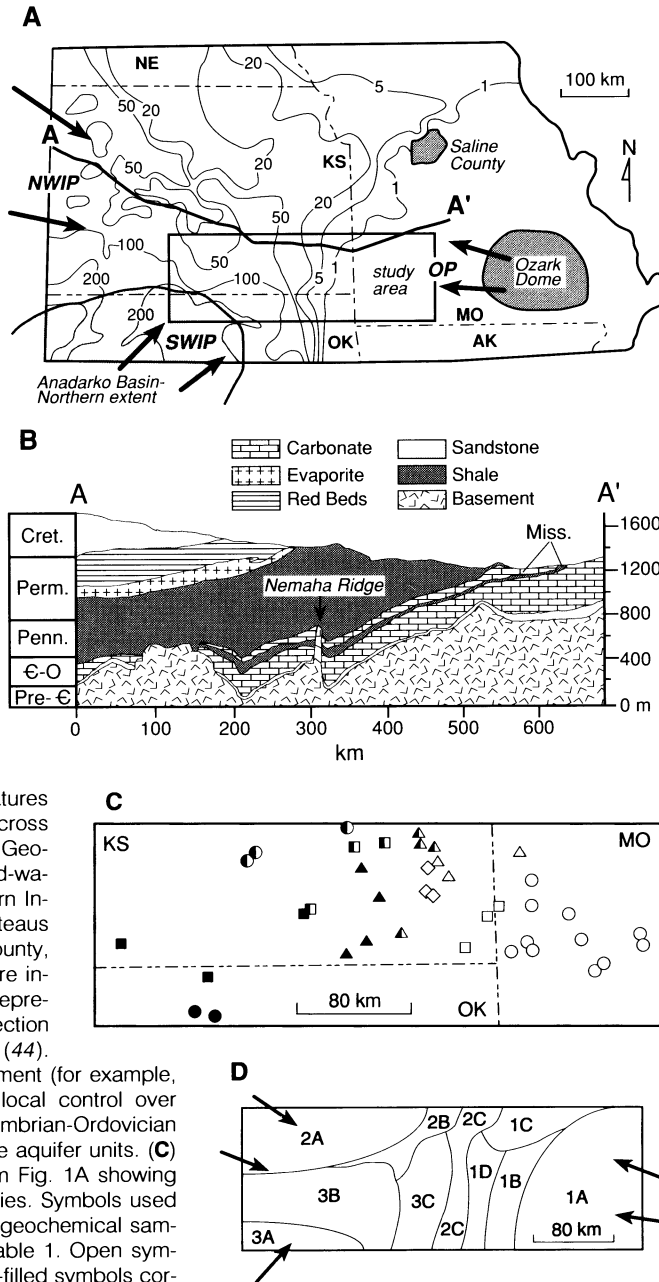
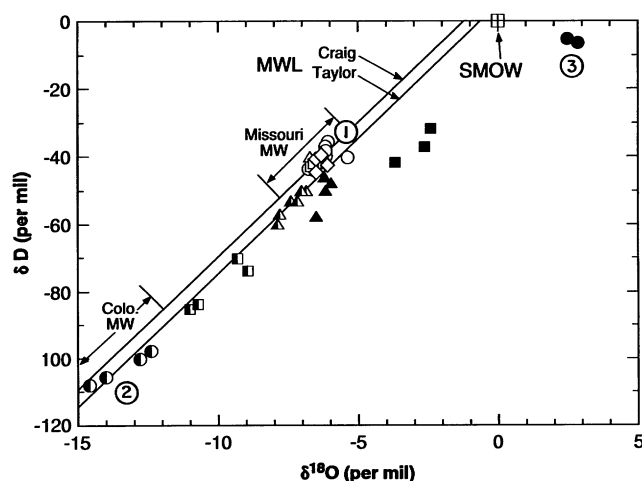


Table 1. Range of geochemical and isotopic parameters for midcontinent ground waters; Temp, temperature. Categorization of groups and respective group endmembers discussed in text. Geochemical data for five

samples from Saline County, Missouri (12), are included in groups 1 and 2. Analytical methods and sample information given in (10). Seawater data from (43). δD and $\delta^{18}O$ values relative to SMOW (11).

	TDS (mg/liter)	Temp (°C)	$\delta^{18}O$ (per mil)	δD (per mil)	$^{87}Sr/^{86}Sr$	Cl (mg/liter)	Br (mg/liter)	Ca (mg/liter)	Sr (mg/liter)
Endmember 1 (1A)	200 to 800	17 to 21	-6.8 to -5.4	-44 to -36	0.70989 to 0.71168	1.5 to 25	<1	7.9 to 101	0.04 to 0.43
Group 1 (1A-1D) <i>n</i> = 21	4,700 to 14,100	15 to 28	-6.8 to -5.4	-43 to -36	0.70989 to 0.71562	1.5 to 7,300	<1 to 17	7.9 to 338	0.03 to 15
Endmember 2 (2A)	21,600 to 35,000	14 to 42	-14.6 to -12.4	-108 to -98	0.71211 to 0.71557	11,600 to 19,300	17 to 28	420 to 1,800	36 to 59
Group 2 (2A-2C) <i>n</i> = 14	6,300 to 63,200	16 to 42	-14.6 to -7.0	-108 to -50	0.71170 to 0.71665	3,400 to 38,200	7 to 75	260 to 3,400	9.0 to 59
Endmember 3 (3A)	230,000 to 250,000	33 to 40	2.5 to 2.8	-6 to -5	0.70911 to 0.70989	170,000 to 184,000	360 to 620	5,900 to 16,100	810 to 1,500
Group 3 (3A-3C) <i>n</i> = 9	62,300 to 250,000	24 to 52	-6.5 to 2.8	-58 to -5	0.70893 to 0.71510	39,000 to 184,000	130 to 620	2,300 to 25,900	83 to 1,500
Seawater	36,000		0	0	0.70917	19,000	67	410	8

Fig. 2. δD versus $\delta^{18}O$ for ground-water samples with respect to the meteoric water line (MWL) of both Craig (45) and Taylor (28); 1, 2, and 3 (circled) refer to ground-water groups as discussed in text. Values for meteoric water for southern Missouri and Colorado are from (28, 45, 46). Symbols as in Fig. 1C.



both the salinity and meteoric signature of endmember 2 and is consistent with Na-Br-Cl systematics for these ground waters (20).

Similar to endmember 2 ground waters, endmember 3 is also a saline Na-Ca-Cl water, but exhibits a distinct isotopic and elemental signature. Values of δD and $\delta^{18}O$ similar to those of endmember 3 have been demonstrated to result from the evaporation of seawater (21). The amount of evaporation can be expressed by a seawater evaporation factor (equal to the ratio of the H_2O in unevaporated seawater to the H_2O remaining in solution, by weight); for the H and O isotope data the evaporation factor is estimated to be in the range of 4 to 12 (21, 22). Similarly, the Br and Cl concentrations of endmember 3 ground waters correspond to an evaporation factor in the range of 5 to 10 (23). These evaporation factors are also consistent with speciation models that indicate that endmember 3 waters are close to halite saturation, which begins at an evaporation factor of 11 (24). These chemical and isotopic variations are similar to trends for fluid inclusions from Permian halite in central Kansas that have been

proposed to be evaporatively concentrated Permian seawater (22, 25).

Two-component mixing between a saline and a dilute endmember ground water has been previously delineated on a local scale in this area (7, 12, 26). Our chloride and δD data show that mixing involves all three endmember ground waters (Fig. 3, A, B, and C). Systematic variations of δD values and salinity across the study area indicate that the endmember ground waters originate in distinct geographic areas (compare Figs. 1D and 3A). The close correspondence among mass-balance model results, ground-water geochemical variations, flow patterns, and sample localities demonstrates that fluid-mixing exerts a fundamental control on ground-water compositions over the 40,000 km² study area. As indicated in Fig. 3C, the freshwater endmember, endmember 1, makes up a greater component of the mixed ground waters in the center of the study area than do the other ground waters. This result is consistent with the higher permeability and ground-water flow rates of the Ozark Plateaus aquifer system relative to the Western

Interior Plains aquifer system (2-4). Jorgensen *et al.* (27) proposed that this mixing zone has migrated outward from the Ozark Dome (that is, westward into the study area) through time as erosion resulting from uplift of the Ozark Dome has decreased the thickness of Pennsylvanian shale overlying the aquifer in southern Missouri.

On the basis that group 1 and 2 ground waters have retained their meteoric δD and $\delta^{18}O$ values, water-rock interaction between carbonate aquifer rocks and these ground waters has been limited, as such interaction would increase the $\delta^{18}O$ values of the water (13, 28). Undersaturation of a ground water with respect to minerals (primarily calcite) in the host aquifer rocks provides a driving mechanism for water-rock interaction and isotopic shifts. Calcite undersaturation in ground waters may result from mixing between ground waters of distinct composition, even when the ground waters that mix are each saturated with respect to calcite (29). Nearly all of the water samples we analyzed are saturated or supersaturated with respect to calcite (Fig. 4). Moreover, calculated saturation indices for mixtures of endmember water compositions approximate saturation indices of the intermediate ground-water samples. These results indicate that ground-water mixing does not produce undersaturation with respect to calcite and support the interpretation that geochemical variations (such as stable isotope values) across the study area are controlled by mixing of ground waters rather than water-rock interactions.

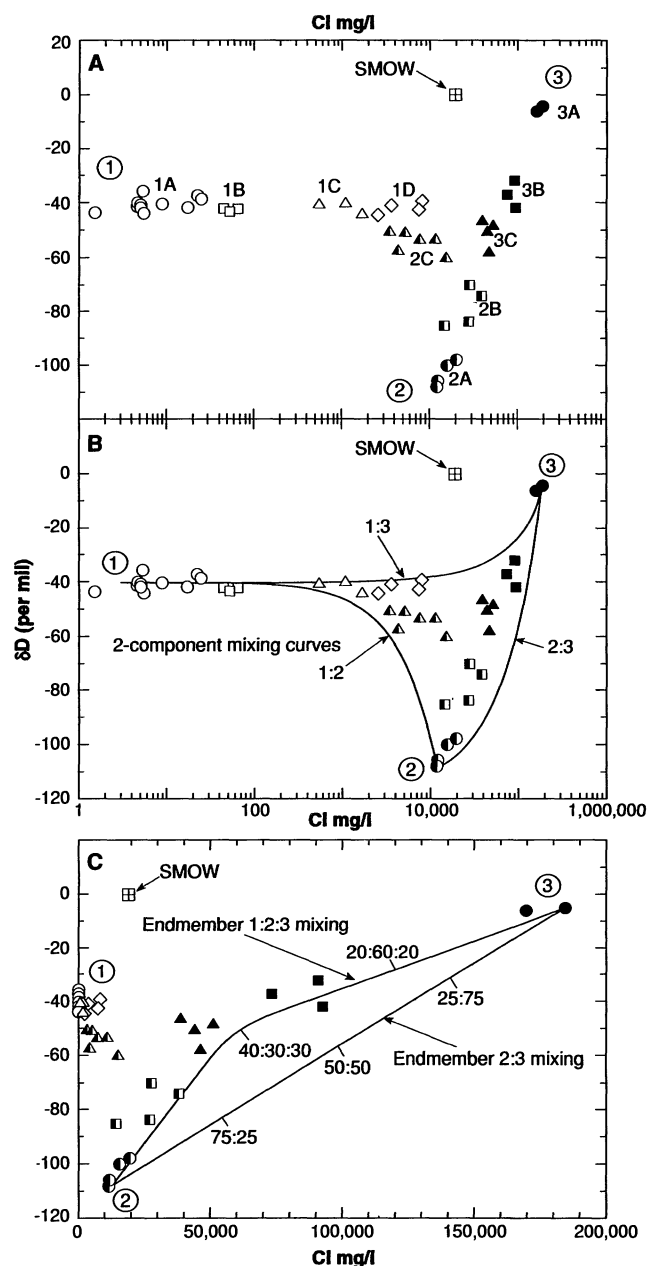
Interaction of ground water with the carbonate or silicate rocks of the aquifer and confining systems may affect the composition of other isotopic systems and elemental concentrations, however. The $^{87}Sr/^{86}Sr$ value of a saline ground water may be altered by low extents of water-rock interaction without significantly altering the $\delta^{18}O$ or δD values of the water (12). Al-

though the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the endmember ground waters are distinct, values for several intermediate (that is, mixed) waters are outside the range of the endmembers (Table 1) and therefore cannot be explained solely by mixing among the three endmember waters. The higher $^{87}\text{Sr}/^{86}\text{Sr}$ values of waters in groups 1 and 2 cannot reflect interaction with carbonate aquifer rocks either. High $^{87}\text{Sr}/^{86}\text{Sr}$ values probably resulted from interaction of ground water with silicate minerals, such as cation exchange with clay minerals (30) and the dissolution or alteration of potassium feldspar and mica (31, 32). Such silicate minerals are present in the underlying granitic basement rocks and argillaceous sedimentary rocks within the aquifer system and overlying confining system.

Hydrologic models and salinity origins. Jorgensen (4) proposed that ground waters in the Western Interior Plains aquifer system are far-traveled and migrate eastward from the Front Range of Colorado by gravity-driven flow. Our results support this model. There is also a clear distinction in geochemical composition between the ground waters in the northern (endmember 2) and southern (endmember 3) sections of this aquifer system.

The geochemical data for endmember 2 ground water, flowing into the study area from the west, indicates an origin involving dissolved halite. In support of this model, bedded halite in subsurface Permian evaporite strata of central Kansas (Fig. 1B) is undergoing dissolution (12, 33). Vertical flow of brines produced by halite dissolution across Pennsylvanian shales in central Kansas would result in elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values by interaction with silicate minerals. On the basis of (i) H, O, and Sr isotopic values and major and trace element concentrations and (ii) the geographic proximity of endmember 2 ground waters to bedded Permian halite (12), we propose that the endmember 2 ground water is itself a mixture of dilute meteoric recharge from the west and downward migrating brines in central Kansas. Dingman and Angino (34) documented the presence of saline fluids in Pennsylvanian shales in central Kansas. The salinity of these fluids exceeds that of ground waters in Cambrian-Ordovician and Mississippian carbonate aquifers in the same areas. An approximate 1:4 mixture of these brines and dilute ground waters with low δD and $\delta^{18}\text{O}$ values migrating eastward in Cambrian-Ordovician and Mississippian rocks can account for the composition of endmember 2 ground waters (20). Additionally, two-dimensional finite-element hydrologic modeling of this system (35) indicates that downward flow is occurring across Pennsylvanian shales in central Kansas.

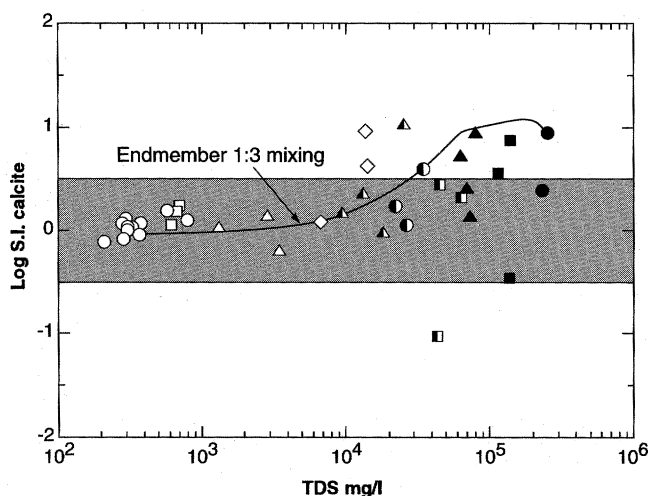
Fig. 3. (A) δD versus Cl concentration, with Cl concentration depicted on a logarithmic scale to illustrate variations of both dilute and saline ground waters. Other geochemical variation diagrams such as δD versus Sr, and $\delta^{18}\text{O}$ versus Na, exhibit similar trends. Group identifications (1A, 1B, 1C, and so forth) correspond to those shown on Fig. 1D. Open symbols represent group 1, half-filled symbols correspond to group 2, and filled symbols are group 3. Circles denote endmember waters, with squares, triangles, and diamonds (for group 1D) delineating progressively mixed intermediate waters in each group. A, B, C, and so forth also delineate progressively mixed intermediate waters in each group. Note correlation between geochemical composition (Fig. 3A) and sample localities (Figs. 1, C and D). **(B)** Same as (A). Curves depict results of mixing models involving endmember ground waters, based on mass-balance relations (47). Simulated mixtures readily encompass natural ground-water compositions. **(C)** Same as (A) with Cl concentration on a linear scale to illustrate relation between two saline ground water groups. Mixing curves compare two-component mixing between saline endmembers 2 and 3 and three-component mixing involving all three endmembers. Percentages of each endmember involved in the mix are depicted at various points along the model curves and are indicative of relative amounts of endmember contributions to mixed ground waters. The three-component mixing model more closely accounts for observed ground-water compositions than does the two-component model.



The origin of the high-salinity waters in the southern part of the Western Interior Plains aquifer system (endmember 3) is not readily explained by the same model. As discussed above, δD and $\delta^{18}\text{O}$ values and the relation of Br and Cl concentrations are consistent with numerous studies in which evaporative concentration of seawater has been proposed as an origin for such geochemical variations. However, the geochemistry of this fluid also must reflect the results of extensive water-rock interaction. Such interaction has been invoked to account for nonmeteoric stable isotope values of saline ground waters (13, 31). Modification of

pore fluids during burial may be sufficient to obscure the original water compositions (31, 36, 37). For example, the marked enrichment of endmember 3 waters in Ca and Sr (Table 1) relative to evaporated seawater is typical of saline fluids from many sedimentary basins [for example (23, 36)] and requires significant fluid-rock interaction. The relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ values indicate that this interaction predominantly involved marine sulfate or carbonate rocks. This would be expected from the long-term residence of these fluids in the Anadarko Basin, which is necessitated by a model involving a Paleozoic marine water

Fig. 4. Logarithm of saturation index (S.I.) for calcite versus total dissolved solids (TDS) for ground waters. $S.I. = ([Ca^{2+}][CO_3^{2-}]/K_{sp})$, where brackets denote ion activities and K_{sp} is the temperature-dependent equilibrium solubility product for calcite. Indices calculated with the thermodynamic equilibrium models PHREEQE (48) and PHRQPITZ (24). Estimated equilibrium range shown for log S.I. values from -0.5 to 0.5. Modeled mixtures between all end-member pairs (endmembers 1 and 3 mix shown) approximate compositions of intermediate (that is, mixed) ground waters from the study area. Symbols as in Figs. 1 to 3. Most samples, as well as modeled mixtures, are saturated to supersaturated with respect to calcite. Calculated dolomite S.I.'s yield similar results as calcite S.I.'s for the ground-water samples and modeled mixtures.



origin for endmember 3. Although the history of water-rock interaction of endmember 3 ground waters is not well constrained, the origin of these fluids is clearly distinct from that of endmember 2, which is readily accounted for by the dissolution of halite by meteoric water. Geochemical study of ground waters from the deep Anadarko Basin may further constrain the evolution of endmember 3.

Paleohydrologic studies indicate that the Ozark Plateaus aquifer system formed during the late Permian (4). Ground water in this system (endmember 1) represents recent local meteoric recharge, as supported by H and O isotope evidence. The present west to east topographically driven flow of the Western Interior Plains aquifer system developed as a result of the Laramide Orogeny (4). In that the onset of the Laramide Orogeny and resulting uplift occurred 65 million years ago (38), flow rates of at least 0.015 m/year are necessary for meteoric recharge to migrate eastward from the Front Range to Missouri, a distance of approximately 1000 km. As discussed in (12), these flow rates fall within a range estimated by regional hydrologic models of gravity-driven flow in similar systems (39) and conservative estimates for present-day flow rates in the Western Interior Plains aquifer system (40). Flow rates in the northern part of the Western Interior Plains aquifer system may be more rapid, up to several meters per year, on the basis of regional hydrologic models of similar ancient gravity-driven flow systems (39). Ground-water flow rates out of the Anadarko Basin should be lower than those for eastward migrating ground waters in the northern, higher porosity and permeability parts of the Western Interior Plains aquifer system (4). These rates may be as low as 1×10^{-5} m/year (40). For the

same time frame of 65 million years, flow rates on the order of 5×10^{-3} m/year are required for water to migrate 350 km out of the deep Anadarko Basin to the center of the study area. Very low flow rates out of the Anadarko Basin are consistent with the long-term residence of marine fluids here. The migration of petroleum from the deep Anadarko Basin to central Kansas has been traced both by linking structural highs of oil and gas fields (41) and hydrocarbon geochemistry (42). This relation between ground-water flow patterns and hydrocarbon migration pathways suggests a common driving mechanism for transmitting both types of fluids from the deep Anadarko Basin to central Kansas.

Implications. The quantification of ground-water mixing processes allows end-member water compositions to be constrained, and hydrologic models for these flow regimes to be evaluated. Regional ground-water flow paths in the Western Interior Plains aquifer system provide a modern analog for models of ancient continental-scale flow systems [for example (39)]. The presence of two geochemically distinct saline ground waters in the same aquifer system, reflecting different origins and evolutions, may have parallels for saline ground water in other sedimentary basins where mixing processes and end-member compositions cannot be clearly defined. The two models proposed to account for the formation of saline ground water (evaporite dissolution and seawater modification) are commonly held as mutually exclusive. However, the mere presence of bedded marine evaporites in any sedimentary sequence indicates that these two processes are closely related and may both operate, albeit at different times, in the same aquifer system.

REFERENCES AND NOTES

- J. S. Hanor, in *Revolution in the Earth Sciences*, S. J. Boardman, Ed. (Kendall/Hunt, Dubuque, IA, 1983), pp. 99–111.
- For a general description of the hydrogeology of the Ozark Plateaus and Western Interior Plains aquifer systems see D. C. Signor and J. L. Imes, in *Regional Aquifer Systems of the United States, Aquifers of the Midwest Region*, L. A. Swain and A. I. Johnson, Eds. (Monogr. Ser. 13, American Water Resources Association, Bethesda, MD, 1989), pp. 149–163.
- J. L. Imes and L. F. Emmett, *U.S. Geol. Surv. Prof. Pap. 1414-F* (in press).
- D. G. Jorgensen, *Okla. Geol. Surv. Circ.* 90, 176 (1989).
- _____, J. O. Helgesen, R. B. Leonard, D. C. Signor, *U.S. Geol. Surv. Map MF-1835-B* (1986).
- T. G. Larson, *Am. Assoc. Petrol. Geol. Mem.* 15, 1043 (1971).
- P. A. Macfarlane and L. R. Hathaway, *Kansas Geol. Surv. Ground Water Ser.* 9 (1987).
- J. E. Carr, H. E. McGovern, T. Gogel, *U.S. Geol. Surv. Open-File Rep.* 86-491 (1986).
- K. S. Johnson, *Okla. Geol. Surv. Cir.* 90, 3 (1989).
- Sample localities were selected to avoid potential anthropogenic effects (for example, downhole chemical additives). Samples were filtered (<0.22 μ m) on-site, and acidified shortly after collection. Temperature, pH, dissolved oxygen, conductivity, Eh, and alkalinity were measured at the wellhead. Sr isotope standard NBS SRM987 gave an average $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710249 ± 10 (1σ , $n = 23$) during the course of this study. A complete listing of analytical methods and results, sample locality information, and collection, filtration, and preservation methods is given in (20).
- The δ (delta) notation expresses isotopic compositions of oxygen ($^{18}\text{O}/^{16}\text{O}$) and hydrogen (D/H) of a sample as the relative parts per thousand, or per mil, difference between the isotopic composition in a sample and in a standard such as SMOW (standard mean ocean water). For example, the δ notation for oxygen is defined as:

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} \right] \times 10^3$$
- J. L. Banner, G. J. Wasserburg, P. F. Dobson, A. B. Carpenter, C. H. Moore, *Geochim. Cosmochim. Acta* 53, 383 (1989).
- R. N. Clayton *et al.*, *J. Geophys. Res.* 71, 3869 (1966); B. Hitchon and I. Friedman, *Geochim. Cosmochim. Acta* 33, 1321 (1969).
- W. H. Burke, R. E. Denison, E. A. Hetherington, R. B. Koepnick, H. Nelson, J. B. Otto, *Geology* 10, 516 (1982).
- S. Chaudhuri, V. Broedel, N. Clauer, *Geochim. Cosmochim. Acta* 51, 45 (1987); J. L. Banner, G. N. Hanson, W. J. Meyers, *J. Sediment. Petrol.* 58, 673 (1988).
- D. T. Long, T. P. Wilson, M. J. Takacs, D. H. Rezac, *Geol. Soc. Am. Bull.* 100, 1568 (1988); E. C. Perry, T. Grundl, R. H. Gilkeson, in *Isotopic Studies of Hydrologic Processes*, E. C. Perry and C. W. Montgomery, Eds. (Northern Illinois Univ. Press, DeKalb, IL, 1982), pp. 35–43.
- D. I. Siegel and R. J. Mandel, *Quat. Res.* 22, 328 (1984).
- W. Dansgaard, *Tellus* 16, 436 (1964); T. Webb III and R. A. Bryson, *Quat. Res.* 2, 70 (1972); C. J. Yapp and S. Epstein, *Earth Planet. Sci. Lett.* 34, 333 (1977).
- J. Ch. Fontes, in *Stable Isotope Hydrology-Deuterium and Oxygen-18 in the Water Cycle*, J. R. Gat and R. Gonfiantini, Eds. (Tech. Rep. Ser. 210, International Atomic Energy Agency, Vienna, 1981), pp. 273–302; A. F. White and N. J. Chuma, *Water Resour. Res.* 23, 571 (1987).
- M. Musgrove, thesis, University of Texas, Austin (1993).
- W. Holser, in *Marine Minerals*, vol. 6 of *Reviews in Mineralogy*, R. G. Burns, Ed. (Mineralogical Society of America, Washington, DC, 1979), pp. 295–

- 346; C. Pierre, L. Ortlieb, A. Person, *J. Sediment. Petrol.* **54**, 1049 (1984).
22. L. P. Knauth and M. A. Beeunas, *Geochim. Cosmochim. Acta* **50**, 419 (1986).
 23. A. B. Carpenter, *Okla. Geol. Surv. Circ.* **79**, 60 (1978).
 24. PHRQPITZ, described in L. N. Plummer, D. L. Parkhurst, G. W. Fleming, S. A. Dunkle, *U.S. Geol. Surv. Water Res. Invest. Rep.* **88-4153** (1988) was used for ground-water speciation modeling for all waters with >20,000 mg/liter TDS. The PHRQPITZ models uses methods and equations outlined in K. S. Pitzer, *J. Physical Chem.* **77**, 268 (1973) to calculate activity coefficients in high ionic strength solutions.
 25. J. Horita, T. J. Friedman, B. Lazar, H. D. Holland, *Geochim. Cosmochim. Acta* **55**, 417 (1991).
 26. A. B. Carpenter and J. C. Miller, *Chem. Geol.* **4**, 135 (1969); J. M. Darr, thesis, University of Missouri, Columbia (1978); D. R. Frick, thesis, University of Missouri, Columbia (1980).
 27. D. G. Jorgensen, J. Downey, A. R. Dutton, R. W. Maclay, in *The Geology of North America*, vol. O-2, *Hydrogeology*, W. Back, J. S. Rosenshein, P. R. Seaber, Eds. (Geological Society of America, Boulder, CO, 1988), pp. 141–156.
 28. H. P. Taylor, Jr., *Econ. Geol.* **69**, 843 (1974).
 29. T. M. L. Wigley and L. N. Plummer, *Geochim. Cosmochim. Acta* **40**, 989 (1976).
 30. A. M. Stueber, P. Pushkar, E. A. Hetherington, *ibid.* **48**, 1637 (1984).
 31. L. S. Land, in *Physics and Chemistry of Porous Media II*, J. R. Banavar, J. Koplik, K. W. Winkler, Eds. (*Conf. Proc. 154, American Institute of Physics*, Ridgefield, CT, 1987), pp. 160–179.
 32. R. H. McNutt, *Geol. Assoc. Can. Spec. Pap.* **33**, 81 (1987).
 33. T. Gogel, *Kans. Geol. Surv. Chem. Qual. Ser.* **9** (1981).
 34. R. J. Dingman and E. E. Angino, *Chem. Geol.* **4**, 325 (1969).
 35. Two-dimensional finite-element modeling performed using the model OILGEN, described in G. Garven, *Am. J. Sci.* **289**, 105 (1989).
 36. L. S. Land and G. L. Macpherson, *Am. Assoc. Petrol. Geol. Bull.* **76**, 1344 (1992); E. P. Moldovanyi and L. M. Walter, *ibid.*, p. 864.
 37. L. M. Walter, A. M. Stueber, T. J. Huston, *Geology* **18**, 315 (1990).
 38. O. Tweto, *Geol. Soc. Am. Mem.* **144**, 1 (1975); B. Bryant and C. W. Naeser, *Geol. Soc. Am. Bull.* **91**, 156 (1980); P. Bird, *Science* **239**, 1501 (1988); K. M. Gregory and C. G. Chase, *Geology* **20**, 581 (1992).
 39. G. Garven, *Econ. Geol.* **80**, 307 (1985); C. M. Bethke, *ibid.* **81**, 233 (1986); D. A. Sverjensky and G. Garven, *Nature* **356**, 481 (1992).
 40. S. C. Christenson and G. P. Adams, *Geol. Soc. Am. Abstr. Progr.* **20**, no. 2, 94 (1988); D. C. Signor, *ibid.*, p. 129.
 41. R. F. Walters, *Am. Assoc. Petrol. Geol. Bull.* **42**, 2133 (1958).
 42. R. C. Burruss and J. R. Hatch, *Okla. Geol. Surv. Circ.* **90**, 53 (1989).
 43. J. D. Hem, *U.S. Geol. Surv. Water-Supply Pap.* **2254** (1989); G. Faure, *Principles of Isotope Geology* (Wiley, New York, 1986).
 44. B. Kellett, *Geologic Cross-section from Western Missouri to Western Kansas* (Kansas Geological Society, Wichita, 1951).
 45. H. Craig, *Science* **133**, 1702 (1961).
 46. J. R. Lawrence and H. P. Taylor, Jr., *Geochim. Cosmochim. Acta* **36**, 1377 (1972).
 47. J. L. Banner and G. N. Hanson, *ibid.* **54**, 3123 (1990).
 48. D. L. Parkhurst, D. C. Thorstenson, L. N. Plummer, *U.S. Geol. Surv. Water Res. Invest. Rep.* **80-96** (1980).
 49. We thank J. Grubb, B. Campbell, P. Bennett, N. Walker, L. Mack, and A. Carpenter for field and laboratory assistance and P. Dobson, L. Land, and J. Sharp for scientific discussions. We also thank G. Garven for assistance and discussions regarding theoretical flow modeling. This work was supported by National Science Foundation grant EAR 90-17660, a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and grants from the Geology Foundation and University Research Institute of the University of Texas, and the National Ground Water Association.

2 October 1992; accepted 15 January 1993