WATER-ROCK INTERACTION HISTORY OF REGIONALLY EXTENSIVE DOLOMITES OF THE BURLINGTON-KEOKUK FORMATION (MISSISSIPPIAN): ISOTOPIC EVIDENCE

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ABSTRACT: Two sequences of pervasive dolomitization are preserved in the Mississippian Burlington-Keokuk Formation of Iowa, Illinois, and Missouri. Cathodoluminescent petrography reveals (1) an early, post-depositional, dolomite-forming episode (dolomite I), and (2) a later dolomite (dolomite II), which replaced the first generation. These texturally and temporally distinct dolomites are correlative over 100,000 km² of outcrop and subsurface (see Cander and others, this volume) and have distinguishing isotopic and trace-element characteristics. Calculation of the simultaneous variations that occur during water-rock interaction demonstrates important differences in the relative rates at which the O, C, Sr, and Nd isotopic compositions of diagenetic carbonates are altered. These quantitative models are used to place constraints on the water-rock interaction history of the Burlington-Keokuk dolomites.

Dolomite I samples have a range of $\delta^{18}O$ (-2.2 to $2.5\%_o$ PDB), $\delta^{13}C$ (-0.9 to $4.0\%_o$ PDB) and ϵ_{Nd} (342) values (-6.0 to -4.7), and initial $^{87}Sr/^{86}Sr$ ratios (0.70757 to 0.70808) that encompass estimated marine dolomite isotopic compositions. These samples also have 107 to 123 ppm Sr, slightly lower than that of modern marine dolomites. Dolomite I formed from predominantly seawater-derived constituents with a small but significant non-marine component. A mixed-marine meteoric-fluid model can quantitatively account for the variations in dolomite I isotope and trace-element compositions, but the origin of the non-marine component is not well constrained.

Compared to dolomite I, dolomite II samples have radiogenic initial $^{87}Sr/^{86}Sr$ ratios (0.70885 to 0.70942), lower $\delta^{18}O$ values (-6.6 to $-0.2\%_o$ PDB), depleted Sr concentrations (50 to 63 ppm), similar $\delta^{13}C$ values (-1.0 to $4.1\%_o$ PDB) and similar ϵ_{Nd} (342) values (-6.5 to -5). The isotopic composition and concentration of Sr in dolomite II preclude a source within the Burlington-Keokuk Formation for the Sr in dolomite II. Dolomite II apparently formed as a result of the recrystallization of the less stoichiometric dolomite I by extraformational subsurface fluids that migrated to shallow burial depths. The results suggest that the recrystallization process effectively exchanged nearly all of the Sr from dolomite I.

Oxygen isotopes equilibrate between dolomite and fluid at relatively low extents of water-rock interaction, and as a result, the $\delta^{18}O$ values of dolomite II may reflect only the last stages of recrystallization. The results of model calculations also suggest that the $^{87}Sr/^{86}Sr$ ratios of dolomite II preserve an earlier and larger record of water-rock interaction, whereas their C and Nd isotopic signatures are inherited from dolomite I precursors. Late-stage, vug-filling carbonates appear to have formed from extraformational fluids that experienced minimal interaction with Burlington-Keokuk host rocks. The petrology and geochemistry of Burlington-Keokuk dolomites document multiple episodes of pervasive water-rock interaction that can be correlated on a regionally extensive scale.

INTRODUCTION

Studies of carbonate diagenesis have endeavored to determine how processes of water-rock interaction have controlled the textural and geochemical evolution of the diagenetic products. Applied to dolomitization, this approach is increasingly complex and important, owing in part to the paucity of dolomite forming in modern settings compared to the extensive dolomite sequences in the Paleozoic and Mesozoic, which are host to significant petroleum and base-metal deposits. Several recent reviews have detailed the controversy regarding models for dolomitization, and some have disputed the utility of geochemical techniques for addressing this controversy (Land, 1980, 1985; Morrow, 1982; Machel and Mountjoy, 1986; Hardie, 1987). The dolomites of the Mississippian Burlington-Keokuk Formation provide a spatially correlative, temporal and textural framework that is well suited to test geochemical approaches for unravelling the water-rock interaction history of this thick-bedded, regionally extensive dolomite sequence.

We present here C, O, and Sr isotope data and Sr concentration data for two major dolomite generations and minor vug-filling carbonates in the Burlington-Keokuk Formation. These data will be used with other geochemical (Nd isotopes, rare-earth element, Fe and Mn concentrations) and petrologic information on the dolomites from previous studies in order to place limits on the processes of dolomitization. Neodymium isotope and trace-element data are treated in detail in Banner (1986) and Prosky and Meyers (1985 and in prep.), and the petrograhic framework of dolomitization is constructed in Harris (1982), Cander and others (this volume), Banner and others (in prep.), and by J. L. Prosky (pers. commun., 1987).

Quantitative models are developed to determine the *simultaneous* variations in several isotopic and elemental parameters as a function of water-rock interaction. This approach reduces the limitations inherent in using a particular geochemical system, such as uncertainties in values for distribution coefficients and fractionation factors. This study employs the method developed in Banner (1986), that of an iterative calculation using mass balance in order to simulate isotopic and elemental exchange during recrystallization. The variation in the isotopic composition and concentration of elements such as O, C, Sr, and Nd in diagenetic fluids and minerals results in important differences in the rates at which the different isotopic systems are altered during the progressive recrystallization of carbonate sediments. The utility of this approach lies not so much in the absolute values of the calculated water:rock ratios as in the *relative* differences calculated between different isotopic systems and between different diagenetic models. These relative differences result in diagnostic alteration trends on isotope-isotope and isotope-element variation diagrams and are used to constrain models for the water-rock interaction history of the Burlington-Keokuk dolomites.

PETROGRAPHY AND GEOCHEMISTRY OF BURLINGTON-KEOKUK DOLOMITES

The Burlington-Keokuk Formation crops out in southeastern Iowa, western Illinois, and eastern, central, and

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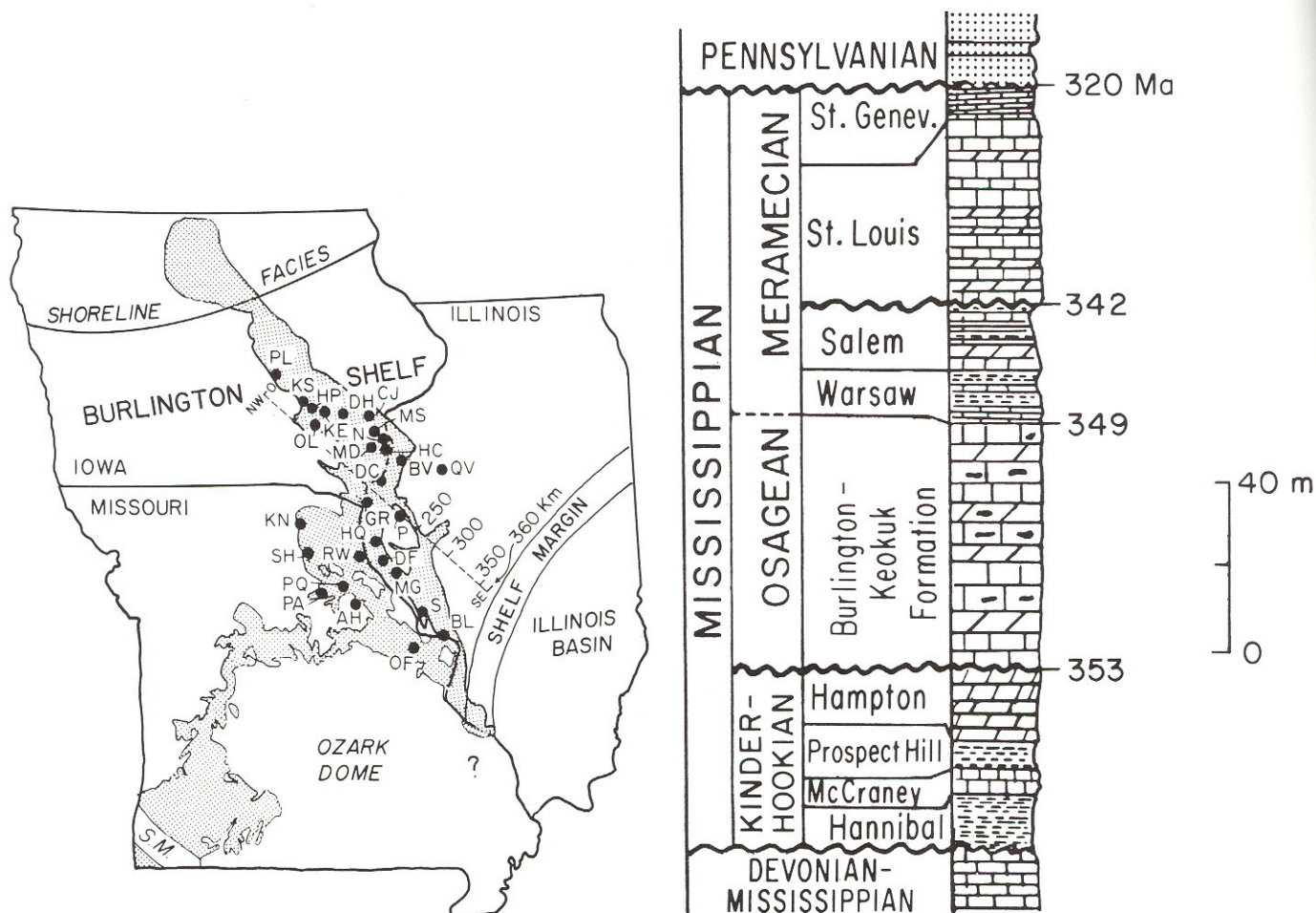
FIG. 1.—Paleogeographic setting of Burlington-Keokuk shelf during Osagean time and localities for samples analyzed in this study and listed in Table 1. Shaded area shows outcrop belt of Mississippian rocks. Paleogeography is taken from Lane and DeKeyser (1980) and Sixt (1983). Stratigraphic section for Iowa and western Illinois from Harris (1982). Time scale from Harland and others (1982).

southern Missouri as part of the Osage Series (Fig. 1). Carbonate deposition occurred on a broad, shallow, subtidal shelf on the southeast flank of the Transcontinental Arch, west of the Illinois Basin, and north and west of the Ozark Dome (Carlson, 1979; Lane and DeKeyser, 1980). Burial history curves indicate a maximum overburden of less than 0.5 km for Burlington-Keokuk strata at the end of Pennsylvanian time (O. A. Cox, unpubl. data). The Burlington-Keokuk Formation is comprised of medium- to thick-bedded, coarse-grained, crinoidal packstone and grainstone and interbedded wackestone and mudstone. A detailed diagenetic history for the Burlington-Keokuk Formation includes multiple episodes of dolomitization, calcite cementation, dedolomitization, chertification, and mechanical and chemical compaction. A paragenetic sequence can be correlated over an area of approximately 100,000 km^2 using calcite and dolomite zonal stratigraphies that are based on cathodoluminescent petrography (Harris, 1982; Cander and others, this volume; Kaufman and others, in prep.).

Two major generations of dolomite can be distinguished on the basis of cathodoluminescent characteristics (Fig. 2). Calcium-rich dolomite I (54.5–56.5 mole percent $CaCO_3$; Prosky and Meyers, 1985), the most common dolomite,

consists of orange to light brown rhombs with concentric zoning. Dolomite I appears to have replaced nearly all lime mud as the earliest diagenetic phase of regional extent in the Burlington-Keokuk Formation. Evidence for the com-
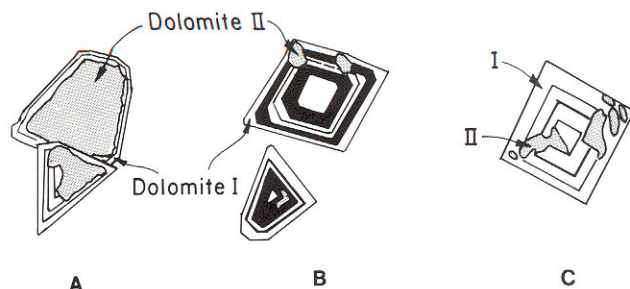

FIG. 2.—Sketches of different cathodoluminescent dolomite types and their morphologies. Pattern of concentric zoning in dolomite I is similar within some measured sections and varies between localities. Samples: (A) HP-4-GR; (B) HP-18-J; (C) MD-13. Replacement nature of dolomite II (shown in grey) is indicated by truncation of fine, concentric zones in dolomite I precursor and by the similar sizes of replaced and unreplaced dolomite I rhombs in the same samples. Most common replacement fabric is shown in (A). Larger rhombs are approximately 100 μm across. Dolomite petrography is detailed in Cander and others (this volume).

position and mineralogy of the precursor sediment to dolomite I has been obliterated by the dolomitization process. In addition to potential aragonite and Mg-calcite precursors, a syndepositional marine dolomite phase, calcium-rich and poorly ordered relative to dolomite I (e.g., Carballo and others, 1987), may have been recrystallized and overgrown by dolomite I.

Dolomite II occurs as a dull red, unzoned replacement of dolomite I and is more stoichiometric (51–52 mole percent $CaCO_3$). Dolomite II′ is less common and occurs as a very dull red to brown replacement of dolomites I and II. A progressive increase in Fe and Mn concentrations is observed through the paragenetic sequence dolomite I − dolomite II − dolomite II′. Iron and Mn concentrations are also correlated to luminescence variations within each dolomite generation (Prosky and Meyers, 1985). Dolomite I, II and II′ have similar $\epsilon_{Nd}(342)$ values and rare-earth element (REE) patterns (Banner, 1986). Two-phase fluid inclusions in dolomites I and II, characterized as primary, yield homogenization temperatures of 90–120°C and bulk salinities of as much as 20 weight percent (Smith, 1984).

In sections that have both dolomite I and II, there is a transition from strata dominated by dolomite II at the bottom to domination by dolomite I higher in the section. Cathodoluminescent petrography and regional stratigraphy have been used to constrain age ranges for the dolomites as follows: (1) dolomite I: post-Burlington-Keokuk deposition to pre-Pennsylvanian deposition (349–320 Ma), and (2) dolomite II: post-dolomite I to pre-Pennsylvanian or pre-Permian (Cander and others, this volume). Calcite spar, saddle dolomite, quartz, pyrite, marcasite, and sphalerite are found in solution vugs and fractures which postdate the major diagenetic episodes in the Burlington-Keokuk Formation.

METHODS

Nearly pure whole rock dolostones, comprised of predominantly one cathodoluminescent dolomite type, and physically separated dolomite (using heavy liquids and magnetic separation methods) from some less pure samples were chosen for analysis. Detailed petrographic descriptions and separation methods are given in Banner (1986). Samples were ground to less than 200 mesh. An approximately 0.2- to 1-mg split of each sample was roasted *in vacuo* at 380°C for 1 hr to remove volatile contaminants. Calcite samples were reacted with anhydrous H_3PO_4 at 50°C in an extraction line coupled to the inlet of a VG 602E ratio mass spectrometer. Dolomite separate and dolostone samples were reacted with anhydrous H_3PO_4 at 50°C in separate off-line vessels for 10 to 18 hr to enable complete digestion. Isotopic enrichments were measured relative to an intralaboratory standard reference gas, which was calibrated to PDB through daily analysis of NBS-20 calcite. All enrichments were corrected for ^{17}O contribution following the method of Craig (1957). No correction was applied for dolomite-phosphoric acid fractionation. Thirty-four analyses of NBS-20 calcite conducted during the course of this study indicate that precision at the one sigma level is ±0.13‰ for oxygen and ±0.09‰ for carbon. Replicate analyses on 14 unknown samples gave a mean deviation of ±0.11‰

for oxygen and ±0.05‰ for carbon. Standard and replicate data are given in Banner (1986).

Strontium and Nd isotope ratios were measured at Stony Brook using a NBS design surface emission mass spectrometer. Precision at the two sigma level for measured ratios was typically ±0.00004 for $^{87}Sr/^{86}Sr$ and ±0.00002 for $^{143}Nd/^{144}Nd$. Details of these methods are given in Banner (1986) and Banner and others (in prep). Fe, Mn, and Ca concentration data are from J. L. Prosky (pers. commun., 1987) and were measured using an ARL-EMX electron microprobe following procedures given in Reeder and Prosky (1986).

RESULTS

Table 1 presents analyses of dolomites I, II, and II′, including whole rock and mineral separate results for some samples. Analyses of vug-filling calcite and dolomite are also given. A comparison of $\delta^{18}O$ values for dolomite separate and whole rock analyses for six samples gives a mean deviation of ±0.57‰, which is greater than the analytical precision. The $\delta^{18}O$ values for all dolomite separates are greater than the corresponding whole rock values. This indicates that a component with a lower $\delta^{18}O$ value was removed during the separation process. The lower $\delta^{18}O$ value of the whole rock may be due to small amounts of late-stage calcite cements, which have $\delta^{18}O$ as low as −11.3‰ (Table 1). Five to 10% of such calcite included in a whole rock dolostone can account for the differences observed between whole rock and dolomite separate analyses. These percentages are higher than the amounts of modal calcite observed in the samples (0–5%). An additional effect may be a systematic removal of dolomite with low $\delta^{18}O$ during the separation procedures. There may be considerable intra-sample variation in dolomite $\delta^{18}O$ values similar to that observed for Ca, Mg, Mn, and Fe (Prosky and Meyers, 1985). $\delta^{13}C$ values for dolomite separate and whole rock analyses are essentially the same for five samples (mean deviation = ±0.15‰), whereas one sample (DH-8) shows a large difference of over 3‰.

The samples analyzed in this study probably all contain small amounts of calcite cements and solid and fluid inclusions with different isotopic compositions compared to the dolomite phase of interest. Based on petrographic criteria and mass balance calculations, the effects of these impurities are limited and will not change inferences or quantitative models based upon the analytical data to any significant degree.

Dolomites I, II, and II′ have the same range in $\delta^{13}C$ values, whereas $\delta^{18}O$ values vary widely between dolomite I and dolomites II and II′ (Fig. 3). For dolomite I, 21 out of 25 samples have $\delta^{13}C$ values between 2 and 4‰, whereas $\delta^{18}O$ values for all dolomite I samples are more evenly distributed over a 5‰ range. Oxygen and C isotope compositions show no distinct correlation for dolomite I samples. Similarly, dolomites II and II′ show a 6‰ span in $\delta^{18}O$ values, whereas most $\delta^{13}C$ values for these samples are between 2 and 4‰. The vug-filling carbonates are distinguished by their low $\delta^{13}C$ and $\delta^{18}O$ values.

The most definitive regional trend in dolomite stable isotope compositions is that in the $\delta^{18}O$ values for dolomite

TABLE 1.—OXYGEN, CARBON, AND STRONTIUM ISOTOPE COMPOSITIONS OF BURLINGTON-KEOKUK DOLOMITES AND ASSOCIATED PHASES

Sample No.	$\delta^{18}O$ PDB	$\delta^{13}C$ PDB	$^{87}Sr/^{86}Sr_i$	Sr, ppm
Dolomite I				
PL-2	−0.95	1.99		
PL-9	−0.33	1.20		
PL-10	0.52	2.73		
PL-J-22	−0.07	2.93		
HP-18-J	1.72	2.41	0.70808	123.3
DH-4	−0.64	0.33		
DH-8-WR*	−0.40	0.15		
DH-8-DS	2.27	3.14	0.70777	108.0
MS-1	2.47	2.97		
MD-F	0.73	3.33	0.70796	110.2
BV-6.8-J-GRWR	0.29	2.85		
BV-6.8-J-GRDS	1.25	3.17		
BV-6.8-J-GFWR	−0.03	2.84		
BV-6.8-J-GFDS	0.98	2.52	0.70787	118.3
BV-11	0.34	3.35	0.70757	106.6
DC-2	−2.23	2.64		
DC-3	−0.36	3.14		
DC-13	−0.76	3.16		
MPA-17	−1.55	2.90		
IP-23	−0.47	3.74		
IQV-10	−1.25	2.16		
MSH-5a	−1.66	2.75		
IHQ-39	−0.37	3.73		
IDF-7	−0.70	3.64		
IDF-8	−0.48	3.54		
IDF-11	−0.31	4.03		
IDF-13	−1.80	2.61		
IDF-K	−1.40	3.54		
MPQ-11	−1.44	1.44		
MAH-14	−0.65	2.58		
IS-20	−2.19	−0.90		
IS-24	−2.20	3.12		
Dolomite II				
KS-2	−2.24	2.06		
KS-5	−3.66	2.49		
KS-6	−2.81	1.36		
KS-8-WR	−3.37	1.04	0.70919	54.2
KS-8-DS	−2.49	1.54		
HP-3-J	−3.09	2.62	0.70942	53.7
HP-4-GRWR	−1.43	1.75		
HP-4-GRDS	−0.24	1.97		
HP-4-GFWR	−1.18	2.35		
HP-4-GFDS	−1.09	2.24	0.70885	62.9
HP-4.1-J	−2.41	2.25		
HP-10.1-J	−2.65	2.25	0.70905	53.5
KE-4	−4.38	2.73		
KE-5	−4.14	3.19		
KE-12	−4.14	2.71		
KE-16	−3.55	2.86		
N-12a	−4.47	2.62		
HC-3	−5.45	2.72		
HC-10	−4.66	3.47		
MKN-8	−4.56	3.41		
MKN-9	−3.52	3.61		
DC-18	−4.30	3.51	0.70931	49.9
GR-14	−4.14	3.79		
MPA-2	−6.43	4.11	0.70907	50.8
MPA-20	−5.03	4.04		
MRW-8	−5.50	3.64		
MRW-18	−5.68	3.55		
IMG-5	−3.94	−1.01		
MOF-16	−5.61	3.72		
IBL-O	−5.25	3.85		
IBL-2	−6.60	3.11		
Dolomite II'				
HP-15-J	−2.31	2.47	0.70925	59.7
DC-7	−3.70	2.84		
DC-23	−4.09	3.58	0.70940	53.2
CJ-2	−3.66	0.63		
CJ-3	−2.00	−0.89		
Vug Dolomite				
GRF-1	−4.96	−2.10	0.71024	91.3
GR5-J	−5.70	−0.56		

TABLE 1.—*Continued*

Sample No.	$\delta^{18}O$ PDB	$\delta^{13}C$ PDB	$^{87}Sr/^{86}Sr_i$	Sr, ppm
Vug Calcite				
KE-5	−6.12	0.24		
DC-3	−5.34	1.75		
GR-6	−11.34	−0.14	0.70987	87.1
MPA-2	−9.81	1.14		

*WR = whole rock; DS = dolomite separate; whole rock analysis, where no designation given. Sample descriptions and localities given in Banner (1986) and Cander (1985) for I-samples and Kaufman (1985) for M-samples. These prefixes are omitted in Figure 1.

For oxygen, $\delta^{18}O = \dfrac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \times 10^3$.

A similar expression can be written for $\delta^{13}C$. The PDB standard is used here. For Sr isotopes, $^{87}Sr/^{86}Sr_i = $ initial $^{87}Sr/^{86}Sr = (^{87}Sr/^{86}Sr)_{measured} - ^{87}Rb/^{86}Sr(e^{\lambda T} - 1)$, where λ is the decay constant for the decay of ^{87}Rb ($\lambda = 1.42 \times 10^{-11}$ y^{-1}), calculated here for 342 Ma. NBS standard SRM 987 gives $^{87}Sr/^{86}Sr = 0.71034$.

II, which decrease from northwest to southeast from central Iowa to southwest Illinois (Fig. 4). These samples have a total range of nearly 6‰, and at any given locality the range is about 2‰ or less. Dolomite I shows a similar but less well-defined trend of decreasing $\delta^{18}O$ southeastward. $\delta^{13}C$ values for all dolomite types have an overall trend of slight depletion to the northwest, but the most striking feature of the dolomite $\delta^{13}C$ data is the restricted range of values for the principal dolomite types (Figs. 4, 5).

Dolomite I samples have initial $^{87}Sr/^{86}Sr$ ratios of 0.70757 to 0.70808, and Sr concentrations of 106.6 to 123.3 ppm (Table 1). Dolomites II and II' have markedly higher initial $^{87}Sr/^{86}Sr$ ratios of 0.70885 to 0.70942 and lower Sr concentrations of 49.9 to 62.9 ppm. A summary of the isotope and trace-element geochemistry of the Burlington-Keokuk dolomites is given in Figure 5.

DISCUSSION

The geologic, petrographic, and geochemical characteristics of the Burlington-Keokuk Formation dolomites will be used toward determining the nature of the fluids and
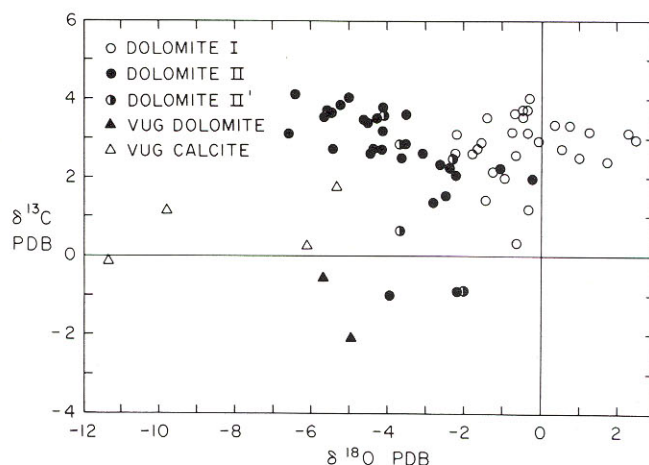

FIG. 3.—Carbon vs. oxygen isotope compositions for all Burlington-Keokuk phases analyzed in this study. In this and all succeeding figures, dolomite separate values are plotted for samples where available.
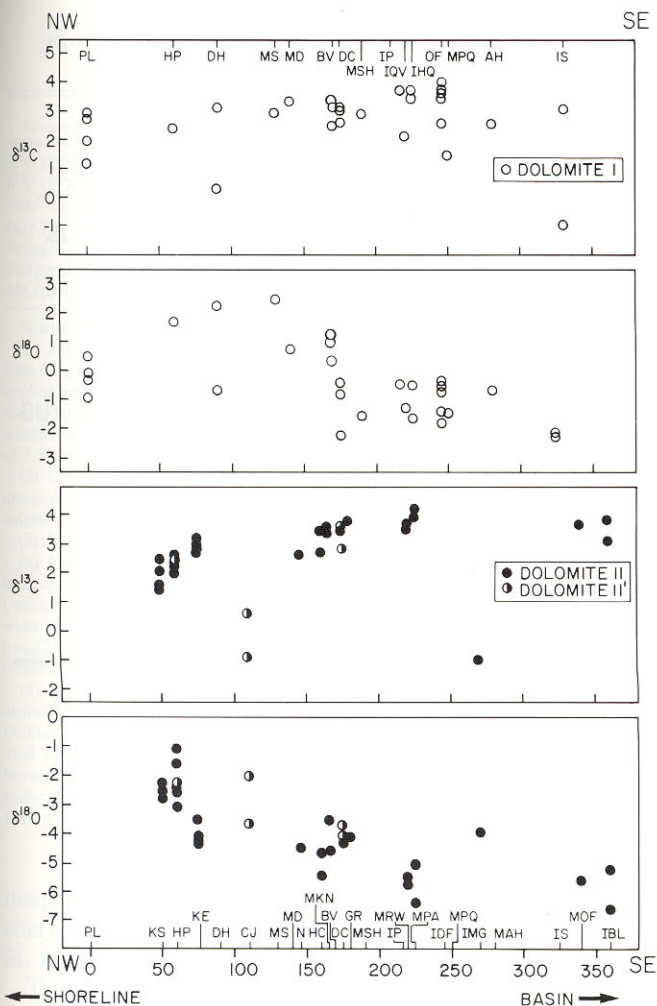
FIG. 4.—Regional variations in C and O isotopic compositions for Burlington-Keokuk dolomites. Sample localities are projected to plot along northwest-southeast transect shown in Figure 1.

processes that generated the dolomites. In order to evaluate the effects of diagenesis on the geochemistry of carbonate sediments, one must be able to estimate the composition of the sediments at the time of their formation in the marine depositional environment. We use the following estimated isotopic compositions for Osagean marine dolomite: $\delta^{18}O = 1.8–2.8‰$ PDB, $\delta^{13}C = 4.0–4.6‰$ PDB, $^{87}Sr/^{86}Sr = 0.7076$, $\epsilon_{Nd}(342) = -7$ to -5, as given in Table 2 and Figure 5.

Calculation of Isotopic Variations During Water-Rock Interaction

The simultaneous variations in O, Sr, C, and Nd isotopic compositions of carbonates that occur during water-rock interaction are portrayed in Figure 6. The model curves were constructed using an iterative calculation procedure and represent changing rock compositions as a function of increasing molar water:rock ratio, $(W/R)_m$. In the model shown, the fluid flows through and recrystallizes the rock in increments. Isotopic exchange during each increment is

calculated using mass balance relationships (Banner, 1986; see also Taylor, 1979, and Land, 1980). The results of the calculations demonstrate the different extents of water-rock interaction required to alter the different isotopic parameters (Fig. 6). It can be seen that these differences arise from the pronounced differences in the concentrations of O, Sr, C, and Nd within and between the fluid and solid phases. These differences are used to construct and evaluate models for the water-rock interaction history of the Burlington-Keokuk dolomites.

Petrogenesis of Dolomite I

Any model for the dolomitization of lime mud to produce dolomite I must account for: (1) the regional extent and early timing of dolomitization; (2) the replacement of lime mud and supply of Mg^{+2} to the site of dolomitization; (3) the calcium-rich, nonstoichiometric compositions; (4) the range of lower $\delta^{13}C$ and $\delta^{18}O$ values of dolomite I compared to the estimated marine dolomite value (EMD); (5) the range of moderately radiogenic Sr isotopic compositions encompassing the EMD and low Sr abundances relative to the EMD; (6) the high Fe and Mn concentrations relative to the EMD; and (7) the high temperatures and salinities of fluid inclusions.

If fluid inclusions have preserved a record of the fluids which crystallized the Burlington-Keokuk dolomites, then any model for the formation of the dolomites requires a fluid with high temperatures and salinities. Alternatively, the leakage of warm saline fluids along fractures in previously crystallized dolomite without recrystallizing the dolomite would produce secondary inclusions with high temperatures and salinities. The common observation of dolomite II replacement of only the inner portions of some dolomite I rhombs (and, less commonly, intra-rhomb pores) indicates that post-crystallization fluids have entered some dolomite I rhombs without leaving an apparent trace of their pathway. Evidence from experimental and natural systems suggests that fluid inclusions in calcite can exchange with post-crystallization fluids (Comings and Cercone, 1986; Goldstein, 1986). Fluid inclusions in the Burlington-Keokuk dolomites may reflect the passage of warm saline fluids through the Burlington-Keokuk Formation subsequent to dolomitization.

Normal sea water and hypersaline dolomitization.—

Models for the formation of ancient dolomites involving sea water or sea water modified by evaporation are based on modern occurrences and can account for the introduction of the large amounts of Mg^{+2} necessary to form dolomite (see review by Land, 1985). Since evaporation of sea water will only increase its $\delta^{18}O$ value and leave its $^{87}Sr/^{86}Sr$ ratio unchanged, these models cannot account for the depleted $\delta^{18}O$ and radiogenic $^{87}Sr/^{86}Sr$ values of some dolomite I samples relative to the EMD.

The migration of marine waters through older sediments has been proposed as a model for dolomitization in the Floridan aquifer (Kohout and others, 1977; Simms, 1984) and in the Enewetak Atoll (Saller, 1984a). Pre-Pennsylvanian sea water did not have the requisite Sr isotopic com-
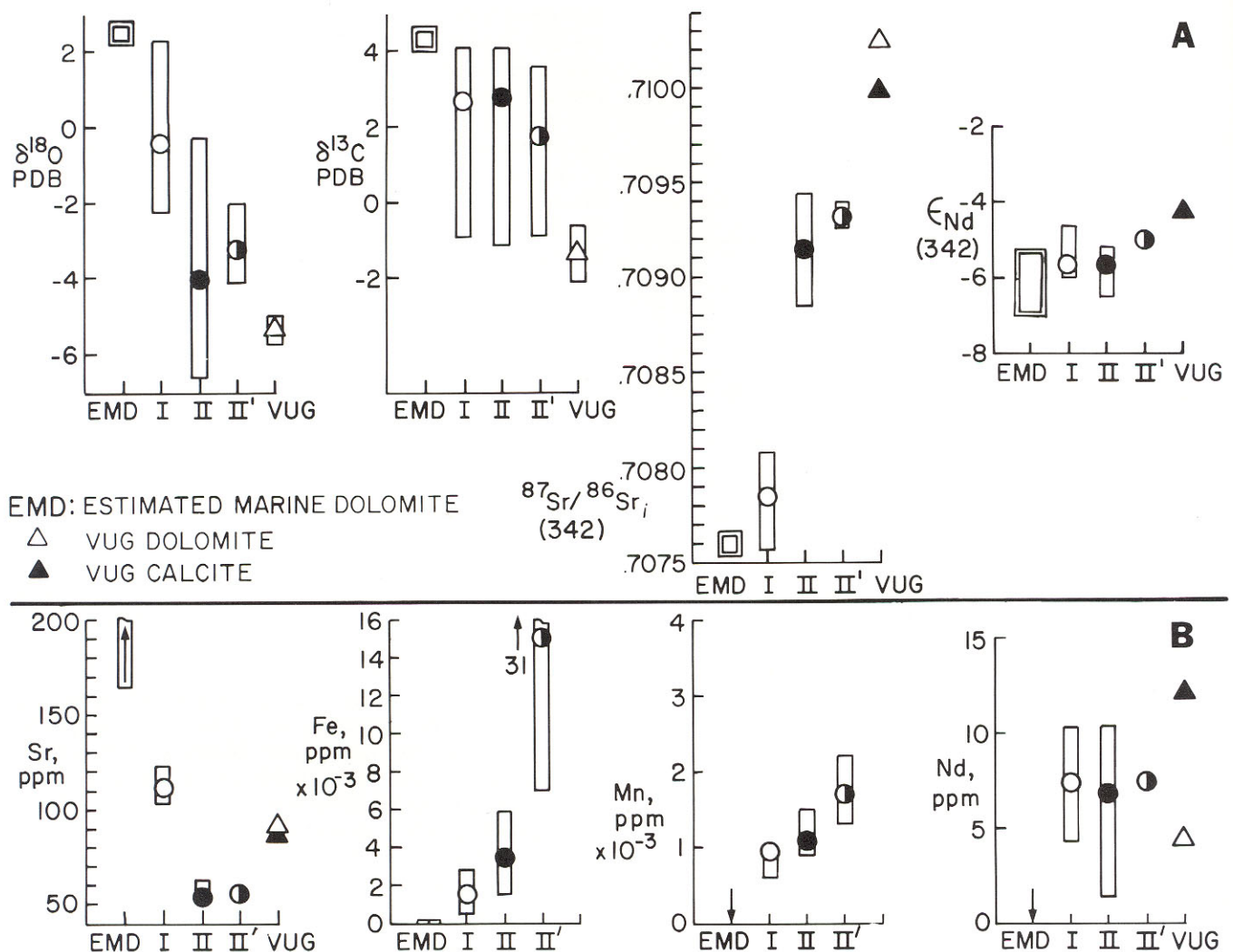
Fig. 5.—Summary of Burlington-Keokuk dolomite geochemistry. Mean and range of values shown for dolomites I, II, and II' for (A) isotopic compositions of O, C, Sr, and Nd, and (B) Sr, Fe, Mn, and Nd abundances. Dolomite III is discussed in Cander and others (this volume). Estimated marine dolomite (EMD) values discussed in Table 2. Neodymium data are from Banner (1986). Iron and Mn data represent sample averages (J. L. Prosky, pers. commun., 1987).

positions to account for the range in Burlington-Keokuk dolomite I values through interaction with marine carbonate precursors with Osagean $^{87}Sr/^{86}Sr$ ratios (Burke and others, 1982; Popp and others, 1986). If pre-Pennsylvanian sea water, circulating through Burlington-Keokuk sediments, was modified by interaction with local clastics such as the Warsaw Shale or the thin argillaceous carbonate seams in Burlington-Keokuk strata, then the sea water could attain slightly higher and locally variable $^{87}Sr/^{86}Sr$ ratios, Fe contents, and $\delta^{13}C$ values and impart these signatures to dolomite I; however, this model cannot account for the dolomite I $\delta^{18}O$ values that range to 4‰ lower than the EMD.

Burial/basinal-brine dolomitization.—

Diagenetic carbonates formed from subsurface saline fluids often have distinctive geochemical signatures relative to contemporaneous marine carbonate. Isotopic data for do-

lomite I samples encompass the estimated marine dolomite values. The deviations in $\delta^{13}C$ values from the EMD for some samples suggest a relativley high water:rock ratio system during dolomite I crystallization (Fig. 6). As will be discussed in a later section, a basinal brine in such a system would be expected to impart lower $\delta^{18}O$ and higher $^{87}Sr/^{86}Sr$ values to the samples. A basinal-brine model for dolomitization is not supported by the geochemical data.

Marine meteoric mixing.—

In this model, dolomitization is facilitated by high rates of circulation and mixing of fluids in coastal seawater-freshwater interfaces (Badiozamani, 1973; Wigley and Plummer, 1976; Magaritz and others, 1980). In evaluating marine meteoric-mixing models for the generation of dolomite I, we consider both proximal coastal sources and more distal sources for the meteoric waters. The Transcon-

TABLE 2.—COMPARISON OF ESTIMATED MARINE DOLOMITE ISOTOPIC COMPOSITION (EMD) AND BURLINGTON-KEOKUK DOLOMITE I

Parameter	EMD*	Method of Estimation	Range of Values for Dolomite I
$\delta^{18}O$ (PDB)	1.8 to 2.8	1	−2.2 to 2.5
$\delta^{13}C$ (PDB)	4.0 to 4.6	2	−0.9 to 4.0
$^{87}Sr/^{86}Sr$	0.7076	3	0.70757 to 0.70808
ε_{Nd} (T)	−7 to −5	4	−6.0 to −4.6
Sr (ppm)	150 to >200	5	108 to 123
Fe (ppm)	16 to 57	5	500 to 3000
Mn (ppm)	19 to 22	5	600 to 1100

*Estimates for theoretical marine dolomite as follows:

(1) Estimated marine calcite $\delta^{18}O$ from concurrence of values for: (a) estimate from Osagean Lake Valley Formation (Meyers and Lohmann, 1985); (b) three heaviest nonluminescent brachiopod analyses (Kaufman, 1985); and (c) convergence of crinoid trends by locality (Chyi and others, 1985). To this value of −1.75 to −1.2‰, a dolomite-calcite fractionation factor of 3.6 to 4.0 was applied to bracket the value of 3.8 proposed by Land (1985).

(2) Estimated marine calcite $\delta^{13}C$ from concurrence of Burlington-Keokuk brachiopod and crinoid and Lake Valley data, similar to oxygen estimate above. No calcite-dolomite fractionation was applied.

(3) Estimated from lowest nonluminescent brachiopod analysis.

(4) No independent estimate from the Burlington-Keokuk or other Osagean formation available. Based on modeling of REE mobility (Banner, 1986), dolomite I samples which have seawater Sr isotopic compositions should also record seawater Nd isotopic compositions. A range was chosen to encompass most dolomite I ε_{Nd}(342) values and the upper end of a range of values for older Mississippian conodonts that preserve marine $^{87}Sr/^{86}Sr$ ratios (Shaw and Wasserburg, 1985).

(5) Analyses of Enewetak dolomites (Saller, 1984b) used for all trace-element estimates. Calculations and observations of Baker and Burns (1985) for Deep Sea Drilling Project dolomites used for lower Sr limit and summary by Land (1980) used for upper Sr limit. The values adopted here are in general agreement with broader studies of secular isotopic variations (e.g., Veizer and Hoefs, 1976; Burke and others, 1982), and are considered the best estimates for the Burlington-Keokuk Formation.

tinental Arch could have provided regionally extensive recharge to the Burlington-Keokuk shelf following the pre-St. Louis or pre-Pennsylvanian regressions.

The depletions in $\delta^{18}O$ and $\delta^{13}C$ values of some Burlington-Keokuk dolomite I samples relative to the EMD may be the result of a freshwater component in the fluid that produced dolomite I. If meteoric waters with relatively low $\delta^{18}O$ and $\delta^{13}C$ values remain largely unmodified during seaward migration, then the mixing of fresh water with sea water will result in a series of curves in $\delta^{13}C$ vs. $\delta^{18}O$ space, which increasingly deviate from linearity as the difference between the total dissolved carbon (TDC) contents of the end-member fluids becomes larger (Fig. 7). Thus, in a mixing zone in which the TDC concentration of the recharging fresh water varied with time or position in the mixing zone, a field of isotopic compositions could be generated that fans out from the composition of sea water to lower $\delta^{13}C$ and $\delta^{18}O$ values.

Interaction between the meteoric water and Mississippian marine carbonates during migration to the zone of mixing would first drive the $\delta^{13}C$ and then the $\delta^{18}O$ value of the fresh water toward the marine values. In addition, dolomitization of lime mud in the Burlington-Keokuk Formation should reflect some buffering of the fluid by the precursor sediment $\delta^{13}C$ and $\delta^{18}O$ values. These water-rock interaction processes will produce an inverted L-shaped compositional trend in $\delta^{13}C$ vs. $\delta^{18}O$ space (Meyers and Lohmann, 1985; Banner, 1986) for each fluid composition. In this manner, the combined processes of fluid-fluid mixing and water-rock interaction that can occur during mixing zone

dolomitization may produce a broad field of C and O isotopic compositions, rather than a distinct trend or composition.

Figure 8 illustrates that Burlington-Keokuk dolomite I samples have a similar range in $\delta^{13}C$ values and lower $\delta^{18}O$ values by about 0–3‰ relative to most Quaternary samples of proposed sea water, evaporite-modified sea water (Abu Dhabi), or mixed seawater-freshwater origin (Yucatan, Jamaica). They also have lower $\delta^{18}O$ values relative to dolomites of Meramecean age from Illinois, which are proposed to have formed in a marine meteoric-mixing zone (Choquette and Steinen, 1980).

Fresh waters that are recharged through soil horizons and fresh waters that have interacted with pre-Mississippian carbonates having $\delta^{13}C <4‰$ (Lohmann, 1983) will have strongly to moderately depleted $\delta^{13}C$ compositions relative to Osagean marine carbonates. Interaction of these fluids with Osagean marine carbonates will produce diagenetic phases with $\delta^{13}C <4‰$ only at relatively high water:rock ratios, as shown in Figure 6. Assuming that the precursor sediment to dolomite I was predominantly lime mud with a marine $\delta^{13}C$ signature of 4.0‰, the calculations suggest that the formation of most dolomite I samples was a relatively high water:rock ratio process (i.e., $(W/R)_m > 3000$). These results are consistent with calculations based upon Mg^{+2} requirements for dolomitization by seawater: freshwater mixtures ranging from 0–90% fresh water [$(W/R)_m = 1100–8900$; Land, 1985].

Fresh waters that are recharged through young marine carbonates will derive their dissolved trace elements almost entirely from interaction with the carbonates, which would have $^{87}Sr/^{86}Sr$ values of contemporaneous sea water. The radiogenic initial Sr isotope compositions of most dolomite I samples relative to the seawater value preclude this type of mixing zone model from being applicable in the case of the Burlington-Keokuk Formation. In contrast to fresh waters with proximal sources, meteoric waters recharging from and interacting with older rocks can have radiogenic $^{87}Sr/^{86}Sr$ ratios relative to the contemporaneous seawater value (see Table 3 for river water and seawater analyses). If the lower Paleozoic rocks of the Transcontinental Arch provided radiogenic Sr to regionally recharged meteoric waters, then a significant source of meteoric water with radiogenic Sr may have been available during late Mississippian time. Because fresh waters have low Sr concentrations (<1 ppm) relative to sea water (8 ppm), mixtures of the two would have only slightly higher $^{87}Sr/^{86}Sr$ ratios compared to sea water and lower Sr concentrations than sea water (Banner, 1986). Interaction of mixtures of continentally derived fresh waters and Osagean sea water with marine carbonates at relatively large water:rock ratios could account for the range in Sr isotope compositions and concentrations in dolomite I samples.

The Fe and Mn concentrations of dolomite I rhombs are orders of magnitude higher than expected for marine dolomite (Fig. 5). The mineral fluid K_D values for Fe and Mn are greater than unity, and these elements have low concentrations in sea water and fresh water (Veizer, 1983), properties that are intermediate between Sr and Nd. By comparison with the models for Sr and Nd in Figure 6, it
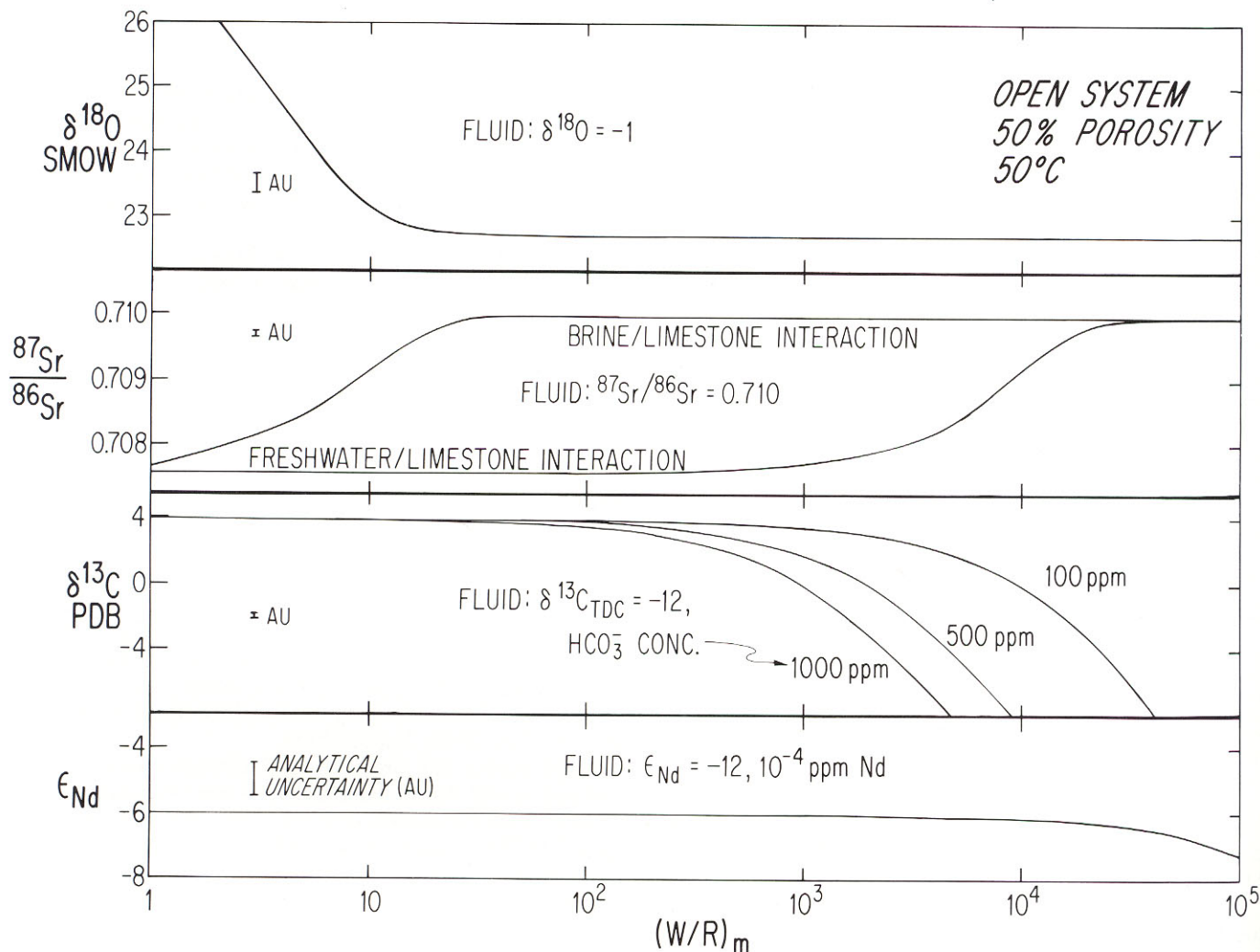
FIG. 6.—Simultaneous variations in the isotopic composition of O, Sr, C, and Nd during open-system recrystallization of a limestone as a function of increasing molar water:rock ratio, $(W/R)_m$ = (moles of water)/(moles of rock). In this model, a fluid is given composition flows through a given volume of rock in increments. Each increment of fluid fills the available porosity and recrystallizes calcite until isotopic equilibrium between the fluid and rock is attained. The resulting changes in the isotopic and trace-element composition of the rock are calculated using mass balance relations. Each new fluid increment displaces the previous one and the process is repeated. The curves illustrate the changes in the composition *of the rock* as a function of the total molar water:rock ratio (i.e., the sum of the increments). Initial isotopic compositions of limestone are: $\delta^{18}O = 28‰$ SMOW, $^{87}Sr/^{86}Sr = 0.7076$, $\delta^{13}C = 4.0‰$ PDB, and $\epsilon_{Nd} = -6.0$, 10 ppm Nd (ϵ_{Nd} as defined in DePaolo and Wasserburg, 1976). Fluid isotopic compositions as follows: $\delta^{18}O = -1.0‰$ SMOW, $^{87}Sr/^{86}Sr = 0.710$, $\delta^{13}C = -12‰$ PDB, $\epsilon_{Nd} = -12$. T = 50°C, porosity = 50%. Two cases illustrated for Sr isotopes: (1) the interaction between a diagenetic carbonate with 200 ppm Sr and a brine with 100 ppm Sr and 20,000 ppm Ca; and (2) the interaction between a marine carbonate with 1,345 ppm Sr and a fresh water with 0.5 ppm Sr and 20 ppm Ca. Calcite-water exchange distribution coefficient is $K_D(Sr/Ca) = (m_{Sr}/m_{Ca})_{calcite}/(m_{Sr}/m_{Ca})_{water} = 0.05$, where m_{Sr}, m_{Ca} are molar concentrations. The water-rock interaction pathways for carbon isotopes demonstrate the effects of dissolved bicarbonate concentrations (in ppm) on the rate at which the $\delta^{13}C$ value of the recrystallizing limestone changes. Note large differences in the water:rock ratios at which the O and C isotopic signatures significantly deviate from the original rock composition. Strontium-isotopic compositions respond at much more variable rates depending on the fluid and rock concentrations. For Nd isotopes, no significant changes from the original rock composition are obtained at water:rock ratios of as much as 5×10^4 using $K_D(Nd/Ca) = 100$ (Palmer, 1985), and fluid concentrations of 0.0001 ppm Nd and 1,500 ppm Ca. For oxygen isotopes, we use the relationship $\Delta_{calcite-water} = 2.78 \times 10^6 T^{-2}$ (°K) $- 2.89$ (Friedman and O'Neil, 1977) in this study for calcite, and the relationship $\Delta_{dolomite-calcite} = 3.8$, as discussed in Land (1985). Model calculations for dolomite recrystallization give very similar results to those shown here for calcite. Equations and procedures of the model are detailed in Banner (1986).

would be expected that relatively high water:rock ratios are needed to produce high Fe and high Mn dolomites in a mixing zone. Uncertainties in the effects of redox control on the supply of locally derived Fe and Mn from sulfides, oxides, hydroxides, and silicates in Burlington-Keokuk strata, however, obscure constraints on the water-rock interaction

history of dolomite I that are based on dolomite Fe and Mn concentrations.

In summary, the petrology and geochemistry of Burlington-Keokuk dolomite I indicate that the dolomites formed from predominantly Late Mississippian marine waters shortly after deposition was complete. A minor but distinctly non-
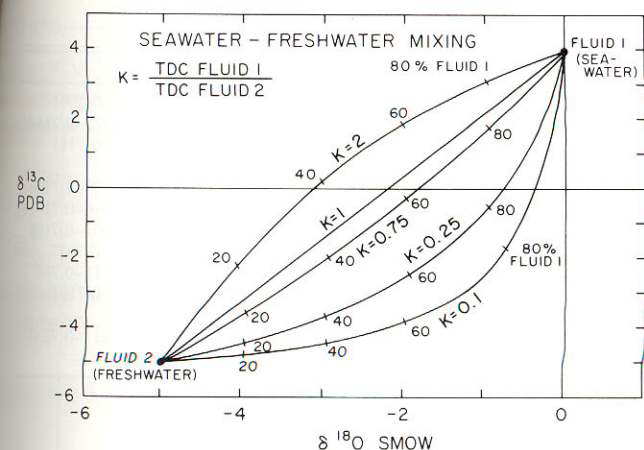
FIG. 7.—Mixing curves of fluid compositions for seawater-freshwater mixing in $\delta^{13}C$ vs. $\delta^{18}O$ space. Fresh water portrayed has typically low $\delta^{18}O$ and $\delta^{13}C$ values relative to sea water (Meyers and Lohmann, 1985). K is the concentration ratio of total dissolved carbon (TDC) as bicarbonate of fluid 1/fluid 2. Sea water has $\delta^{18}O = 0‰$ (SMOW), $\delta^{13}C = 4‰$ (PDB); fresh water has $\delta^{18}O = -5‰$ and $\delta^{13}C = -5‰$. Mixtures of fluids with equal TDC concentrations will define a straight line. For end members with different TDC concentrations, fluid mixtures describe a curve that will be concave up if the lighter $\delta^{13}C$ end member also has the higher TDC concentration. Method of curve calculation discussed in Banner (1986).

marine component in the water-rock interaction history of dolomite I is required by the isotopic and trace-element data. Although the source of this non-marine component is not clear, meteoric waters recharging through distal, older formations that mixed with sea water may have had the appropriate compositions for the genesis of dolomite I.

Petrogenesis of Dolomite II and II'

The geochemistry of dolomites II and II' is summarized in Figure 5. From the close similarities in C, O, and Sr isotope compositions, Sr and major-element concentrations, and replacement textures between dolomites II and II', it is evident that these two phases were formed by very similar processes. Any model for the generation of dolomites II and II' must satisfy the constraints of the following observations:

(1) the replacement of dolomite I by dolomites II and II', the closer approximation to stoichiometry of dolomites II and II', and the higher Fe and Mn concentrations in dolomites II and II' compared to those in dolomite I;

(2) the vertical (upsection) transition from dolomites II and II' to dolomite I, indicating that the fluid that formed dolomites II and II' migrated laterally and upward or simply upward into the Burlington-Keokuk Formation from older formations;

(3) the significant enrichment of radiogenic Sr in dolomites II and II', and the relatively large range in $\delta^{18}O$ values over a narrow range of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations. Mass balance calculations show that the relatively low $^{87}Sr/^{86}Sr$ ratios of shale horizons in the Burlington-Keokuk Formation during Mississippian time, combined with their composing $\leq 5\%$ of the strata, make these shale ho-

rizons an insufficient source of radiogenic Sr to account for the $^{87}Sr/^{86}Sr$ ratios of dolomites II and II' (Chyi and others, 1985). In addition, the juxtaposition of strata dolominated by dolomite I in between strata dominated by dolomite II and the Warsaw Shale makes this extensive clastic sequence an unlikely source of constituents for dolomites II and II'. Significant amounts of Sr must have been introduced from allochthonous sources.

(4) the low $\delta^{18}O$ values for dolomites II and II', as much as 9‰ lower than the heaviest dolomite I sample, and the same mean and range of $\delta^{13}C$ values between 29 dolomite I samples and 28 dolomite II samples;

(5) similar ranges of Nd-isotopic compositions and REE abundances between dolomites I, II, and II'.

Two considerations should be borne in mind throughout the following discussion. First, one can determine from cathodoluminescence that dolomite II and II' samples are all related by the process of dolomite I recrystallization. Therefore, there is a precise knowledge of the initial rock composition and porosity and an indication of the process involved for constructing quantitative models of water-rock interaction. Second, since the formation of dolomites II and
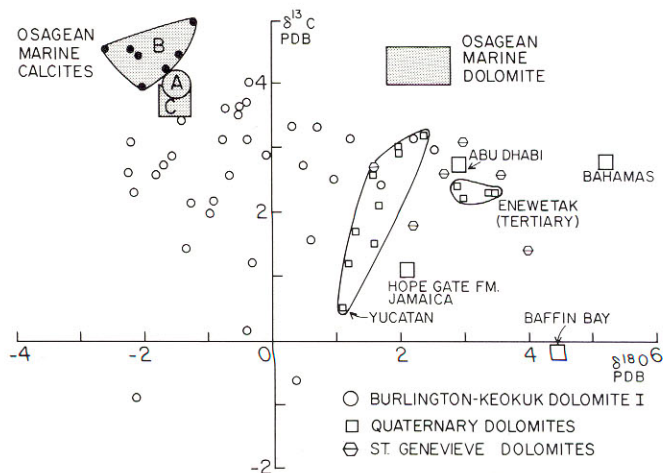

FIG. 8.—$\delta^{13}C$ vs. $\delta^{18}O$ for Burlington-Keokuk dolomite I and other ancient and Quaternary dolomites. Estimated Osagean marine calcite values are: A = Lake Valley Formation, New Mexico (Meyers and Lohmann, 1985); B = Burlington-Keokuk nonluminescent brachiopods, individual analyses shown (Kaufman, 1985); and C = Convergence of trends for Burlington-Keokuk crinoids (Chyi and others, 1985). Dolomite-calcite fractionation of 3.6 to 4.0‰ for oxygen used to estimate Osagean marine dolomite isotopic composition (see Table 2).

Mississippian dolomites from the St. Genevieve Formation (Meramecean) of Illinois are from Choquette and Steinen (1980). Mean values for Quaternary dolomite suites (large squares) are taken in part from compilation in Ward and Halley (1985) and include Baffin Bay, Texas (Behrens and Land, 1972); Little Bahama Bank (Mullins and others, 1985); Abu Dhabi, Persian Gulf (McKenzie, 1981); and the Hope Gate Formation, Jamaica (Land, 1973a). Unstippled fields enclose data for Pleistocene Yucatecan dolomites (Ward and Halley, 1985) and Tertiary to Recent dolomites from Eocene strata in Enewetak atoll (Saller, 1984a). Analyses of proposed mixing zone dolomites from Jamaica (Land, 1973b) and Israel (Magaritz and others, 1980) lie between $\delta^{13}C = -10$ to -7 and $\delta^{18}O = -3$ to -1 and are not shown here. Accounting for a 1‰ difference between modern and Mississippian carbonate, Burlington-Keokuk dolomite I samples have approximately 0–3‰ lower $\delta^{18}O$ values compared to most Quaternary dolomites.

TABLE 3.—Sr ISOTOPE COMPOSITIONS AND Rb, Sr, AND Ca CONCENTRATIONS (mg/l) OF SELECTED NATURAL WATERS

Sample/Locality	Rb	Sr	Ca	Sr/Ca-molar	$^{87}Sr/^{86}Sr$
1. Sea water	0.12	8.0	411	0.00885	0.7091
2a. North American Rivers	—	0.01–0.16	1.4–183	0.001–0.007	0.7077–0.71549
2b. Canadian Rivers	—	0.01–0.08	0.8–29	0.0005–0.006	0.7111
3. Illinois Basin:					
a. Mississippian	—	128–745	2,109–14,790	0.0041–0.060	0.7079–0.7104
b. Devonian	—	177–424	2,694–11,735	0.030–0.0164	0.7096–0.7101
c. Silurian	—	2–908	45–5,499	0.018–0.082	0.7091–0.7108
4. Miocene, Israel	0.168	57	1,400	0.019	0.7087
5. Canadian Shield	<1	1.7–2,060	19,000–64,000	0.001–0.024	0.711–0.740
6. Jurassic, Arkansas	—	2,930	44,200	0.0301	0.7101
7. Texas	0.15	97	1,320	0.033	
8. Osagean-Meramecian, Kansas	0.8–0.9	40–46	1,440–1,670	0.012–0.013	0.7221–0.7230
9. Osagean, Missouri	<1	8.6	315	0.012	—

Sample Key
1. Present-day seawater from Drever (1982) and Burke and others (1982).
2a. North American rivers from Goldstein and Jacobsen (1987).
2b. Canadian rivers from Wadleigh and others (1985). Ranges for concentrations and weighted mean for isotopic composition.
3. Ranges for brines sampled from Missippian through Silurian strata, Illinois Basin (Hetherington and others, 1986 and A. M. Stueber, pers. commun., 1987).
4. Brine sampled from Mavqiim clastics, evaporites, and clastics, Upper Miocene, Israel coastal plain (Starinsky and others, 1983).
5. Range for brines sampled from Precambrian Shield (Frape and others, 1984; McNutt and others, 1984).
6. Brine sampled from Kerlin Field, Upper Jurassic Smackover Formation (Stueber and others, 1984, and Trout, 1974).
7. Brine sampled from High Island Field, Offshore Texas (Kharaka and others, 1985).
8. Ranges for brines sampled from Osagean to Meramecian carbonates, Hodgeman County, Kansas (Chaudhuri and others, 1987).
9. Ground water sampled from Burlington-Keokuk Formation, Saline County, Missouri (Carpenter and Miller, 1969).

II′ is a dolomite-to-dolomite recrystallization process, an external source of Mg^{+2} is not required. The nonstoichiometric composition of dolomite I was probably a driving mechanism in the formation of dolomite II, as calcium-rich dolomites are susceptible to recrystallization by a range of fluid compositions (Land, 1985).

Marine meteoric mixing.—

The high $^{87}Sr/^{86}Sr$ ratios of dolomites II and II′ are difficult to explain in terms of a mixing zone model. A fresh water with 1 ppm Sr and a $^{87}Sr/^{86}Sr$ ratio of 0.710 (Table 3) requires mixtures of more than 90 percent fresh water in order to exceed mixture values of 0.7088. The interaction of such a fluid with dolomite I would produce dolomites with $^{87}Sr/^{86}Sr$ ratios of less than 0.7089, the minimum dolomite II value. Fresh waters typically range to less than 0.1 ppm Sr. Using these low concentrations would lead to mixtures requiring greater than 99 percent fresh water to give $^{87}Sr/^{86}Sr$ ratios of 0.7089 in dolomites forming from the mixture.

Fresh water dolomitization.—

The end-member fresh water could produce the Sr isotopic compositions for dolomites II and II′ by recrystallization of dolomite I. Figure 9 graphically illustrates the results of model calculations simulating the recrystallization of dolomite I by various fluids, in the same manner as the results of calculations presented in Figure 6.

Owing to the small Sr concentrations in fresh waters, this recrystallization process would require approximately 12,000 moles of water for each mole of rock (Fig. 9A), or nearly 20,000 pore volumes of fresh water at 15 percent porosity to produce dolomites with the $^{87}Sr/^{86}Sr$ ratios and Sr concentrations of dolomites II and II′. Accounting for the distance over which an extraformational fluid had to have traveled to produce the regional distribution pattern for dolomites II and II′ (>360 km), and the amount of time during which

these dolomites were probably generated (≤20 million years), a calculated water:rock ratio will determine a fluid flow velocity. The water:rock ratio for the freshwater, open-system model gives a flow velocity of >250 m/yr, which is more than an order of magnitude higher than flow rates in sedimentary aquifers, as determined by Back and Hanshaw (1970) and Bethke (1986). A Sr-Ca-rich brine, with the same m_{Sr}/m_{Ca} ratio as fresh water will exchange more Sr with a mineral during water-rock interaction than an equivalent amount of fresh water (Fig. 9B), thus requiring orders of magnitude less fluid (and geologically realistic flow rates) to achieve dolomite II and II′ compositions.

Normal, hypersaline, and sulphate-reduced seawater dolomitization.—

Normal seawater and sea water that has been modified by evaporation or sulphate reduction will all bear a marine $^{87}Sr/^{86}Sr$ ratio. The initial $^{87}Sr/^{86}Sr$ ratios determined for dolomites II and II′ have a maximum at 0.70942, which is higher than all estimated seawater compositions for Phanerozoic time (Burke and others, 1982). Most other chemical signatures—Fe, Mn, Sr contents, and C, O isotopes— also show significant depletion or enrichments from the estimated marine value. The failure of a seawater model to account for nearly all geochemical features of the later replacement dolomites II and II′ make most seawater models untenable.

Burial-compaction/basinal-brine dolomitization.—

Burial history curves for the Burlinton-Keokuk Formation limit maximum burial depths to less than 0.5 km (O. A. Cox, unpubl. data). If basinal brines were the dominant diagenetic agent in the formation of dolomite II, then they had to have migrated to these shallow burial depths from a deeper, allochthonous source. This is consistent with the conclusions that the intraformational shales and the Warsaw Shale were not important sources of Sr for dolomite II.
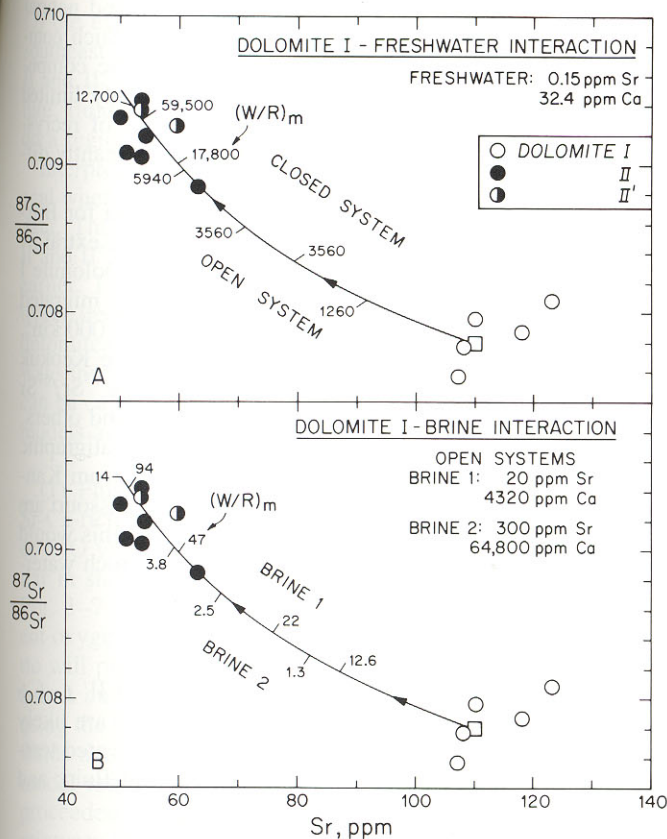
FIG. 9.—$^{87}Sr/^{86}Sr$ vs. Sr abundance for Burlington-Keokuk dolomites I, II, and II′, shown as open, filled, and half-filled circles, respectively. Curves show calculated pathways of changing dolomite compositions during water-rock interaction between dolomite I and diagenetic fluids for dolomite-water $K_D(Sr/Ca) = 0.05$. Porosity = 15%. Fluid $^{87}Sr/^{86}Sr = 0.7095$ in all models. Curve shape and position is dependent on $K_D(Sr/Ca)$, fluid composition and starting rock composition. Method of model calculation presented in Figure 6. Molar water:rock ratios, $(W/R)_m$, are numbered on all curves. Square indicates starting parameters for dolomite I in all models: $^{87}Sr/^{86}Sr = 0.7078$; 110 ppm Sr. (A) Curves illustrate open- and closed-system water-rock pathways for fresh water with 0.15 ppm Sr and 32 ppm Ca. (B) Water-rock curves for brine-dolomite I interaction. Brine 1 has 20 ppm Sr and 4,320 ppm Ca. Brine 2 has 300 ppm Sr and 64,800 ppm Ca. Note differences in water:rock ratios required to produce dolomite II and II′ compositions between the different diagenetic fluid regimes and between open and closed systems.

Subsurface waters have a spectrum of major- and trace-element concentrations and isotopic compositions that often is distinct compared to those of sea water and fresh waters (Table 3; Hanor, 1979). Qualitatively, the marked increases in $^{87}Sr/^{86}Sr$ ratios and Fe concentrations, and the decreases in $\delta^{18}O$ values of dolomites II and II′ relative to the EMD are expected for the recrystallization of carbonates by basinal fluids at elevated temperatures. The following section will examine the effects of subsurface fluids on the chemical and textural evolution of shelf carbonates and attempt to quantify these effects in the case of the Burlington-Keokuk Formation. Recognizing the wide range of salinities and sources of subsurface fluids, we use the term "brine" herein to connote a subsurface fluid that is enriched in certain cations relative to sea water (e.g., Sr, Ca) for comparative purposes in evaluating models.

Quantitative Models for Brine-Rock Interaction

Integrated studies of the geology, petrology, and geochemistry of carbonate-hosted lead-zinc ore deposits in the midcontinent region have proposed hypotheses for the origin of these Mississippi Valley-type (MVT) deposits involving the migration of warm saline brines from distant, deep basinal sources to carbonate shelves. Case studies have documented the large scale on which some fluid migration events appear to have occurred (Gregg, 1985; Leach and Rowan 1986), and various hydrologic models have been proposed (Jackson and Beales, 1967; Cathles and Smith, 1983; Garven, 1985; Bethke, 1986; Oliver, 1986). Calcite and dolomite cements associated with ore deposits (Kessen and others, 1981; Sverjensky, 1981; Gregg, 1985) and deep burial environments (Mattes and Mountjoy, 1980; Moore, 1985; Scholle and Halley, 1985) have had their origins attributed to the interaction of basinal brines with carbonate host rocks. These minerals may have preserved the isotopic signatures of the brines that crystallized them.

Strontium isotopes and Sr concentrations.—

Many gangue carbonates have significantly higher $^{87}Sr/^{86}Sr$ ratios relative to their host rocks, which have close to the estimated marine value (Fig. 10). Basinal brines are inferred to be the source of radiogenic Sr (Kesson and others, 1981; Chaudhuri and others, 1983). Late calcite and dolomite cements (vug-filling carbonates) in the Burlington-Keokuk Formation have similar high $^{87}Sr/^{86}Sr$ ratios (Fig. 10). In contrast to the results of other studies, however, Burlington-Keokuk Formation dolostone host rocks can have *both* radiogenic (dolomites II and II′) and near-marine Sr isotopic compositions (dolomite I). As discussed earlier, the radiogenic Sr in the replacement dolomites was likely derived from sources external to the Burlington-Keokuk Formation. Consider that dolomite composes roughly one-third to one-half of the Burlington-Keokuk Formation over nearly the entire 100,000 km² study area, and that dolomites II
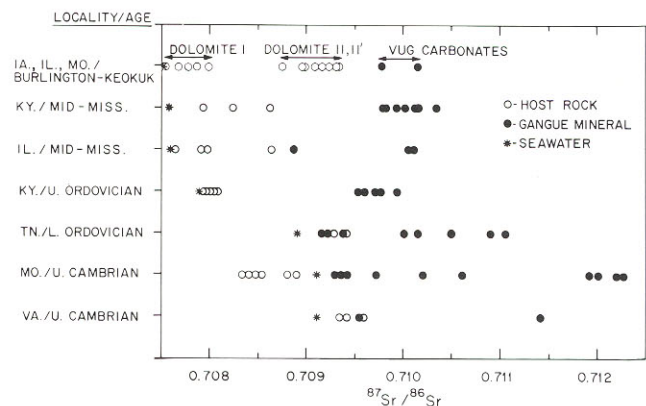

FIG. 10.—Comparison of $^{87}Sr/^{86}Sr$ ratios for gangue minerals associated with Mississippi Valley-type mineralization in host carbonate rocks of various age in the central United States and in Burlington-Keokuk carbonates. Data sources: Kessen and others (1981), Chaudhuri and others (1983), and this study. Burlington-Keokuk data adjusted to a value of $^{87}Sr/^{86}Sr = 0.71014$ for the NBS 987 Sr standard for comparative purposes. Sea water estimates for other studies are from Burke and others (1982).

and II' compose one-third to one-half of all dolomite. If the radiogenic Sr in dolomites II and II' was derived through the interaction of extraformational brines as they migrated through previously dolomitized (dolomite I) sediments, then the Burlington-Keokuk Formation may contain the most regionally extensive and correlative record of pervasive brine-rock interaction in carbonates yet reported.

Examination of the covariation of Sr abundances and Sr isotopic compositions for dolomites I and dolomites II and II' shows relatively narrow and distinct ranges for the two parameters for the different dolomite generations. Pathways of water-rock interaction for various fluids interacting with dolomite I can be determined in order to model these two parameters in dolomite II. For a closed system, higher water:rock ratios are required to attain the same Sr isotopic compositions and Sr abundances relative to open-system calculations (Fig. 9A). As discussed earlier, the freshwater model gives approximately two to three orders of magnitude higher water:rock ratio values in both open and closed systems, compared to the results of the same calculations using various brine compositions (Fig. 9B).

The narrow range of Sr concentrations and isotopic compositions in dolomite II and II' samples, with six of eight values within the range 49.9–54.2 ppm and $^{87}Sr/^{86}Sr$ = 0.7091–0.7094, for localities covering a distance of 160 km is indicative of an open system in which the diagenetic phases record the unbuffered m_{Sr}/m_{Ca} and $^{87}Sr/^{86}Sr$ ratios of the fluid. In such a system, the recrystallization has progressed to a stage in which the original Sr from dolomite I has essentially been completely removed from the system. If this advanced stage had not been reached, then the lower extents of fluid-rock interaction would have produced a wider range in Sr abundances and $^{87}Sr/^{86}Sr$ ratios, unless all samples from a 160-km regional extent have experienced the same amounts of water-rock interaction with similar fluids. The summary of data in Table 3 shows that present subsurface brines from both sedimentary sequences and granitic basement have high $^{87}Sr/^{86}Sr$ ratios relative to marine values. Brines extracted from Silurian through Devonian strata in the Illinois Basin have $^{87}Sr/^{86}Sr$ ratios of 0.7091 to 0.7108, similar to the range of values determined for dolomites II, II', and the vug carbonates. In contrast, brines extracted from Keokuk and Warsaw strata in western Kansas have quite radiogenic and uniform isotopic compositions ($^{87}Sr/^{86}Sr$ = 0.7221–0.7230). It was suggested earlier that Sr isotopic compositions in dolomites II and II' are the result of crystallization in an open system from an end-member fluid composition, making brines with isotopic compositions similar to those from the Illinois Basin more appropriate for the formation of dolomites II and II'.

In order to crystallize dolomite with 50 ppm Sr for a dolomite-fluid exchange K_D(Sr/Ca) = 0.05, a fluid with a molar Sr/Ca ratio of less than 0.005 is required (Fig. 9). Nearly all of the subsurface fluids listed in Table 3, including some sampled from the Burlington-Keokuk Formation, have molar Sr/Ca ratios that are considerably higher than 0.005. To invoke such fluids in the formation of dolomites II and II' would require a K_D of <0.01, which is considerably lower than any published values. Similar discrepancies in other diagenetic carbonate systems have been

attributed to differences between experimental and natural systems (Bein and Land, 1983; Moore, 1985). Such comparisons involving the trace-element and isotopic compositions of present subsurface fluids are necessarily limited by the fact that the fluids available at the time of recrystallization of the dolomites may have had significantly different compositions.

In summary, Sr isotope and concentration data for Burlington-Keokuk dolomites II and II' indicate an extraformational, older source of Sr for the dolomites. Dolomite I recrystallization was likely effected by brines that migrated to shallow burial depths on a scale of nearly 100,000 km², probably prior to Pennsylvanian time. Subsurface Keokuk and Warsaw dolomites from western Kansas have $^{87}Sr/^{86}Sr$ ratios of 0.7091–0.7095 (data from Chaudhuri and others, 1987; adjusted to SRM 987 = 0.71034). If the stratigraphic and isotopic similarities between the dolomites from Kansas and the dolomites from Iowa, Illinois, and Missouri are the result of related fluid migration events, then this would increase by a factor of two the large scale on which water-rock interaction appears to have occurred.

Oxygen isotopes.—

The depleted $\delta^{18}O$ values for dolomites II and II' (−6.6 to −0.2‰) relative to dolomite I (−2.2 to 2.5‰) are likely due to a combination of the influences of: (1) elevated temperatures; (2) the $\delta^{18}O$ value of the replacement fluid; and

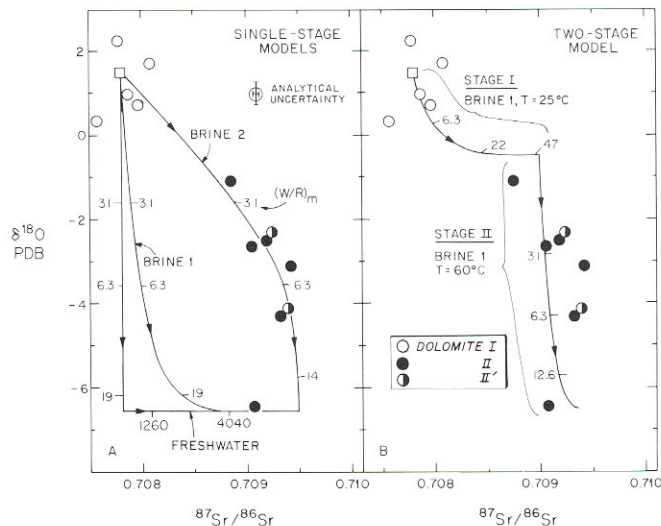FIG. 11.—$^{87}Sr/^{86}Sr$ vs. $\delta^{18}O$ for Burlington-Keokuk dolomites I, II, and II', illustrating narrow range of Sr isotopic compositions relative to oxygen-isotopic compositions for second generation dolomites. Calculated curves illustrate changing dolomite compositions during progressive water-rock interaction. (A) Single-stage water-rock interaction models shown are calculated for the recrystallization of dolomite I by three different fluids: fresh water, brine 1 and brine 2. (B) A two-stage model is shown for the recrystallization of dolomite I by brine 1. A single-stage model involving a saline brine and a multistage model involving increasing temperature and a dilute brine of constant composition can account for the dolomite II and II' data. All models are for open systems. Fluid compositions, porosities, and K_D's as in Figure 9. All fluids have $\delta^{18}O$ = −2‰ SMOW. T = 60°C, except where noted otherwise.

(3) the extent of water-rock interaction. The northwest to southeast gradient of decreasing $\delta^{18}O$ values of dolomites II and II′ (Fig. 4) can be ascribed to changes in temperature, fluid composition, or extent of water-rock interaction on a regional scale.

Interpretation of the oxygen isotope data is least equivocal when examined in conjunction with other geochemical data. The covariation of $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ for dolomites II and II′ can be modeled in the same manner as presented earlier. Figure 11 illustrates that $^{87}Sr/^{86}Sr$ ratios are relatively invariant compared to the range of $\delta^{18}O$ values for dolomites II and II′. Several possible evolutionary pathways involving fluid-rock interaction and fluid-fluid mixing can be calculated to give a reasonable fit to the data. These models are:

(1) Fluid-fluid mixtures of <80% sea water and >20% Sr-Ca-rich brine will produce mixing trends with a range of $\delta^{18}O$ values and a narrow range of $^{87}Sr/^{86}Sr$ ratios, similar in shape to the brine 2 curve in Figure 11A (see also Fig. 3–7 in Banner, 1986). Mixtures of brines with different oxygen isotope compositions and the same $^{87}Sr/^{86}Sr$ ratio will produce the same trend. Separate water-rock interaction curves could produce the dolomite II and II′ trend using the range of these fluid-fluid mixtures as end-member fluids and dolomite I as the initial rock composition. This model requires that the water-rock interaction process has proceeded to the same extent for each sample and that the mixtures have maintained their integrity for the duration of the process.

(2) Using a saline fluid with high Sr and Ca contents in the recrystallization calculation (brine 2, Fig. 11A) would produce a water-rock interaction curve that would change the $^{87}Sr/^{86}Sr$ ratio of the recrystallized product faster than it would change $\delta^{18}O$ during progressive water-rock interaction. This model produces a range of $\delta^{18}O$ and constant $^{87}Sr/^{86}Sr$ at low (<20 molar) water:rock ratios. Note that a minimum fluid salinity is required in order for this model to account for the dolomite data.

(3) Several stages of water-rock interaction involving a brine with moderate Sr and Ca contents (brine 1, Fig. 11B) can also explain the dolomite II and II′ trend. A water-rock pathway for such a brine recrystallizing dolomite I will be nearly L-shaped (brine 1 pathway in Fig. 11A). Extensive water-rock interaction will drive the replacement dolomites first to low $\delta^{18}O$ at low water:rock ratios (beginning of stage I in Fig. 11B) and then to higher and fairly uniform $^{87}Sr/^{86}Sr$ ratios at higher water:rock ratios (end of stage I in Fig. 11B). If there was a change in the temperature or the $\delta^{18}O$ value of the fluid during the last stages of recrystallization (stage II in Fig. 11B), then a range of $\delta^{18}O$ values could have been imposed on dolomites II and II′ through small extents (water:rock ratio <20) of water-rock interaction. Due to the low water:rock ratio, $^{87}Sr/^{86}Sr$ ratios in the recrystallized products will change only slightly during this stage. As a consequence, a new vertical limb of an L-curve (stage II) would be extended from the end of the horizontal limb of the previous L-curve (stage I). In this manner, the regional gradient in $\delta^{18}O$ for dolomites II and II′ could be accounted for by progressively increasing water-rock inter-

action from northwest to southeast during the last stages of recrystallization. In this multistage model, it can be seen that the $\delta^{18}O$ values of the dolomites record a relatively small and late segment in the water-rock interaction history of the dolomites, whereas dolomite Sr isotope signatures reflect an earlier and larger segment of the same history.

Carbon isotopes.—

In contrast to the oxygen isotope results for the Burlington-Keokuk dolomites, carbon-isotopic compositions of 28 samples of dolomites II and II′ have nearly the identical mean and range of values as observed for 29 samples of dolomite I (Fig. 5). For the few localities for which isotope analyses are available for samples of dolomite I, II, and II′, there are small but distinguishable differences between the average $\delta^{13}C$ values of each locality (Fig. 12). Dolomite I, II, and II′ samples from the same localities have similar ranges of values. Only the vug carbonates show significantly different $\delta^{13}C$ compositions. This suggests that dolomites II and II′ inherited their carbon-isotopic signatures from dolomite I and that the recrystallization process did not affect these values.

Quantitative modeling of the change of $\delta^{13}C$ values as a function of progressively increasing water:rock interaction during recrystallization supports these general observations. During the recrystallization of dolomite, oxygen in the dolomite will equilibrate with oxygen in the fluid at much lower water:rock ratios compared to the values required for carbon equilibration (Fig. 12). This produces an inverted L-shaped curve in $\delta^{13}C$ vs. $\delta^{18}O$ space. For a fluid that has total dissolved carbon (as bicarbonate) with $\delta^{13}C = -12‰$ and concentrations of 300 mg/l, a molar water:rock ratio value of approximately 3,000 is needed to establish a 2‰ change in the isotopic composition of the rock. Thus, because $\delta^{13}C$ values are essentially unchanged between dolomites I, II, and II′, the recrystallization process probably involved less than 3,000 moles of fluid for each mole of rock. The water-rock calculations for Sr contents and Sr isotopes predicted that replacement dolomitization via brine 1 required on the order of 50 to 100 moles of fluid for each mole of rock reacting. The independent constraints of the two isotopic systems are consistent and indicate geologically reasonable fluid flow velocities as discussed earlier.

An alternative explanation for the distribution of carbon isotopes in the Burlington-Keokuk dolomites is that the fluid that recrystallized dolomite I had dissolved bicarbonate with an isotopic composition similar to the $\delta^{13}C$ values of dolomite I (via interaction with older marine carbonates), and therefore any exchange that may have taken place during the formation of dolomite II would not be detectable. This hypothesis is less tenable than the model of retention of original dolomite I carbon in dolomite II because: (1) small but distinct differences in $\delta^{13}C$ are retained at several localities for dolomites I, II, and II′ (Fig. 12), as well as for crinoids (Chyi and others, 1985), and (2) as discussed in the final section, the low $\delta^{13}C$ and $\delta^{18}O$ values and high $^{87}Sr/^{86}Sr$ ratios of the vug carbonates indicate that extraformational fluids with light $\delta^{13}C$ migrated to the Burlington-Keokuk Formation without being buffered by carbon from older marine carbonates.
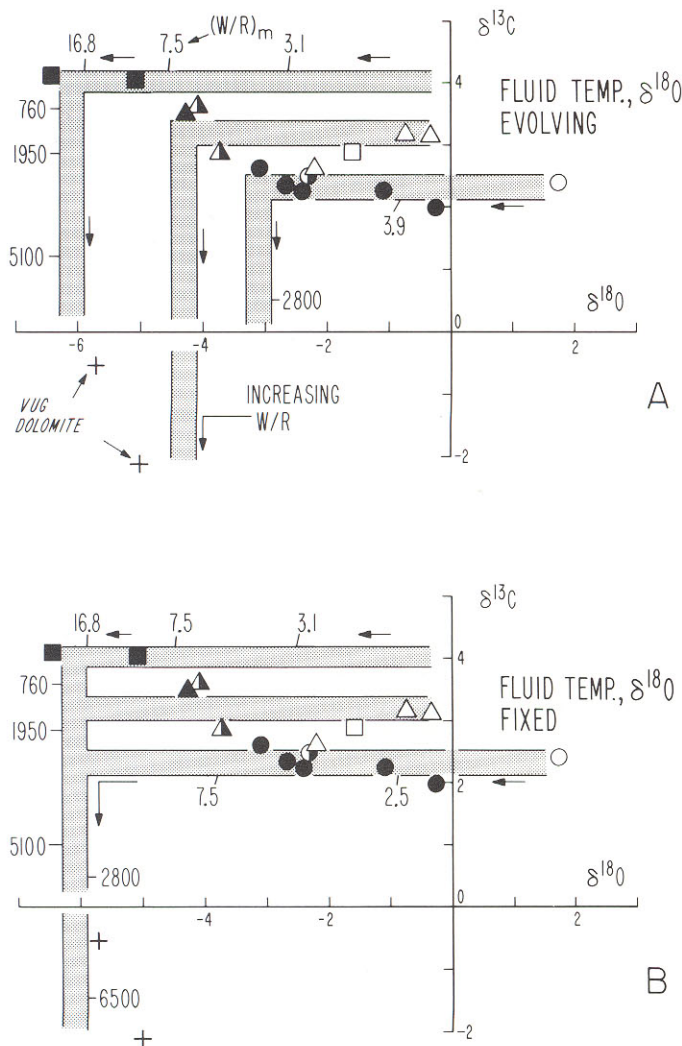
DOLOMITE I-BRINE INTERACTION

FIG. 12.—$\delta^{13}C$ vs. $\delta^{18}O$ (PDB) for localities where dolomites I, II, and II′ have been analyzed. Localities as follows: circles—HP; squares—MPA; triangles—DC. Dolomites I, II, and II′ are open, filled, and half-filled symbols respectively. Vug dolomites are from locality GR. Shaded trends are calculated pathways of water-rock interaction between brine and dolomite. Arrows indicate direction of increasing water-rock interaction. All models are for open systems. Three separate starting dolomite I compositions are used in both (A) and (B): (1) $\delta^{18}O = -0.5$, $\delta^{13}C = 4$; (2) $\delta^{18}O = -0.5$, $\delta^{13}C = 3.25$; (3) $\delta^{18}O = 1.75$, $\delta^{13}C = 2.3$ (all in ‰). The fluid has $\delta^{13}C = -12$ and 300 ppm HCO_3^- and the rock has 15% porosity in all models. (A) Water-rock pathways evolve to distinct dolomite $\delta^{18}O$ values. The curve extending from the dolomite I composition at $\delta^{18}O = -0.5$, $\delta^{13}C = 4$ (MPA locality) is a pathway calculated using a fluid $\delta^{18}O$ value of -1.6‰ (SMOW) and a temperature of 60°C. Differences in second generation dolomite $\delta^{18}O$ values between localities can be accounted for by either a progressive increase in fluid $\delta^{18}O$ values of 3‰ or a progressive 20°C decrease in temperature between the MPA and HP localities. (B) A single-fluid isotopic composition and temperature will produce similar isotopic variations in second generation dolomite. Differences between localites are a function of local variations in extents of water-rock interaction. Fluid $\delta^{18}O = -1.6$‰ (SMOW), T = 60°C at all localities. The similar $\delta^{13}C$ values among different dolomite types at individual localities suggest that dolomite I recrystallization occurred at moderate $(W/R)_m$ values of $\leqslant 3,000$.

Rare-earth elements.—

The similarities in REE patterns and Nd isotopic compositions between dolomites I, II, and II′ are consistent with the invariance in $\delta^{13}C$ values between the dolomites, because even higher water:rock ratios would be required to change the REE distributions during the recrystallization of dolomite I compared to the results for carbon, as shown in Figure 6.

Final stages of brine-rock interaction.—

Although only limited analyses have been performed on the late-stage carbonates from solution vugs in Burlington-Keokuk strata, quantitative modeling of their isotope geochemistry suggests that they crystallized in a fluid-dominated environment with only a minor influence from the host rock. The vug carbonates have elevated $^{87}Sr/^{86}Sr$ ratios of 0.7099–0.7102, suggesting that they formed from similar but distinct fluids compared to those that formed dolomites II and II′. The vug dolomites have depleted $\delta^{18}O$ (-5.7 to -5.0‰) and $\delta^{13}C$ values (-2.1 to -0.6‰) relative to most dolomite II and II′ samples, and lie on a vertical limb of an inverted L-shaped brine-dolomite I interaction curve in $\delta^{13}C$ vs. $\delta^{18}O$ space (Fig. 12). The calculated alteration pathway transects the dolomite II and II′ data at low water:rock ratios and extends through the vug dolomites at high water:rock ratios.

Basinal hydrocarbon sources of light $\delta^{13}C$ have been proposed in many cases of MVT gangue and burial carbonate cements. As the calculations in Figure 12 demonstrate, significant depletions in carbon-isotopic signatures that are attributable to water-rock interaction imply relatively large water:rock ratios during crystallization. The solution vugs developed late in the diagenetic history of the Burlington-Keokuk Formation, after most cementation and recrystallization occurred and thus at a time when the rocks were least porous. Such high water:rock ratios do not require especially large volumes of fluid. Rather, they may reflect vanishingly small amounts of host rock taking part in the interaction. As observed for the C isotopic data, the REE patterns and ϵ_{Nd} value for the vug carbonates (Banner, 1986) are distinct relative to the overlapping values in dolomites I, II, and II′, consistent with higher water:rock ratios during vug carbonate formation.

Whereas the vug carbonates may preserve the C and REE signatures of an extraformational fluid, dolomites II and II′ that have replaced pre-existing sediments appear to record the C and REE signatures of the precursor dolomite I. If the majority of constituents for the vug calcites and dolomites is fluid-derived with little host rock influence, then these fluids would also have been capable of dolomitization. In contrast, the source of Mg for dolomites II and II′ could have been predominantly autochthonous.

CONCLUSIONS

(1) Two major episodes of regionally extensive (100,000 km^2) dolomitization can be correlated in the Burlington-Keokuk Formation of Iowa, Illinois, and Missouri. Dolomite I and its recrystallized product, dolomite II, have dis-

tinctive isotopic compositions and trace- and major-element concentrations.

(2) The results of model calculations that simulate isotopic exchange during water-rock interaction illustrate important differences in the relative rates at which different isotopic systems are altered during carbonate diagenesis. During dolomite recrystallization, dolomite $\delta^{18}O$ values are reset at relatively low water:rock ratios, whereas several orders of magnitude larger extents of water-rock interaction are required to alter dolomite $\delta^{13}C$ values. Strontium-isotopic compositions are changed at variable extents of water-rock interaction, depending on the Sr isotopic compositions and Sr and Ca concentrations of the dolomite and fluid.

(3) Burlington-Keokuk dolomite I samples have O, C, and Sr isotopic compositions that encompass estimated marine dolomite values and range to slightly lower $\delta^{18}O$ and $\delta^{13}C$ values and slightly higher $^{87}Sr/^{86}Sr$ ratios. These results can be explained by a marine meteoric-mixing model in which the diagenetic constituents that comprise dolomite I are predominantly marine derived.

(4) Dolomite II samples preserve a petrographic and geochemical record of the recrystallization of the nonstoichiometric dolomite I. This process imparted lower $\delta^{18}O$ values and Sr concentrations and higher $^{87}Sr/^{86}Sr$ ratios and Fe concentrations to the recrystallized dolomites. It appears that extraformational subsurface fluids migrated into Burlington-Keokuk strata at shallow burial depths during dolomite II formation. The results of quantitative modeling suggest that these fluids exchanged nearly all of the original Sr in the dolomites during recrystallization, and that the Sr signature of dolomite II samples reflects a large segment of their water-rock interaction history. In contrast, the $\delta^{18}O$ values of the dolomites may have been reset during the last stages of recrystallization, whereas their C and Nd isotopic signatures were probably inherited from dolomite I precursors. Dolomitization in the Burlington-Keokuk Formation occurred via water-rock interaction processes that can be correlated on a regionally extensive scale.

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