

Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis

JAY L. BANNER¹ and GILBERT N. HANSON²

¹ Department of Geological Sciences, University of Texas, Austin, TX 78713-7909, USA

² Department of Earth and Space Sciences, State University of New York, Stony Brook, NY 11794, USA

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Abstract—Equations are developed for the calculation of the simultaneous variations in trace element concentrations and radiogenic and stable isotopic compositions that occur during water-rock interaction. The equations are of general use for modeling chemical and isotopic variations in porous media and are applied here to the diagenesis of carbonate rocks and sediments. The variables which control the ultimate geochemical composition of diagenetic carbonates include the composition of the original sediment and fluid, water:rock ratio, fractionation factors, distribution coefficients, open vs. closed system behavior, and porosity.

Owing to the extreme differences in the concentrations of oxygen and carbon in diagenetic fluids, carbonate minerals equilibrate with fluid $\delta^{18}\text{O}$ values at three orders of magnitude lower water:rock ratios (<10) than the water:rock ratios at which they equilibrate with fluid $\delta^{13}\text{C}$ values (10^3). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are affected at variable rates. In order to reset the $^{87}\text{Sr}/^{86}\text{Sr}$ value of a marine limestone during freshwater diagenesis, water:rock ratios similar to those calculated for equilibration of $\delta^{13}\text{C}$ values are required, while Sr-Ca-rich brines can reset the $^{87}\text{Sr}/^{86}\text{Sr}$ value of a limestone at low water:rock ratios, similar to those calculated for equilibration of $\delta^{18}\text{O}$ values. Water:rock ratios exceeding 10^3 are required to affect the rare earth element (REE) patterns and Nd isotopic compositions of carbonate sediments during diagenesis.

These large, relative differences in the response of different isotopic systems to water-rock interaction translate into characteristic trends on isotope and trace element covariation diagrams that can be used to distinguish between (1) different models for water-rock interaction and (2) different processes such as water-rock interaction, mixing of fluids, and mixing of mineral endmembers. An example is the use of simultaneous variations of O and Sr isotopes in modeling the freshwater diagenesis of limestones. Freshwater-limestone interaction pathways are independent of Sr-Ca exchange distribution coefficient ($K_D^{\text{Sr-Ca}}$) values over an order of magnitude range of 0.01 to 0.15, because of the large differences in the water:rock ratios necessary to equilibrate the two isotopic systems. Carbon vs. oxygen isotopic variations in the same system can be used to distinguish between water-rock interaction, mixing of fluids, and mixing of end-member calcites.

These modeling approaches are applied to the regionally extensive dolomites of the Mississippian Burlington-Keokuk Formation. Compared to its early dolomite precursor (dolomite I), second-generation replacement dolomite (II) in the Burlington-Keokuk Formation has higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, lower $\delta^{18}\text{O}$ values and Sr concentrations, and similar $\delta^{13}\text{C}$ values, Nd isotopic compositions, and REE patterns. A multistage model calculation can account for the dolomite II data via recrystallization of dolomite I, whereby the $\delta^{18}\text{O}$ values of dolomite II record a relatively minor and late portion of the water-rock interaction history of the samples while Sr in the dolomites preserves an earlier and larger segment of the same history. The recrystallization process was effected by extraformational brines in a relatively open system with respect to Sr, while C and the REE were unaffected.

INTRODUCTION

DIAGENETIC STUDIES HAVE come to rely on geochemical techniques such as trace element, radiogenic isotope, and stable isotope systems for interpreting the conditions of formation of diagenetic phases, the compositions of diagenetic fluids, and the nature of interactive processes between fluid and rock in porous media. Despite this emphasis, quantitative geochemical modeling of variations in these parameters during diagenetic processes has been limited compared with studies of igneous and metamorphic systems. This is in part due to uncertainties in the experimentally determined values for trace-element distribution coefficients and isotopic fractionation factors applicable to low temperature sedimentary systems (see reviews by LAND, 1980, and VEIZER, 1983). However, quantitative models can demonstrate the limits of

a particular geochemical system and can then be used to obtain valuable information within these limits, especially when a range of isotopic and trace element systems are used. The purpose of this contribution is to develop a set of similar mass balance equations for the calculation of the simultaneous changes in elemental abundances and radiogenic and stable isotope values that occur during fluid-rock interaction in diagenetic systems. The results of these calculations will enable the direct comparison of a variety of geochemical data toward testing models for diagenesis. A key feature of this approach is that often only the relative values of distribution coefficients, fractionation factors, and water:rock ratios are necessary for evaluating such models. While the absolute values for fluid:rock ratios determined by mass balance methods may not be directly pertinent to the parameters of natural diagenetic systems (e.g., BAUMGARTNER and RUMBLE,

1988), this relative information enables the calculation of characteristic trends on covariation diagrams using isotopic and trace element parameters.

For the model calculations, a porous mineral-fluid system is defined. The infiltration of a fluid through a given volume of rock is simulated by passing successive increments of fluid into the available porosity. Assuming that a thermodynamic drive for the appropriate mineral-fluid reaction exists, each fluid increment reacts with the rock until isotopic and elemental equilibrium is achieved before it is displaced by the next increment of unreacted fluid. The process is then repeated through any number of iterations, similar to the approach used by SPOONER et al. (1977) and LAND (1980), and the progressive changes in the trace element and isotopic compositions of the given volume of rock are calculated. In this manner, the evolution of carbonate sediment and rock compositions during dissolution-recrystallization is modeled in the present study. As examples of such a process in a natural system, we will consider the recrystallization of calcite and dolomite to more stable compositions. The methodology of the calculations is easily modified to take into account additional factors such as limited interaction of fluid with rock at each step, diffusion, changes in porosity during dissolution and cementation, and mineralogic changes (e.g., high-Mg calcite to low-Mg calcite). The equations have been applied to a variety of porous fluid-rock systems (e.g., BANNER et al., 1988a; MEYERS, 1989; MONTANEZ and READ, 1989; GAO, 1990) and can be used as well for modeling the evolution of the fluid (e.g., BANNER et al., 1989).

The equations are similar to those developed for other systems by TAYLOR (1977), HASKIN (1984), and NABELEK (1987), in that they are based on mass balance relationships, distribution coefficients, and fractionation factors. These earlier studies develop equations for water-rock interaction that describe the infiltration of infinitesimally small increments of fluid through a given volume of rock and as such do not provide information about the effects of porosity on the system considered.

After developing the equations, calculated examples are used to (1) evaluate the relative importance of open vs. closed systems, porosity, extents of fluid-rock interaction, and uncertainties in determining distribution coefficient values in the various systems, and (2) determine which geochemical covariation diagrams may be most informative for placing constraints on the composition of fluids and the process(es) responsible for diagenesis. As a case study, geochemical data for two regionally extensive dolomite generations in the Mississippian Burlington-Keokuk Formation of Iowa, Illinois, and Missouri are compared to calculated models for diagenesis involving a range of fluid compositions.

The quantitative approach used here is for equilibrium fluid-rock interaction. It should be considered as an end-member process. The application of these calculations does *not* require that the rocks or mineral phases studied have reached chemical equilibrium with the diagenetic fluid. In most situations it is adequate to recognize that the rock or mineral compositions have advanced toward equilibrium during the diagenetic process considered. Geochemical data for a suite of rocks that has undergone a range of extents of

diagenesis can then be compared with theoretically modeled isotopic and trace element variations in order to determine whether simple, open-system fluid-rock interaction is a viable process to explain the data. If so, it should be possible to place constraints on the composition of the fluid(s) responsible for a given diagenetic reaction and to approximate the relative magnitude of the fluid:rock ratios. In addition, alternatives to simple fluid-rock interaction, such as (1) multiple fluid-rock interaction events, (2) evolving fluid compositions, (3) mixing of fluids, and (4) mixing of mineral endmembers within multiphase samples, should also be evaluated to explain geochemical variations in a suite of samples.

ITERATIVE CALCULATION OF ELEMENT CONCENTRATIONS

A model system is defined by a fixed volume of a porous solid phase and a fluid phase occupying the available porosity. Mass balance and equilibrium partitioning relationships can be used to describe the distribution of elemental and isotopic concentrations in this system both prior to and after the solid has equilibrated with the fluid in a single step reaction. Open system water-rock interaction is simulated by successive iterations of the one-step reaction. The reacted pore fluid is displaced upon the introduction of unreacted fluid after each iteration. The following two sections outline the equations necessary to calculate changes in the elemental and isotopic composition of a rock during such a water-rock interaction process.*

The symbols used are defined in Table 1. Equation 1 defines the exchange reaction distribution coefficient, $K_D^{I,J}$, for two elements or components, I and J , equilibrated between a solid and fluid phase. The relation between $K_D^{I,J}$ and the single element (or single component) distribution coefficients, D^I and D^J , and the concentrations at equilibrium of the elements I and J in solid, C_s^I and C_s^J , and fluid, C_f^I and C_f^J , is given by

$$K_D^{I,J} = \frac{D^I}{D^J} = \frac{C_s^I/C_f^I}{C_s^J/C_f^J} \quad (1)$$

Although C_s^I , C_f^I , C_s^J , and C_f^J are commonly expressed in molar units, the numerical value of $K_D^{I,J}$ is the same in weight or molar units because the units of concentration and the atomic weights cancel. Weight concentration units, ppm, will be used in this paper.

In calculations involving calcite or aragonite, it is convenient to select the element of interest as element I and to select Ca as element J . For the fluid-rock modeling presented here, it is assumed that there is no net gain or loss of carbonate during diagenesis so that the fluid interacts with calcite (or dolomite) without changing its Ca (or Ca and Mg) or total carbon concentration. Thus, for a system in which calcite is

* A BASIC computer code that employs these equations in water-rock interaction calculations is available upon request from the editorial office of *Geochimica et Cosmochimica Acta*.

the solid phase, $C_s^J = C_s^{Ca} = 4 \times 10^5$ ppm, and the single element distribution coefficient, D^J , from Eqn. (1) is

$$D^J = D^J \times K_D^{J-J} = \frac{C_s^J \times K_D^{J-J}}{C_f^J} = \frac{C_s^{Ca} \times K_D^{J-Ca}}{C_f^{Ca}} = \frac{4 \times 10^5 \times K_D^{J-Ca}}{C_f^{Ca}} \quad (2)$$

For calculating D^J for dolomite, depending on the crystal chemical characteristics of element I , element I could be considered to substitute more readily in either the Ca ($J = Ca$) or Mg ($J = Mg$) site, or for both Ca and Mg ($J = Mg + Ca$). Stoichiometric dolomite has 2.17×10^5 ppm Ca and 1.32×10^5 ppm Mg. Thus, depending on the element and the extent to which ideal stoichiometry is approached, an appropriate value would be substituted for 4×10^5 in Eqn. (2).

Upon infiltration of a fluid into the porosity of a given volume of rock, and prior to any interaction, the concentration of element I in this fluid-rock system, C_o^I , is given by mass balance

$$C_o^I = F \times C_{f,o}^I + (1 - F) \times C_{s,o}^I \quad (3)$$

F is the weight fraction of fluid in this system for any one iteration, $C_{f,o}^I$ is the concentration of element I in the fluid before interaction, and $C_{s,o}^I$ is the concentration of I in the solid before interaction.

F is related to porosity using the densities of the fluid and rock by

$$F = \frac{P \times \rho_f}{P \times \rho_f + (1 - P)\rho_s} \quad (4)$$

where P is porosity in volume fraction, and ρ_s and ρ_f are the densities of the solid and fluid, respectively.

The compositions of the fluid and solid after equilibration can be calculated in a manner similar to that given by SCHILLING (1966) for batch melting in igneous systems. The single element distribution coefficient, D^I , is used to calculate the concentration of element I in the fluid, C_f^I , after equilibration with the solid:

$$C_f^I = C_s^I / D^I \quad (5)$$

Using the equilibrium concentrations of element I in the fluid and solid (C_f^I and C_s^I) in a mass balance equation where C_o^I is given from Eqn. (3),

$$C_o^I = F \times C_s^I / D^I + (1 - F) \times C_s^I \quad (6)$$

Solving for C_s^I ,

$$C_s^I = \frac{C_o^I}{F/D^I + (1 - F)} \quad (7)$$

Thus, the calculation of elemental exchange during water-rock interaction involves two successive steps: (1) calculation using Eqn. (3) of the concentration of element I in the entire system, C_o^I , upon addition of the fluid to the initial rock, and (2) calculation of the concentration of element I in the rock (C_s^I) after equilibration with the fluid using the calculated C_o^I and the appropriate D^I in Eqn. (7). This two-step calculation represents closed-system behavior.

Table 1. Definition of symbols

α_{s-f}^{m-n}	Isotope fractionation factor for isotope ratio m/n of element I between solid and fluid phase.
C_A^I	Concentration of element I in phase A .
$C_{s,o}^I$	Initial concentration of element I in solid prior to fluid-rock interaction.
C_s^I	Concentration of element I in solid phase after a given increment of fluid-rock interaction.
$C_{s,e}^I$	Concentration of element I in solid in equilibrium with initial fluid (see Eq. 10).
C_f^I	Concentration of element I in fluid.
C_o^I	Concentration of element I in total system of fluid phase plus solid (see Eq. 3).
$(\delta^{mI})_f$	Isotope ratio mI/nI of fluid expressed in delta notation. For $^{18}O/^{16}O$, $\delta_f^{18O} = \left(\frac{(^{18}O/^{16}O)_f}{(^{18}O/^{16}O)_{STD}} - 1 \right) \times 10^3$, where $(^{18}O/^{16}O)_{STD}$ is the oxygen isotope composition of a standard such as standard mean ocean water (SMOW).
$(\delta^{mI})_o$	Isotope ratio mI/nI of system expressed in delta notation.
$(\delta^{mI})_s$	Isotope ratio mI/nI of solid expressed in delta notation.
D^I	Single element distribution coefficient (see Eqs. 1 and 2).
EQ	Extent to which solid has approached equilibrium with the fluid (see Eq. 11), expressed as a fraction of unity.
f	Parameter designation for fluid phase.
F	Weight fraction of fluid in system.
FW	Formula weight of a specified phase (e.g., s or f).
IEQ	Extent to which $(mI/nI)_s$ has approached value in isotopic equilibrium with fluid (see Eq. 30).
mI	Isotope m of element I .
nI	Isotope n of element I .
$(mI/nI)_f$	Isotope ratio mI/nI for element I in fluid.
$(mI/nI)_s$	Isotope ratio mI/nI for element I in solid.
$(mI/nI)_o$	Isotope ratio mI/nI for element I in total system of fluid plus solid.
K	Correction factor for the effects of porosity, α and D^I values on the fluid:rock ratio required to reach a given value of IEQ relative to a non-porous system (see Eq. 45).
K_D^{I-J}	Exchange reaction distribution coefficient for elements I and J (see Eq. 1).
N	Cumulative water:rock weight ratio at a given stage in the interaction process (see Eq. 8).
N_e	Cumulative water:rock weight ratio, N , at which EQ = 0.99.
N_i	Cumulative water:rock weight ratio, N , at which EQ = 0.01.
P	Porosity of system expressed in volume fraction.
Q	Ratio of N values for porous vs. non-porous media at a given value of EQ for element I (see Eq. 32).
ρ	Density of a specified phase (e.g., s or f) in grams per cc.
s	Parameter designation for solid phase.
X^{mI}	Mole fraction of isotope mI in a given phase.
$(W/R)_m$	Cumulative water:rock ratio, in molar units.

Calculation of the progressive changes in the composition of the rock upon repeated additions of fluid with the same initial composition simulates open-system water-rock interaction. These changes can be determined by iterative calculations, using first Eqn. (3) and then Eqn. (7) in which the composition of the rock in Eqn. (3), $C_{s,o}^I$, is derived from

the previous calculation of C_s^I using Eqn. (7). For each iteration, all of the solid interacts and equilibrates with the fluid, and the porosity of the rock does not change during the interaction. The effects of partial equilibration between fluid and rock during each step are discussed in a later section.

The cumulative fluid:rock ratio for any stage in the interaction process is expressed on a weight basis as the term N , where

$$N = n \times (F/(1 - F)) \quad (8)$$

where n is the number of iterations, and $F/(1 - F)$ is the incremental fluid:rock ratio. In molar units,

$$(W/R)_m = \frac{\text{moles fluid}}{\text{moles rock}} = n \times \left(\frac{F/FW_f}{(1 - F)/FW_s} \right) \quad (9)$$

where FW_f and FW_s are the formula weights of the fluid and solid phases, respectively. The n term also represents the number of pore volumes of fluid that has reacted with the rock.

The concentration of element I in calcite that ultimately will equilibrate with the original fluid as an endmember product of extensive fluid-rock interaction is defined as $C_{s,e}^I$. By combining Eqns. (2) and (5) we obtain

$$C_{s,e}^I = D^I \times C_f^I = \frac{4 \times 10^5 \times K_D^{I, Ca} \times C_f^I}{C_{Ca}^I} \quad (10)$$

We define here the term EQ as a measure of the extent to which fluid-rock interaction has taken place, or the extent to which C_s^I approaches $C_{s,e}^I$. EQ is given by

$$EQ = \frac{C_s^I - C_{s,o}^I}{C_{s,e}^I - C_{s,o}^I} \quad (11)$$

where $C_{s,o}^I$ is the initial composition of the solid before the water-rock interaction has begun. Initially, $EQ = 0$, and, at equilibrium, $EQ = 1$. EQ is a useful measure of progressive water-rock interaction with which to monitor changes in C_s^I .

ITERATIVE CALCULATION OF ISOTOPIC ABUNDANCES

In this section we consider the isotope systematics during fluid-rock interaction for systems that undergo isotope fractionation in nature as well as for those that do not. For the Sr, Nd, Pb, and U isotope systems, isotopic fractionation is either negligible or corrected for by normalization during mass spectrometric analysis to a nonradiogenic isotope ratio. For an isotopic system in which mI and nI are the isotopes of element I of interest, the isotopic composition of the system is given by mass balance equations for each of the isotopes:

$$\left(\frac{^mI}{^nI} \right)_o = \frac{^mI_o}{^nI_o} = \frac{(X^m I_{f,o})(C_{f,o}^I)F + (X^m I_{s,o})(C_{s,o}^I)(1 - F)}{(X^n I_{f,o})(C_{f,o}^I)F + (X^n I_{s,o})(C_{s,o}^I)(1 - F)} \quad (12)$$

where $X^m I_{f,o}$, $X^n I_{f,o}$, $X^m I_{s,o}$, and $X^n I_{s,o}$ are the mole fractions of the isotopes m and n of element I in the fluid and solid

before interaction. $C_{s,o}^I$ and $C_{f,o}^I$ may be expressed in weight units if the difference in the isotopic ratios for the fluid and solid are sufficiently small such that differences in the atomic weight of the element between the fluid and solid are less than or equal to the uncertainties in determining $C_{s,o}^I$ and $C_{f,o}^I$ or F and $1 - F$ ($\sim 1\%$). This is usually the case.

If the difference in the isotope ratios of the fluid and solid is such that the resulting differences among the mole fractions $X^m I_f$ and $X^m I_s$, and $X^n I_f$ and $X^n I_s$ are less than the uncertainties for $C_{f,o}^I$ and $C_{s,o}^I$ or F and $(1 - F)$, then $(^mI/^nI)_o$ may be approximated by

$$\left(\frac{^mI}{^nI} \right)_o = \frac{((^mI/^nI)_{f,o})C_{f,o}^I F + ((^mI/^nI)_{s,o})C_{s,o}^I(1 - F)}{C_o^I} \quad (13)$$

$(^mI/^nI)_{f,o}$ and $(^mI/^nI)_{s,o}$ are the initial isotope compositions of element I of the fluid and solid for each iteration. If there is no fractionation of the isotopes between the solid and fluid, both phases will have the same isotope ratio after equilibration, that of the system, $(^mI/^nI)_o$. If there is fractionation, the solid and fluid will have different isotope ratios which are related by a fractionation factor. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{18}\text{O}/^{16}\text{O}$ variations during water-rock interaction are calculated below as examples of the two types of systems.

Strontium Isotope System

For homogeneous equilibrium, the Sr isotope ratio in the solid, fluid, and entire system will be the same. Therefore, a mass balance expression for $(^{87}\text{Sr}/^{86}\text{Sr})_o$ will also give the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the solid upon equilibration. Following Eqn. (12),

$$\begin{aligned} (^{87}\text{Sr}/^{86}\text{Sr})_o &= \frac{(X^{87}\text{Sr}_{f,o})(C_{f,o}^{\text{Sr}})F + (X^{87}\text{Sr}_{s,o})(C_{s,o}^{\text{Sr}})(1 - F)}{(X^{86}\text{Sr}_{f,o})(C_{f,o}^{\text{Sr}})F + (X^{86}\text{Sr}_{s,o})(C_{s,o}^{\text{Sr}})(1 - F)} \quad (14) \end{aligned}$$

In order to calculate the mole fractions of ^{87}Sr and ^{86}Sr , it is necessary to use the isotope ratios of all the Sr isotopes:

$$^{88}\text{Sr}/^{86}\text{Sr} = 8.37521;$$

$$^{86}\text{Sr}/^{86}\text{Sr} = 1.00000; \quad ^{84}\text{Sr}/^{86}\text{Sr} = 0.0565.$$

For example, the mole fraction of ^{87}Sr in the solid prior to any interaction, $X^{87}\text{Sr}_{s,o}$, can be expressed as

$$X^{87}\text{Sr}_{s,o} = ((^{87}\text{Sr}/^{86}\text{Sr})_{s,o})(X^{86}\text{Sr}_{s,o}) \quad (15)$$

where $(^{87}\text{Sr}/^{86}\text{Sr})_{s,o}$ is the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the solid prior to interaction. The mole fraction of ^{86}Sr in the solid, $X^{86}\text{Sr}_{s,o}$, is

$$X^{86}\text{Sr}_{s,o} = \frac{(^{86}\text{Sr}/^{86}\text{Sr})_{s,o}}{[(^{88}\text{Sr}/^{86}\text{Sr})_{s,o} + (^{87}\text{Sr}/^{86}\text{Sr})_{s,o} + (^{86}\text{Sr}/^{86}\text{Sr})_{s,o} + (^{84}\text{Sr}/^{86}\text{Sr})_{s,o}]} \quad (16)$$

Substituting the values of the constant isotope ratios gives

$$X^{86}\text{Sr}_{s,o} = \frac{1}{(^{87}\text{Sr}/^{86}\text{Sr})_{s,o} + 9.432} \quad (17)$$

Similar relations can be expressed for the mole fractions

of ^{87}Sr and ^{86}Sr in the fluid. Substituting for the mole fractions of ^{87}Sr and ^{86}Sr in Eqn. (14) from Eqns. (15) and (17) gives

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_o = \frac{\left\{ \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{f,o} (C_{f,o}^{\text{Sr}}) F / \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{f,o} + 9.432 \right) \right] + \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{s,o} (C_{s,o}^{\text{Sr}}) (1-F) / \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{s,o} + 9.432 \right) \right] \right\}}{\left\{ \left[(C_{f,o}^{\text{Sr}}) F / \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{f,o} + 9.432 \right) \right] + \left[(C_{s,o}^{\text{Sr}}) (1-F) / \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{s,o} + 9.432 \right) \right] \right\}} \quad (18)$$

If the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the fluid and original solid are between 0.700 and 0.800, which is the case for most fluid-carbonate systems, then the differences in the values of $(^{87}\text{Sr}/^{86}\text{Sr})_{s,o} + 9.432$ and $(^{87}\text{Sr}/^{86}\text{Sr})_{f,o} + 9.432$ will be less than 1%. In most systems the uncertainties in the concentrations of Sr in the solid and fluid and the uncertainty in F and $1-F$ will be equivalent to or larger than 1%. Thus, for such systems we can assume that

$$(^{87}\text{Sr}/^{86}\text{Sr})_{s,o} + 9.432 = (^{87}\text{Sr}/^{86}\text{Sr})_{f,o} + 9.432. \quad (19)$$

These terms cancel from Eqn. (18), which becomes equivalent to Eqn. (13), i.e.,

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_o = \frac{(^{87}\text{Sr}/^{86}\text{Sr})_{f,o} (C_{f,o}^{\text{Sr}}) F + (^{87}\text{Sr}/^{86}\text{Sr})_{s,o} (C_{s,o}^{\text{Sr}}) (1-F)}{(C_{f,o}^{\text{Sr}}) F + (C_{s,o}^{\text{Sr}}) (1-F)}. \quad (20)$$

Substituting for the denominator using Eqn. (3)

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_o = \frac{(^{87}\text{Sr}/^{86}\text{Sr})_{f,o} (C_{f,o}^{\text{Sr}}) F + (^{87}\text{Sr}/^{86}\text{Sr})_{s,o} (C_{s,o}^{\text{Sr}}) (1-F)}{C_o^{\text{Sr}}}. \quad (21)$$

Thus, the simultaneous changes in the Sr isotope composition and Sr concentration of a diagenetic carbonate during water-rock interaction can be calculated by iteration using Eqns. (3) and (7) for Sr concentrations, and Eqn. (21) and the Sr concentration results for Sr isotopes. Analogous equations can be written for other radiogenic isotope and trace element systems, such as Nd, U, and Pb.

Oxygen Isotope System

Upon equilibration during fluid-rock interaction, the solid and fluid phase will have oxygen isotope compositions dependent on the isotope composition of the total system, the fractionation factor for the solid and fluid, and the proportion of solid and fluid in the system. The equilibrium fractionation factor, α_{s-f}^{m-n} , is equivalent to the exchange reaction, $K_D^{f,j}$, in Eqn. (1), except that it refers to the relative distribution of

two isotopes rather than two elements. It may also be expressed using the single element distribution coefficient notation for each isotope, as given in the BASALTIC VOLCANISM STUDY PROJECT (1981), where

$$D^{16\text{O}} = C_s^{16\text{O}}/C_f^{16\text{O}}, \text{ and } D^{18\text{O}} = C_s^{18\text{O}}/C_f^{18\text{O}} \quad (22)$$

and

$$\alpha_{s-f}^{m-n} = \alpha_{s-f}^{18-16} = (^{18}\text{O}/^{16}\text{O})_s / (^{18}\text{O}/^{16}\text{O})_f = \frac{D^{18\text{O}}}{D^{16\text{O}}}. \quad (23)$$

Using an approach similar to that for Sr isotopes, the analogous term for oxygen in Eqn. (19) is $(^{18}\text{O}/^{16}\text{O})_s + 1.00037$. Because oxygen consists predominantly of ^{16}O , ranges in $\delta^{18}\text{O}$ values from -200 to $+200\%$ result in changes in $(^{18}\text{O}/^{16}\text{O})_s + 1.00037$ of less than 0.1%. δ -notation is defined in Table 1. Thus, an equation similar to Eqn. (21) for Sr is appropriate for calculating the oxygen isotope value of the fluid-rock system, $\delta_o^{18\text{O}}$, for each iteration:

$$\delta_o^{18\text{O}} = \frac{(\delta_{f,o}^{18\text{O}})(C_{f,o}^{\text{O}})F + (\delta_{s,o}^{18\text{O}})(C_{s,o}^{\text{O}})(1-F)}{C_o^{\text{O}}} \quad (24)$$

where C_o^{O} is a constant for a given F , because $C_{f,o}^{\text{O}}$ and $C_{s,o}^{\text{O}}$, the concentrations of oxygen in the fluid and carbonate, are constant (see Eqn. 3). After equilibration, $\delta_s^{18\text{O}}$ and $\delta_f^{18\text{O}}$ are related by $\delta_s^{18\text{O}} = (\alpha_{s-f}^{18-16})(\delta_f^{18\text{O}} + 1000) - 1000$, and $\delta_s^{18\text{O}}$ is given by

$$\delta_s^{18\text{O}} = \frac{(\delta_o^{18\text{O}})C_o^{\text{O}}(\alpha_{s-f}^{18-16}) - 1000(C_f^{\text{O}})F(1 - (\alpha_{s-f}^{18-16}))}{C_s^{\text{O}}(1-F)(\alpha_{s-f}^{18-16}) + C_f^{\text{O}}(F)}. \quad (25)$$

This is analogous to the closed system equation of TAYLOR (1977). For the next iteration step, $\delta_s^{18\text{O}}$ from Eqn. (25) is substituted into Eqn. (24) to calculate a new $\delta_o^{18\text{O}}$, etc.

Therefore, given an initial fluid and solid oxygen isotope composition prior to water-rock interaction, a final solid isotopic composition can be calculated and will be dependent on the cumulative water:rock ratio, N , and the temperature-dependent fractionation factor, α_{s-f}^{18-16} . This formula can be used for other elements with stable isotope compositions that undergo fractionation in nature, given similar considerations concerning the range of δ values in the system.

EVOLUTION OF FLUID COMPOSITIONS DURING WATER-ROCK INTERACTION

The evolution of a fluid infiltrating through and successively recrystallizing a rock of uniform composition can also be evaluated in the same manner as was the evolution of the solid. For each iteration, Eqn. (3) gives C_o^I . C_f^I is then given by

$$C_f^I = \frac{C_o^I}{D^I(1-F) + F}. \quad (26)$$

For the isotopic composition, Eqn. (13) and an equivalent expression of Eqn. (24) give $(^mI/^nI)_o$ and δ_o^mI , respectively. $(^mI/^nI)_f$ values are given by $(^mI/^nI)_o$ for each iteration, analogous to the determination of $(^mI/^nI)_s$ values. For isotopic

systems involving fractionation, $(\delta^m I)_f$ for each iteration is given by

$$(\delta^m I)_f = \frac{(\delta^m I)_o C_o^I - (1000 C_s^I (1 - F))[(\alpha_{s,f}^{m,n}) - 1]}{(\alpha_{s,f}^{m,n}) C_s^O (1 - F) + (C_f^I) F} \quad (27)$$

CALCULATION OF ISOTOPIC VARIATIONS DURING WATER-ROCK INTERACTION USING ENDMEMBER MIXING CALCULATIONS

An alternative method to iteration for determining the isotope ratio of the evolved solid phase makes use of the EQ term defined in Eqn. (11). The change in the isotope ratio of the solid phase during fluid-rock interaction follows a curve, in $(^m I/^n I)_s$ vs. C_s^I space, representing mixing between the solid equilibrated with the fluid and the original solid. In this manner, the isotope ratio in the solid phase, $(^m I/^n I)_s$, can be calculated by the following mass balance equation for the point at which fluid-rock interaction has proceeded to a given fraction EQ (see Eqn. 11):

$$\left(\frac{^m I}{^n I}\right)_s = \frac{(X^m I_{s,o})(C_{s,o}^I)(1 - EQ) + (X^m I_{s,e})(C_{s,e}^I)EQ}{(X^n I_{s,o})(C_{s,o}^I)(1 - EQ) + (X^n I_{s,e})(C_{s,e}^I)EQ} \quad (28)$$

$X^m I_{s,o}$, $X^m I_{s,e}$, $X^n I_{s,o}$ and $X^n I_{s,e}$ are the mole fractions of the isotopes $^m I$ and $^n I$ in the original solid and in the solid equilibrated with the fluid, respectively. If the variation of the isotope ratios between these two endmember solids is not large (see discussions leading to Eqns. 13 and 20), then Eqn. (28) can be approximated by

$$\left(\frac{^m I}{^n I}\right)_s = \frac{(^m I/^n I)_{s,o}(C_{s,o}^I)(1 - EQ) + ((^m I/^n I)_{s,e})(C_{s,e}^I)EQ}{C_{s,o}^I(1 - EQ) + (C_{s,e}^I)EQ} \quad (29)$$

The value of EQ from Eqn. (11) is a measure of how close the concentration of element I in the solid has approached the value of the solid that would ultimately be in equilibrium with the fluid after large extents of fluid-rock interaction. The equivalent term for the isotope ratios, IEQ , is

$$IEQ = \frac{(^m I/^n I)_s - (^m I/^n I)_{s,o}}{(^m I/^n I)_{s,e} - (^m I/^n I)_{s,o}} \quad (30)$$

where $(^m I/^n I)_{s,e}$ is the value for the solid in equilibrium with the original fluid; i.e., $(^m I/^n I)_{s,e} = (\alpha_{s,f}^{m,n})(^m I/^n I)_{f,o}$. For systems in which the element I has the same concentration in the original and final carbonate (e.g., $C_{s,o}^O = C_{s,e}^O$), EQ is not defined and IEQ is used instead as a measure of the extent to which the carbonate has approached the value in equilibrium with the fluid.

SIMULTANEOUS VARIATIONS: ISOTOPIC COMPOSITION VS. CONCENTRATION

Simultaneous variations in the concentration and isotopic composition of the same element can yield distinctive water-rock interaction trends. The relative responses of the Sr iso-

tope ratios and Sr concentrations in two limestones interacting with the same fluid are compared using Eqns. (3), (7), and (21) in an iterative calculation (Fig. 1). The limestones originally have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and different Sr concentrations. As shown in Fig. 1, the Sr concentrations of both limestones are altered toward and attain the value in equilibrium with the fluid ($C_{s,e}^{\text{Sr}} = 200$ ppm) at the same cumulative water:rock ratio values (N). The rate of change of the Sr contents of the altered limestones with increasing N values is controlled not by the original Sr content of the limestones, but rather by the $K_D^{\text{Sr-Ca}}$ and C_f^{Ca} values, which are the same in cases A and B. In contrast, the Sr isotope ratio of each limestone follows a distinct path and approaches the equilibrium $^{87}\text{Sr}/^{86}\text{Sr}$ value at different N values. The Sr isotope ratio for limestone A, which has the lower original Sr concentration, is affected by the fluid at much lower N values than is the Sr isotope ratio for limestone B, which has the higher original Sr concentration.

Figure 2 illustrates the covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration for the interaction of two limestones and two fluids, using endmember mixing calculations (Eqns. 29 and 11). Both limestones originally have $^{87}\text{Sr}/^{86}\text{Sr} = 0.708$ and both fluids have $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$. Limestone I originally has 200 ppm Sr and interacts with a fluid in equilibrium with calcite with 40 ppm Sr (i.e., fluid Sr/Ca = 0.002, $K_D^{\text{Sr-Ca}} = 0.05$). Limestone II originally has 40 ppm Sr and interacts with a fluid in equilibrium with calcite with 200 ppm Sr (i.e., fluid Sr/Ca = 0.01). The curves in Fig. 2 show the distinct pathways of water-rock interaction for limestones in rock- and water-dominated systems. The Sr isotopic composition of high-Sr limestone is reset toward the value of the fluid at a higher N value compared with the alteration pathway of the low-Sr limestone.

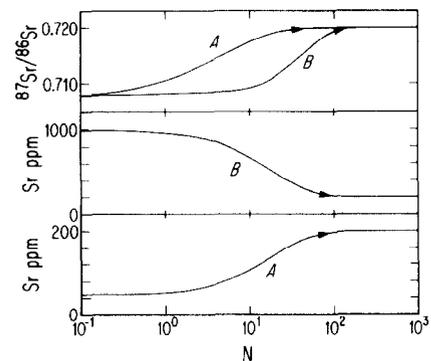


FIG. 1. Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration with increasing N (cumulative fluid:rock ratio, Eqn. 8) for the recrystallization of two limestones, each with 50% porosity and a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.708. Initially, limestone A has 40 ppm Sr and limestone B has 1000 ppm Sr. The curves delineate the changes in composition of each rock during interaction with a fluid with 10 ppm Sr, 1000 ppm Ca, and a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.720. $K_D^{\text{Sr-Ca}} = 0.05$. This fluid is in equilibrium with calcite with 200 ppm Sr, and $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$. The arrows indicate direction of progressive fluid-rock interaction and denote fluid:rock ratio at which isotopic composition or concentration of Sr has reached 99% of the equilibrium value (i.e., EQ , $IEQ = 0.99$; see Eqns. 11 and 30). Note that the Sr concentrations of the two limestones equilibrate with the fluid at the same N values, while the Sr isotope ratios equilibrate at different rates, depending on the relative differences in Sr concentrations between solid and fluid in each system.

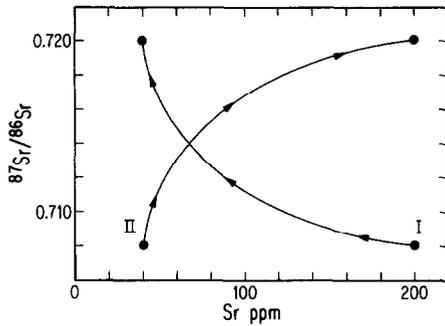


FIG. 2. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr concentration for two limestones with 50% porosity interacting with two fluids to compare water-rock interaction curves for a rock-dominated system, I, and a fluid-dominated system, II. The arrows indicate the direction of progressive water-rock interaction (i.e., increasing N values) along each path from the initial rock composition to the trace element and isotopic composition that is in equilibrium with the fluid. The paths, which are equivalent to those of mixing of mineral endmembers, are not affected by porosity, distribution coefficients, or concentrations of Ca or Sr when the end-member concentrations and isotopic compositions are fixed.

EFFECTS OF SYSTEM PARAMETERS

In this section, several examples of fluid-rock interaction are used to evaluate the relative effects of variations in parameters such as porosity, open versus closed systems, values of distribution coefficients, extents of fluid-rock interaction, and fluid and solid compositions.

Porosity

For non-porous media, NABELEK (1987) has shown that there is a direct relationship between the fluid:rock ratio divided by the single element distribution coefficient and the extent to which fluid-rock interaction has affected the composition of the original rock. By rearrangement of Eqn. (9) in NABELEK (1987), and substituting our EQ term (Eqn. 11), the following expression for non-porous media is obtained:

$$e^{-N/D^I} = 1 - EQ. \quad (31)$$

For 1% reaction, $N/D^I = 0.01$; for 99% reaction, $N/D^I = 4.6$.

In order to evaluate the effects of porosity in determining the water:rock ratio at which an altered rock attains a given value of EQ , a comparison is made between N calculated for porous media using the iterative method described earlier and N calculated for non-porous media using Eqn. 31. The comparison is made for a range of values for F and D^I . We define the term Q as

$$Q = \frac{N[\text{porous media}]}{N[\text{non-porous media}]}. \quad (32)$$

Q is plotted as a function of D^I and F in Fig. 3, where it can be seen that the effect of porosity, as monitored by the Q value, increases with decreasing D^I and increasing F . While Q is a function of D^I and F , it is not dependent on the extent of reaction. Figure 4 is a plot of EQ versus water-rock ratio, N , for a range of D^I values and for F values of 0 and 0.5. For D^I values of about 4 or less, rocks with a high porosity ($F = 0.5$ curves) require higher fluid:rock ratios to reach the

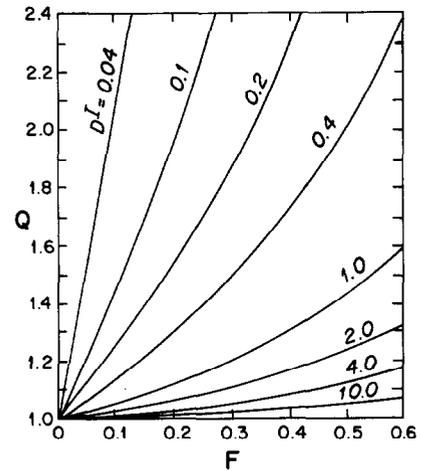


FIG. 3. Plot of Q , the ratio of N for porous rocks relative to non-porous rocks, versus F , the weight fraction of the fluid phase in the system, for a range of single component distribution coefficients, D^I , labeled on each curve. See text for explanation.

equivalent value of EQ as compared to rocks with lower porosity ($F = 0.0$ curves). For D^I greater than 4 and F less than 0.5, porosity does not affect the extent of water-rock interaction (i.e., $Q \cong 1$) and the equation of NABELEK (1987) can be used.

Empirically, it was found that for the portions of the curves in Fig. 3 with F less than 0.5 and D^I greater than 0.4, Q can be approximated by a third-order polynomial using curve-fitting parameters as follows:

$$Q = aF^3 + bF^2 + cF + 1 \quad (33)$$

where

$$a = \exp[-0.807(\ln(D^I)) + 0.637] \quad (34)$$

$$b = \exp[-0.897(\ln(D^I)) - 1.806] \quad (35)$$

$$c = \exp[-0.995(\ln(D^I)) - 0.663]. \quad (36)$$

Thus, for porous media with D^I greater than 0.4 and F less

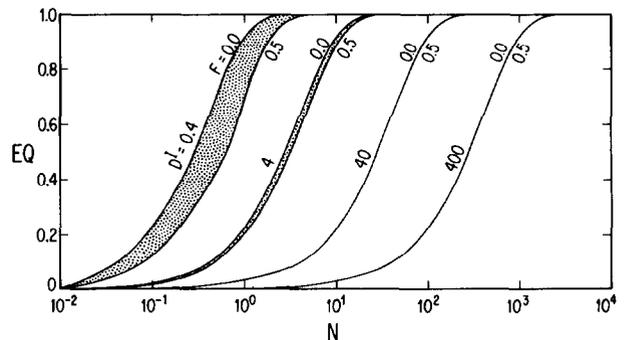


FIG. 4. Covariation of the extent of reaction, EQ (see Eqn. 11), vs. fluid:rock ratio, N , for weight fractions of the fluid phase, F , ranging from 0 to 0.50 (= 0–75% porosity in limestone) for a range of single component distribution coefficient values, D^I , labeled on each curve. For D^I values greater than 4, the difference between porous and non-porous rocks during fluid-rock interaction is negligible for F less than 0.5.

than 0.5 (e.g., porosity of less than about 75% for limestone), a generalized form of Eqn. (31) that incorporates the Q term can be written as

$$N/D^I = -Q[\ln(1 - EQ)]. \quad (37)$$

For porous calcite-fluid systems, combining Eqns. (2) and (37) gives the following expression for N :

$$\begin{aligned} N &= -D^I Q [\ln(1 - EQ)] \\ &= -(4 \times 10^5 (K_D^{I\text{Ca}}/C_f^{\text{Ca}})) [Q \ln(1 - EQ)]. \end{aligned} \quad (38)$$

From this relation, it can be seen that the fluid:rock ratio for a given extent of reaction is directly proportional to the $K_D^{I\text{Ca}}$ and inversely proportional to the Ca concentration of the fluid, C_f^{Ca} . C_s^I for a given fluid:rock ratio, N , from Eqns. (11) and (37) is given by

$$C_s^I = C_{s,e}^I - (C_{s,e}^I - C_{s,o}^I)(e^{-N/D^I Q}). \quad (39)$$

Use of this equation allows direct calculation of the concentrations in the solid phase of a set of elements with different D^I or $K_D^{I\text{Ca}}$ values for a given fluid:rock ratio, N .

Fluid:Rock Ratio

Trace elements

In considering which elements to use in a diagenetic study, it would be useful to know the approximate fluid:rock ratios at which the concentration of a given element in the rock is (1) measurably affected, relative to its initial value, by interaction with the fluid (i.e., N value when $EQ = 0.01$) and (2) essentially equivalent to the value in equilibrium with the fluid (i.e., N value when $EQ = 0.99$). Using Eqn. (37), we can define N_e as the fluid:rock ratio required to reach 99% of equilibrium as

$$N_e = 4.6(D^I Q). \quad (40)$$

Likewise, N_i is defined as the fluid:rock ratio for which $EQ = 0.01$:

$$N_i = 0.01(D^I Q). \quad (41)$$

For limestones, we can substitute for D^I from Eqn. (2), giving

$$N_e = 1.84 \times 10^6 (K_D^{I\text{Ca}}/C_f^{\text{Ca}}) Q \quad (42)$$

$$N_i = 4000 (K_D^{I\text{Ca}}/C_f^{\text{Ca}}) Q. \quad (43)$$

Thus, the fluid:rock ratio required for the solid to reach the initial and final stages of reaction for cation substitution in carbonates is a function of $K_D^{I\text{Ca}}$ and the Ca content of the fluid, and not a function of the trace element concentration of the fluid or the rock (see Fig. 1). It is therefore possible to evaluate, for a suite of elements whose $K_D^{I\text{Ca}}$ values are known, the relative extents of fluid:rock interaction at which they would be affected.

Oxygen isotopes

For the stable isotope systems that undergo fractionation in nature, variations in D^I , α_{s-f}^{m-n} , and F are found to produce small but significant differences in the N values calculated by iteration in porous media and the N values calculated

using an equivalent expression to Eqn. (31) for stable isotopes in non-porous media (TAYLOR, 1977; NABELEK, 1987). In order to take these effects into account, a correction factor K , which is a modification of the Q term, was empirically determined in a manner similar to the derivation of the Q term. A modified version of Eqn. (37) can be expressed using IEQ (Eqn. 30) for isotope compositions:

$$N = -D^I \times Q \times K \times \ln(1 - IEQ) \quad (44)$$

where

$$K = 1 - \frac{0.4F[(\alpha_{s-f}^{m-n}) - 1]}{D^I}. \quad (45)$$

For oxygen, D^I is written as D^O , and each carbonate will have a D^O of constant value, (e.g., $D^O = 0.54$ for calcite: water). The correction factor K is applicable for any stable isotope system and will produce fluid:rock ratios within 1% of those calculated by iteration where F is less than 0.5, D^I is greater than 0.4, and α_{s-f}^{m-n} is between 0.85 and 1.15. Iteration is required for conditions where this correction factor is not applicable. The range of N values necessary to reach IEQ values of 0.01 and 0.99 for $\delta^{18}\text{O}$ is strongly dependent on porosity. For fluid-limestone interaction at 75% porosity, N_i and N_e are 0.01 and 4.6; and at 0% porosity, N_i and N_e are 0.005 and 2.5, respectively.

Carbon isotopes

The C content of a given carbonate is fixed and D^C in most systems is usually greater than 100; thus Q and K values are close to unity, and N_i and N_e are dependent only on the C content of the fluid. For calcite-fluid systems,

$$N_e = 4.6 D^C = 4.6 (C_s^C/C_f^C) = (5.5 \times 10^{-5})/C_f^C \quad (46)$$

$$N_i = 0.01 D^C = 1200/C_f^C. \quad (47)$$

Open vs. Closed Systems

Figure 5 compares closed and open system model calculations for Sr abundance and oxygen isotope variations during the recrystallization of a limestone. Closed system behavior at different fluid:rock ratios is given by a single iteration of Eqns. (3) and (7) for the Sr abundance at varying $F/(1 - F)$ ratios (i.e., $n = 1$ in Eqn. 8) and similarly using Eqns. (24) and (25) for oxygen. This type of single-step behavior is probably not followed in most diagenetic systems. However, the closed system curves also represent the changes in the composition of a rock as a given amount of fluid is recycled through a given volume of rock with a progressive increase in the fraction of fluid reacting during each cycle (e.g., TAYLOR, 1977). In all closed system calculations, the original rock and fluid constituents remain in the system.

For open system behavior, each curve describes the path that an individual rock may follow during progressive water-rock interaction. The infinitesimal or 0% porosity curves are calculated following NABELEK (1987). It can be seen in Fig. 5 that there is a significant difference between open and closed systems, and that there are smaller but resolvable differences between the open system calculations that model porous vs. non-porous media. The minimum fluid:rock ratio required

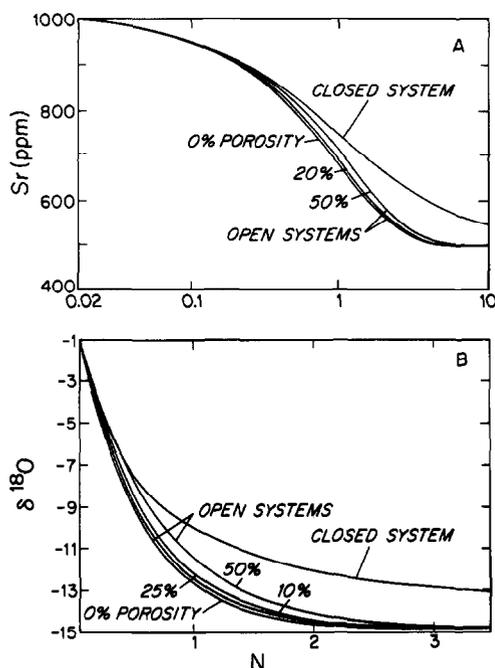


FIG. 5. (a) Strontium concentration vs. fluid:rock ratio (N) showing paths for recrystallization of a marine limestone with 1000 ppm Sr by a diagenetic fluid with 500 ppm Sr and 20,000 ppm Ca. $K_D^{\text{Sr-Ca}} = 0.05$. The closed system curve is calculated using a single iteration of Eqns. (3) and (7), for each specific value of F . The paths for an open system with 20 and 50% porosity use Eqns. (3) and (7) in iterative calculations. The 0% porosity curves in (a) and (b) are calculated following Nabelek (1987), which models the infiltration of a fluid through a rock in infinitesimally small increments, as discussed in text. (b) $\delta^{18}\text{O}$ (PDB) vs. fluid:rock ratio (N), illustrating paths for recrystallization of a marine limestone with $\delta^{18}\text{O} = -1\text{‰}$ (PDB) by a fluid with $\delta^{18}\text{O} = -3\text{‰}$ (SMOW) at 100°C . The closed system curve uses Eqns. (24) and (25) in a single iteration for each specific F value. The paths for an open system at 10, 25, and 50% porosity use Eqns. (24) and (25) in iterative calculations. The fractionation factor is calculated from the expression given by Friedman and O'Neil (1977).

to achieve equilibration in a fluid-rock system is given by the infinitesimal porosity model, and the maximum value is given by the closed system model.

EVALUATING FLUID-ROCK INTERACTION IN DIAGENETIC CARBONATES

As suggested by Brand and Veizer (1980) and Veizer (1983), it can be illustrative to evaluate the effects of fluid-rock interaction on two trace elements with greatly different K_D values, such as Sr with a $K_D^{\text{Sr-Ca}}$ of about 0.05 and Mn with a $K_D^{\text{Mn-Ca}}$ of about 30. The approach outlined in the present study is used to quantitatively delineate these effects and to evaluate how different processes affect a given geochemical system.

Marine calcites are typically Sr-rich and Mn-poor, while diagenetic, non-marine calcites are relatively Sr-poor and Mn-rich. Figure 6 shows the simultaneous variations in Mn and Sr abundances that occur during (1) the recrystallization of an original marine calcite by freshwater and (2) the physical mixing of the two endmember calcites. The endmember mixing line represents the effects of obtaining impure samples

from multi-phase rocks. Due to the large differences in the values of $K_D^{\text{Sr-Ca}}$ and $K_D^{\text{Mn-Ca}}$, the Sr abundances of carbonates will be affected during recrystallization by much smaller fluid:rock ratios than are the Mn abundances. The large, relative differences in the water:rock ratios at which the two trace elements are affected during water-rock interaction will be the same whether the process involves brines, seawater, or freshwater. This K_D^I (or D^I) control on the simultaneous variations of trace elements during water-rock interaction can also be deduced from Eqns. (42) and (43) and Fig. 4. The Sr vs. Mn diagram provides a straightforward discrimination between fluid-rock interaction and two-component endmember mixing as dominant processes. If both processes are important, data for a suite of recrystallized samples would lie within the field defined by the mixing and water-rock interaction curves. Whereas trace element covariations such as Sr vs. Mn can depict the influence of K_D values on water-rock interaction trends, isotopic covariations considered below can elucidate additional controls of model parameters on the geochemistry of diagenetic phases.

An L-shaped plot similar to that of Sr vs. Mn in Fig. 6 would be found for any pair of elements in which the carbonate nears complete equilibration with the fluid for one element ($C_{s,e}^I$) while retaining its near-initial composition for the other element ($C_{s,o}^I$). From Fig. 4 and Eqn. (2) it can be seen that such a situation would arise when there is about a factor of 10 difference in D^I or $K_D^{\text{Sr-Ca}}$. The basis for the selection of the elements to be analyzed should include those with a large variation in $K_D^{\text{Sr-Ca}}$ and those that might have distinguishing C_f^I/C_r^I ratios in the diagenetic fluids under consideration. The more elements considered, the more

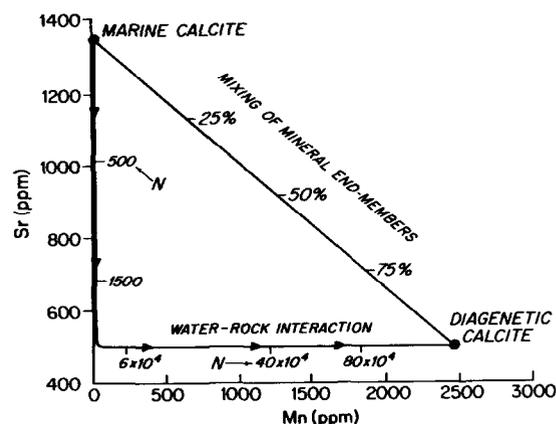


FIG. 6. Strontium vs. manganese variations in limestones related by water-rock interaction and mixing of calcite endmembers. For water-rock interaction, the original limestone composition is represented by the marine calcite values (1345 ppm Sr, 1 ppm Mn, and 50% porosity). The water-rock interaction curve illustrates changing limestone compositions during recrystallization by freshwater with 20 ppm Ca, 0.5 ppm Sr, and 0.0041 ppm Mn. $K_D^{\text{Sr-Ca}} = 0.05$, $K_D^{\text{Mn-Ca}} = 30$, $D^{\text{Sr}} = 1000$, and $D^{\text{Mn}} = 6 \times 10^5$. Numbers on tick marks along water-rock interaction curve are water:rock ratios (N). Samples comprised of mixtures of marine calcite (1345 ppm Sr, 1 ppm Mn) and diagenetic calcite (500 ppm Sr, 2460 ppm Mn) endmembers plot along straight line. From these results, one can discriminate between a suite of carbonate rocks related by varying extents of water-rock interaction and a suite of carbonates with varying proportions of different generations of calcite.

Table 2. Concentrations, in ppm, of selected elements in sedimentary carbonates and natural waters, and calcite-water exchange distribution coefficients, K_D^{I-J} .

Element	Limestone	Seawater	Riverwater	Groundwater, Brine	K_D^{I-J}
Oxygen	480,000	889,000	889,000	889,000	$K_D^{O-O} = 1$
Carbon	120,000	29	10	20-2000	$K_D^{C-C} = 1$
Calcium	400,000	415	13	20-74,000	$K_D^{Ca-Ca} = 1$
Strontium	20-10,000	8	0.06	0.1-2000	$K_D^{Sr-Ca} = 0.05-0.14$
Neodymium	0.01-100	$10^{-6}-10^{-5}$	$10^{-6}-10^{-3}$	$10^{-6}-10^{-4}$	$K_D^{Nd-Ca} \geq 100$
Manganese	0.1-10,000	0.0002	0.008	0.1-350	$K_D^{Mn-Ca} = 5-30$

Data sources (exclusive of Nd): limestone, Veizer (1983); average seawater, Drever (1982) and Quinby-Hunt and Turekian (1983); average riverwater, Drever (1982) and Veizer (1983); groundwater and brine, Carpenter et al. (1974) and Drever (1982); K_D^{I-J} values, Veizer (1983). Nd data sources: limestone, Shaw and Wasserburg (1985) and Banner et al. (1988b); seawater, Elderfield (1988); riverwater, Goldstein and Jacobsen (1987); groundwater, brine, Michard et al. (1987) and Banner et al. (1989); K_D^{Nd-Ca} values, Palmer (1985).

probable that one can evaluate whether fluid-rock interaction is the process responsible for the geochemical variation in the suite of samples. Knowledge of precise K_D^{I-Ca} values is less important for such an evaluation than an understanding of the relative K_D^{I-Ca} values. As described earlier, the computed fluid-rock interaction pathways presented here are for complete interaction during each iteration. Model calculations that simulate only partial interaction of the bulk rock with the fluid during each iteration produce water-rock interaction pathways of similar shape to those calculated using a model involving complete interaction. For example, both methods generate similar L-shaped plots to that shown in Fig. 6. The differences in the two calculation methods result in larger N values required for the partial interaction model to attain a given value of EQ as compared with N values computed for the complete interaction model.

For any element, one must consider the possibility that it was not introduced by the diagenetic fluids, but rather was derived from local non-carbonate minerals and redistributed on a small scale during diagenesis. This would be of particular concern for elements with large K_D^{I-Ca} (e.g., Nd and Mn, Table 2), for which the fluid will have a much lower concentration than the rock. For example, BANNER et al. (1988b) found that the rare earth element (REE) concentrations in secondary dolomites from the Burlington-Keokuk Formation were locally enriched where the dolomites occurred in strata with high contents of REE-rich detrital apatite. Care must also be taken in assessing the concentrations of trace elements in carbonates that can have multiple valence states under diagenetic conditions, such as Mn, Fe, and U. For example, Mn has two common valence states, +2 and +4, of which only Mn^{+2} readily substitutes in the carbonate lattice. Local variations in Eh are commonly inferred to play an important role in determining the Mn concentrations in carbonates. This role is especially important if Mn is not introduced with

the fluid, but is derived by reduction of Mn-rich oxide minerals within the rock. A suite of diagenetic carbonates may have high Mn concentrations, indicative of high EQ values (e.g., Fig. 6), yet independent evidence may indicate that diagenesis proceeded at fluid:rock ratios which are too low to have affected the Mn concentrations by extraformational fluids with low Mn/Ca ratios. In such a case, the Mn is likely autochthonous and has been remobilized due to redox fluctuations.

Figure 7 compares simultaneous variations during fluid-limestone interaction for the isotopic compositions of O, Sr, C, and Nd, illustrating important differences in the relative rates at which the various systems attain equilibrium with the diagenetic fluid. As oxygen is an essential structural constituent that fills a structural site in each phase in the system (see SUN and HANSON, 1975), the value of the fluid:rock ratio at which the $\delta^{18}O$ value of the limestone approaches equilibrium with the fluid ($N < 10$) is constrained by the stoichiometry of the fluid and the rock. This value will therefore not vary as a function of fluid or rock composition in any fluid-limestone system in the context of the model calculation. In contrast, Sr isotopic signatures are affected at variable N values. If the diagenetic fluid is a Sr-Ca-rich brine, Sr in the limestone may attain isotopic equilibrium with the fluid at a similar low fluid:rock ratio as oxygen, but for fluids with lower Sr and Ca concentrations, a higher fluid:rock ratio is required for isotopic equilibration. Freshwater (low Sr, low Ca) recrystallization of marine limestones requires fluid:rock ratios on the order of 10^3 to reset the Sr isotope composition of the limestone. Carbonates will equilibrate with fluid $\delta^{13}C$ values at similar fluid:rock ratios to those calculated for Sr isotope equilibration in the freshwater diagenesis model. These fluid:rock ratios are significantly higher than those required to equilibrate oxygen isotopes between fluid and carbonate. Owing to the low REE contents of most fluids and

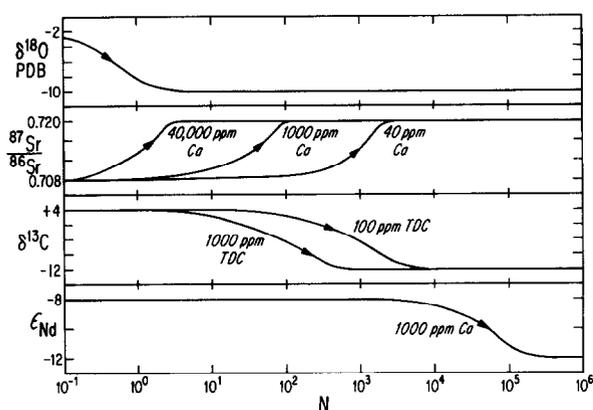


FIG. 7. Comparison of fluid:rock ratios, N , required to affect the O, Sr, C, and Nd isotopic systems during fluid-rock interaction for a variety of fluids. Initial isotopic compositions and trace element concentrations of the limestone are $\delta^{18}\text{O} = -2\text{‰}$ (PDB), $^{87}\text{Sr}/^{86}\text{Sr} = 0.708$, $\delta^{13}\text{C} = 4.0\text{‰}$ (PDB), and $\epsilon_{\text{Nd}} = -8.0$; and 1000 ppm Sr and 10 ppm Nd. The isotopic compositions of the fluid are $\delta^{18}\text{O} = -5.0\text{‰}$ (SMOW), $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$, $\delta^{13}\text{C} = -12\text{‰}$ (PDB), and $\epsilon_{\text{Nd}} = -12$. The temperature of the system is 50°C , porosity = 50%, $K_D^{\text{Sr-Ca}} = 0.05$, and $K_D^{\text{Nd-Ca}} = 100$. Curves showing the effect of Ca concentrations of 40, 1000, and 40,000 ppm for the fluid are shown for the Sr isotope system. In each fluid, Sr/Ca = 0.01. Curves showing the effect of 1000 and 100 ppm total dissolved carbon (TDC) in the fluid are shown for the carbon isotope system. Final trace element concentrations in the limestone are 200 ppm Sr and 4 ppm Nd. Table 2 gives abundance data and $K_D^{\text{I-J}}$ values for the O, C, Sr, and Nd systems.

the high values for $K_D^{\text{REE-Ca}}$ (Table 2), higher fluid:rock ratios are necessary to attain Nd isotope equilibration compared with all of the other systems shown in Fig. 7.

An understanding of the relative fluid:rock ratios that the different isotope systems require to approach equilibrium can be particularly useful in covariation diagrams for evaluating the nature of the diagenetic process involved, the extent of fluid-rock interaction, and the composition of the diagenetic fluids. Figure 8 shows the simultaneous variations in Sr and O isotopes during fluid-rock interaction between a limestone and three fluids: a freshwater, a dilute brine, and a saline brine. For the freshwater model, three fluid-rock interaction curves are drawn for three different $K_D^{\text{Sr-Ca}}$ values of 0.01, 0.05, and 0.15. The curves all overlap. Only the fluid:rock ratios are different along each path. The L-shape of the reaction path shows that the rock attains the oxygen isotope value in equilibrium with the fluid before the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio begins to change significantly. In view of the significant uncertainties associated with determining trace element $K_D^{\text{I-J}}$ values in carbonate systems (LAND, 1980; VEIZER, 1983), the invariance of the shape of the water-rock interaction curves over a ten-fold change in distribution coefficient values points out the utility of using combined isotopic systems to examine diagenetic processes. The water-rock interaction curves for two brines reacting with the same rock composition show significant differences between each other and the freshwater curve. These curve shapes are principally governed by relative differences in the Ca:Sr:O proportions between the fluids and the rock. It can be seen that fluid salinity can be critical in determining the relative response of different isotopic signatures to fluid-rock interaction.

Figure 9 shows calculated variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values during three processes: (1) fluid-rock interaction, (2) mixing of two fluids, and (3) mixing of two mineral endmembers. Open-system fluid-rock interaction between a marine limestone ($\delta^{18}\text{O} = 2\text{‰}$ PDB; $\delta^{13}\text{C} = 4\text{‰}$ PDB) and a groundwater ($\delta^{18}\text{O} = -1\text{‰}$ SMOW; $\delta^{13}\text{C} = -5\text{‰}$ PDB) follows an inverted L-shaped curve, even at an atypically high concentration of 10,000 ppm bicarbonate in the fluid. As shown qualitatively for closed system behavior by MEYERS and LOHMANN (1985), this curve shape results from the high O:C ratio in the water relative to the limestone (Table 2). TAYLOR (1977) demonstrated that the disparity in O:H ratios in rock and fluid reservoirs yields similar model curves for the hydrothermal alteration of granitic batholiths. Also shown in Fig. 9 is a path for the endmember calcite compositions resulting from seawater-freshwater mixing in which the freshwater has four times the dissolved carbon content as does seawater. Fluid mixtures would crystallize carbonates that define curves having concavities dependent on the relative concentrations of dissolved carbon in each fluid (see

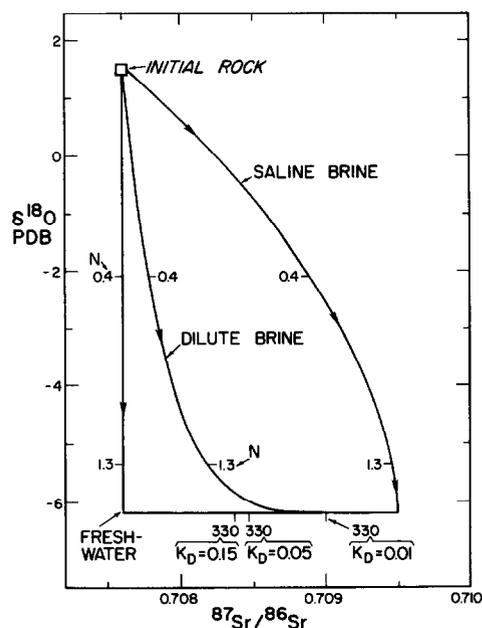


FIG. 8. Oxygen vs. strontium isotope variations illustrating three water-rock interaction models involving the recrystallization of a limestone by freshwater and two brine compositions. Porosity = 20%; $T = 40^\circ\text{C}$. The original limestone has $\delta^{18}\text{O} = 1.5\text{‰}$ (PDB), $^{87}\text{Sr}/^{86}\text{Sr} = 0.7076$, and 300 ppm Sr. In the freshwater model, the fluid has 0.6 ppm Sr, 30 ppm Ca, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7095$, and $\delta^{18}\text{O} = -1\text{‰}$ (SMOW). Values of $K_D^{\text{Sr-Ca}} = 0.15, 0.05$, and 0.01 were used to construct three freshwater diagenesis curves, which all overlap. The shape of the curve is not affected by the value of $K_D^{\text{Sr-Ca}}$. Only the fluid:rock ratios (N) along the curve are different. For an equivalent N value ($N = 330$ is used as an example), a lower $K_D^{\text{Sr-Ca}}$ value results in a carbonate that more closely approaches the endmember isotope composition. The other curves show water-rock interaction models involving the same starting rock composition and two brines with different salinities. Each brine has the same $^{87}\text{Sr}/^{86}\text{Sr}$, Sr/Ca, and $\delta^{18}\text{O}$ values as the freshwater. The dilute brine has 90 ppm Sr and 4500 ppm Ca. The saline brine has 1200 ppm Sr and 60,000 ppm Ca. Both the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ values of the limestone are significantly affected by the high-Sr, high- Ca brine at similar low N values, which is in contrast to the more dilute fluids.

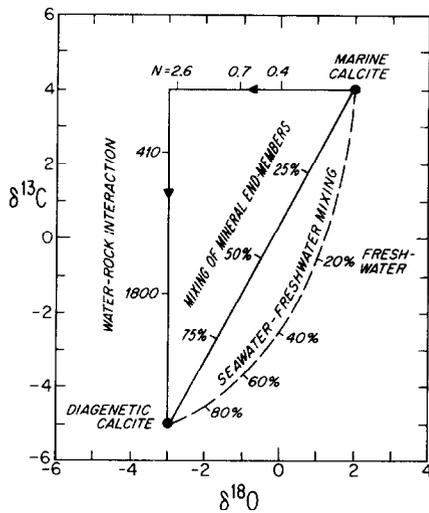


FIG. 9. Covariation of carbon vs. oxygen isotopic compositions during water-rock interaction involving a limestone (represented by the marine calcite composition) with 50% porosity, a $\delta^{18}\text{O}$ value of 2‰ (PDB), and a $\delta^{13}\text{C}$ value of 4‰ (PDB), and a fluid with a $\delta^{18}\text{O}$ value of -1‰ (SMOW), a $\delta^{13}\text{C}$ value of -5‰ (PDB), and 60 ppm total dissolved carbon ($= 305 \text{ ppm HCO}_3^-$). $T = 23^\circ\text{C}$. Water-rock interaction curve shapes are similar for fluids with up to ~ 2000 ppm total dissolved carbon ($10,000 \text{ ppm HCO}_3^-$) or less. The water:rock ratio, N , necessary to achieve the endmember diagenetic calcite value is inversely proportional to the dissolved carbon content of the fluid. Distinct pathways are calculated for water-rock interaction, fluid endmember mixing, and mineral endmember mixing. The curve showing seawater-freshwater mixing gives the endmember calcite compositions that would crystallize from a given fluid mixture. For this example, the freshwater ($\delta^{13}\text{C} = -5\text{‰}$) has a dissolved carbon content four times that of seawater ($\delta^{13}\text{C} = 4\text{‰}$). The shape of the seawater-freshwater mixing curve will vary as a function of the relative dissolved carbon concentrations in each fluid. For water-rock interaction between limestone and seawater-freshwater mixtures, the resulting carbonates would lie between the water-rock interaction and seawater-freshwater mixing curves. Mixtures of endmember marine calcite and diagenetic calcite lie along a straight line.

Fig. 7 in BANNER et al., 1988a). A suite of carbonates that are related by fluid mixing will produce a linear correlation if the two fluids have the same dissolved carbon content. If seawater-freshwater mixing and subsequent fluid-rock interaction occur in this system, data for diagenetic carbonates would lie between the two curves. These rock compositions would result from a set of L-shaped curves beginning at the marine limestone composition and ending at the various fractions along the seawater-freshwater mixing curve. A linear correlation in $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ space is a likely consequence of mixing between two carbonate mineral endmembers, as shown for marine and diagenetic calcite mixtures in Fig. 9.

In summary, calculation of the simultaneous variations in a range of isotopic and elemental systems that occur during water-rock interaction can be used to determine the effects of variations in porosity, closed system versus open system behavior, uncertainties in K_D^{I-Ca} values, and variations in fluid and rock compositions. Upon evaluation of these parameters, one can select covariation diagrams that can be best used to constrain and discriminate between different models for diagenesis.

BURLINGTON-KEOKUK DOLOMITES: A CASE STUDY

The regionally extensive, fine-grained dolomites of the Mississippian Burlington-Keokuk Formation provide a natural setting to apply quantitative fluid-rock interaction models. Two major dolomite generations, dolomites I and II, as well as several minor dolomite generations, have been distinguished by their cathodoluminescent characteristics and have been correlated over an area of $100,000 \text{ km}^2$ in Iowa, Illinois, and Missouri (HARRIS, 1982; BANNER et al., 1988a,b; CANDER et al., 1988; KAUFMAN et al., 1988). Orange to light brown, concentrically zoned dolomite I rhombs ($50\text{--}150 \mu\text{m}$) pervasively replaced lime mud in mudstone through grainstone lithologies. Red to brown, unzoned dolomites II and II' replaced dolomite I. Dolomites II and II' are texturally and chemically similar and will be collectively referred to here as dolomite II. Table 3 presents geochemical data for dolomites I and II. Compared to dolomite I, dolomite II samples have more stoichiometric major element compositions, higher $^{87}\text{Sr}/^{86}\text{Sr}$ values and Fe abundances, lower $\delta^{18}\text{O}$ values and Sr abundances, and similar $\delta^{13}\text{C}$ and ϵ_{Nd} values and REE patterns. Based on mass balance constraints and lithologic variations in the Burlington-Keokuk Formation, the Sr in dolomite II must have been derived from a predominantly extraformational source (BANNER et al., 1988a). Modeling the process of replacement of dolomite I by dolomite II is a straightforward application of the quantitative method presented above because analyses of dolomite I samples provide precise information on the isotopic and trace element composition and porosity of the starting rock, and petrographic relationships indicate that dolomite II samples are related by the recrystallization of dolomite I. Thermodynamic stabilization of the non-stoichiometric composition of dolomite I was likely the driving mechanism for the recrystallization process (see LAND, 1985).

The covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr abundances for dolomites I and II is shown in Fig. 10. The model curves shown represent the results of calculations simulating the recrystallization of dolomite I by three different fluids, a freshwater and two brines, in open and closed systems. In

Table 3. Ranges of isotopic and elemental concentration data for Burlington-Keokuk dolomites.

	Dolomite I	Dolomite II
$\delta^{18}\text{O}$ (‰, PDB)	-2.2 to 2.5	-6.6 to -0.2
$\delta^{13}\text{C}$ (‰, PDB)	-0.9 to 4.0	-1.0 to 4.1
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70757-0.70808	0.70885-0.70942
ϵ_{Nd}	-6.0 to -4.7	-6.5 to -5.0
Sr, ppm	104-123	50-63
Nd, ppm	4.3-10.2	1.4-10.4
Fe, ppm (mean)	1500	3500
Mn, ppm (mean)	1000	1200
mole% CaCO_3	54.5-56.5	51-52.5

Data from Banner et al. (1988a,b). Reported Sr and Nd isotopic compositions are initial values, corrected for estimated time of diagenesis (342 Ma).

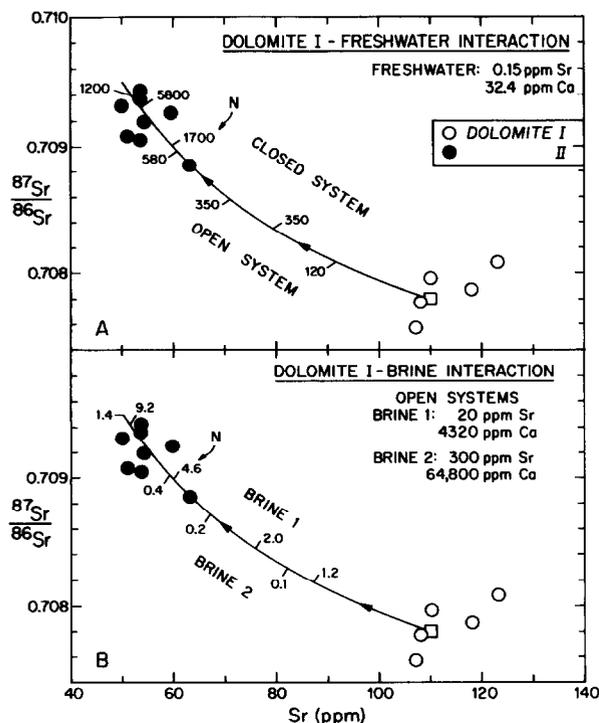


FIG. 10. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr. abundances for Burlington-Keokuk dolomites I and II. Curves are for water-rock interaction between representative dolomite I composition (open square) and diagenetic fluids using $K_D^{\text{Sr-Ca}} = 0.05$ at 15% porosity. In (a), the curve represents both open and closed systems for diagenesis by the freshwater composition shown. The fluid:rock ratios (N) for the two systems are given along the curves. In (b), curves for the interaction of two brines and dolomite I are shown. Note that all curves are identical, because the two endmember compositions are fixed (see Fig. 2). The fluid:rock ratios, however, are quite different. The fluids with the higher Sr and Ca concentrations require lower fluid:rock ratios to achieve the same alteration of the trace element concentration and isotopic composition of the dolomite. Dolomite data for Figs. 10 and 11 are from Banner et al. (1988a).

such calculations, we have assumed that Sr substitutes only for Ca in the dolomite structure. As discussed for Figs. 1 and 2, the curves are all identical because the $K_D^{\text{Sr-Ca}}$ values and the values for Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ in the fluids are the same. Only the fluid:rock ratios along the curves are different. Thus, such model curves whose shapes are independent of water:rock ratios can be useful in placing constraints on the Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ values of the diagenetic fluids. The narrow range of Sr isotopic compositions and concentrations in dolomite II samples from a 160 km regional transect indicates that either (1) the diagenetic process effected nearly complete exchange of Sr between dolomite I and the fluid (i.e., $EQ \cong 1$ for Sr in dolomite II), or (2) the dolomite samples have experienced nearly identical extents of water-rock interaction over this large regional scale (i.e., EQ is less than 1 and essentially the same value for all samples).

The narrow range in Sr concentration and isotopic composition in dolomite II is in contrast to the 6‰ range in $\delta^{18}\text{O}$ values (Fig. 11). Water-rock interaction models using the same three fluid compositions from Fig. 10 show that if the

distribution of data is a result of a single-stage fluid-rock interaction process, then neither the freshwater nor the dilute brine can account for the isotopic and trace element variations in dolomite II. However, fluid-rock interaction involving the high-Sr, high-Ca brine (64,800 ppm Ca) can produce a range in $\delta^{18}\text{O}$ values and equilibrated Sr abundances at low water:rock ratios of $N \sim 2$ (Fig. 11a).

While a model involving a concentrated brine can explain the diagenetic conversion of dolomite I to dolomite II, brines with such high Ca concentrations are near the upper limit of concentrations observed for natural fluids (Table 2). Multiple stages of fluid-rock interaction involving the dilute brine with lower Sr and Ca concentrations can also explain the dolomite II trend (Fig. 11b). The same brine is used in the two stages, but at two different temperatures. During Stage I, recrystallization of dolomite I by brine 1 occurs at 25°C, producing dolomites with 50 to 60 ppm Sr and $\delta^{18}\text{O}$ values shifted by only $\sim 2\%$ from the original dolomite I value. During this stage, essentially complete exchange of Sr and O occurs between brine 1 and dolomite I (i.e., $EQ, IEQ \cong 1$) at moderate water:rock ratios of $N \sim 5$. Continued interaction between brine 1 and the recrystallized dolomite product of Stage I occurs during Stage II at 60°C. Assuming a negligible difference in the value for $K_D^{\text{Sr-Ca}}$ between 25 and 60°C, the Sr abundances of the dolomite do not change because the Sr/Ca ratio of the fluid is the same. However, the oxygen isotope fractionation factor at 60°C is smaller, and the $\delta^{18}\text{O}$ values of the recrystallizing dolomites will change. A key aspect of the two-stage model is that during the last influx of reacting fluid (Stage II), a range of $\delta^{18}\text{O}$ values could be imposed on dolomite II through small extents of water-rock interaction ($N \leq 2$). Similar results are obtained using constant temperature and varying fluid $\delta^{18}\text{O}$ values between the two stages. If the multistage model presented in Fig. 11b is applicable, it suggests that the concentration and isotopic composition of Sr in dolomite II samples record a relatively early and large segment of the recrystallization history of the dolomites while the dolomite $\delta^{18}\text{O}$ values reflect a smaller and more recent extent of the same fluid-rock interaction history.

It is likely that the fluids that imparted high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $\delta^{18}\text{O}$ values to dolomite II also had different $\delta^{13}\text{C}$ and ϵ_{Nd} values and REE signatures compared with dolomite I. If so, then the similar C and Nd isotopic signatures and different REE patterns for dolomites I and II (Table 3, and BANNER et al., 1988b) are consistent with the low water:rock ratio values given by the models in Figs. 10 and 11. This can be seen by inspection of Fig. 7. The different geochemical parameters appear to have been affected quite differently by the same fluid-rock interaction process in this Mississippian aquifer. Carbon and REEs in dolomite II were likely derived from dolomite I precursors within Burlington-Keokuk strata. In contrast, dolomite II appears to record large-scale, open system exchange of Sr with extraformational fluids, while dolomite $\delta^{18}\text{O}$ values may reflect only the final segment in a multistage water-rock interaction sequence.

SUMMARY

In the approach presented here, variations in the elemental abundances and isotopic values for an evolving rock or fluid

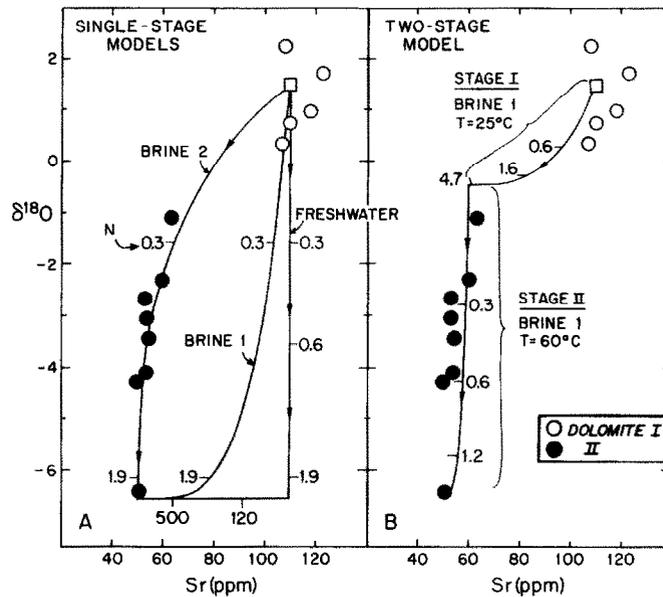


FIG. 11. $\delta^{18}\text{O}$ (PDB) vs. Sr abundances for Burlington-Keokuk dolomites. Symbols are the same as in Fig. 10. (a) Single-stage water-rock interaction curves ($T = 60^\circ\text{C}$) calculated using the same freshwater and brine compositions from Fig. 10, all of which have $\delta^{18}\text{O} = -2\text{‰}$ (SMOW). The single-stage model involving brine 2 can account for the dolomite II data. (b) Two-stage model involving only brine 1 at two different temperatures. During stage I, brine 1 interacts with dolomite I producing a dolomite with 50 to 60 ppm Sr and $\delta^{18}\text{O} = -0.5\text{‰}$ at N values ≥ 5 ($T = 25^\circ\text{C}$). During stage II, brine 1 interacts with the dolomite end product from stage I at N values < 2 ($T = 60^\circ\text{C}$). Stage II dolomites have a wide range of $\delta^{18}\text{O}$ values and a narrow range in Sr contents that are produced at low N values. Similar results are obtained at constant temperature and evolving fluid $\delta^{18}\text{O}$ values.

during water-rock interaction are derived from similar and related mass balance equations, and the variations can be calculated simultaneously. Modifying this approach to evaluate the effects upon the various elemental and isotopic systems of changes in fluid composition, temperature, porosity, fraction of rock reacting with the fluid, and changing mineralogy during diagenesis is a straightforward process. Choosing the appropriate covariation diagrams (e.g., O vs. Sr isotopic variations for the freshwater diagenesis of limestones) permits the construction of fluid-rock interaction trends that are independent of the absolute values of the distribution coefficients (e.g., $K_D^{\text{Sr-Ca}}$) over an order of magnitude range. Processes such as fluid-rock interaction vs. mixing of mineral or fluid endmembers may also be distinguished in this manner. The incorporation of this approach into numerical codes may prove useful for modeling geochemical variations in diagenetic carbonates as a function of regional gradients in lithology, fluid composition, mineral-solution equilibria, and flow rates in sedimentary basins.

Owing to the relative differences in (1) the concentrations of O, C, Sr, Mn, and Nd in carbonates and in diagenetic fluids, and (2) the values of their distribution coefficients, these elements and their isotopic compositions will be reset at different fluid:rock ratios during progressive fluid-rock interaction. During open system diagenesis, calcite will equilibrate with the oxygen isotope value of the fluid at a low water:rock ratio (< 10). The low concentrations of C (10 to 1000 ppm) and REEs (10^{-6} to 10^{-4} ppm) in fluids relative to their concentration in carbonates, and the large K_D^{C} values for the REEs, result in the requirement of water:rock ratios on the order of 10^3 or higher to effect C or Nd isotopic changes

in diagenetic carbonates. The Sr isotope system is affected at variable fluid:rock ratios, depending on the Sr and Ca concentrations of the fluid and the rock. Application of these calculations to recrystallized dolomites from the midcontinent illustrates that the $\delta^{18}\text{O}$ values of the dolomites may record a relatively late segment of their water-rock interaction history. Dolomite $^{87}\text{Sr}/^{86}\text{Sr}$ values reflect a larger and earlier segment of the same history, while $\delta^{13}\text{C}$ and REE distributions preserve the compositions of the unrecrystallized precursor dolomites.

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