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A MODEL OF ISOTOPE FRACTIONATION IN REACTING GEOCHEMICAL SYSTEMS

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ABSTRACT. We present a numerical technique that predicts how the stable isotopes ^{2}H, ^{13}C, ^{18}O, and ^{34}S fractionate among solvent, aqueous species, minerals, and gases over the course of a geochemical reaction process. Our model is based on mass balance techniques similar to those already presented in the literature but differs from previous techniques in that it allows minerals to be segregated from isotopic exchange instead of remaining in isotopic equilibrium. Such an approach allows us to simulate the fractionation of isotopes between rock and fluid resulting solely from mineral dissolution and precipitation. We test our technique by modeling isotopic fractionation during several reaction processes, including (1) dolomitization of limestone by a migrating pore fluid, (2) diagenetic alteration of the Permian Lyons sandstone in the Denver basin, and (3) hydrothermal alteration of the Okanagan Batholith in southern British Columbia. The results of calculations in which we segregate minerals from isotopic exchange compare well to isotopic trends observed in nature but differ markedly from calculations that assume isotopic equilibrium.

INTRODUCTION

Geochemists have come to rely on geochemical modeling techniques to study the nature of water-rock interaction and the chemical evolution of natural waters. Helgeson (1968) and Helgeson and others (1970) were the first to use a computer to trace the irreversible reaction of a geochemical system. Since then, geochemists have developed a number of numerical models to study processes in geochemical systems that are open to mass or heat transfer .(Wolery, 1979, 1983; Reed, 1982; Parkhurst, Thorstenson, and Plummer, 1980; Plummer, Parkhurst, and Thornstenson, 1983; Plummer and others, 1988; Bethke, 1994). Reaction path models have found widespread application, for example, in the studies of weathering, diagenesis, fluid mixing, hydrothermal alteration, and ore deposition.

In general, a geochemical model predicts how a fluid's chemistry evolves and which minerals precipitate or dissolve over the course of a geochemical process. Bowers and Taylor (1985) and Bowers (1989) showed how the modeling techniques can be modified to trace the fractionation of stable isotopes. They incorporated into the calculation

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mass balance equations to predict how isotopic mass is distributed among fluid and minerals over the course of a reaction path. Such predictions are useful because they give insight into how isotopes fractionate in reacting systems and, when the results can be compared to analytical measurements, provide checks on the correctness of chemical reactions predicted.

In this paper, we consider how isotopic fractionation might be further integrated with reaction path modeling. We present a method of tracing over the course of a reaction path the fractionation of the stable isotopes ^{2}H, ^{13}C, ^{18}O, and ^{34}S among solvent, aqueous species, minerals, and gases. Our model is based on the mass balance techniques of Bowers and Taylor (1985) and Bowers (1989) but differs from previous models in the manner in which isotopes are assumed to fractionate among fluid and minerals. In nature, isotopes fractionate among fluid and minerals by isotopic exchange as well as dissolution and precipitation reactions. At low temperature, isotopic exchange is so slow that even over geologic time it may have little effect on the composition of fluids and minerals, let alone allow them to approach isotopic equilibrium (Gregory and Taylor, 1981; Criss and Taylor, 1983; Cole and Ohmoto, 1986). When isotope exchange is slow, dissolution and precipitation reactions provide the dominant control on the distribution of isotopic mass.

Our technique allows the modeler to segregate minerals from isotopic exchange instead of requiring that they remain in isotopic equilibrium with the evolving fluid. Similar approach of sequestering the interiors of minerals has been used in studying transfer reactions of metamorphism (Chamberlain, Ferry, and Rumble, 1990; Chamberlain and Conrad, 1991; Young and Rumble, 1993). When a mineral precipitates over a step in reaction progress, only the mineral mass that forms over the step is taken in isotopic equilibrium with the fluid; any mass present at the beginning of the step maintains its composition. Conversely, when a mineral dissolves, it alters the fluid's isotopic composition, but any mineral mass remaining at the end of the step is unchanged. In this way, the modeler can simulate the fractionation resulting from chemical reaction in the absence of isotopic exchange. Our model also differs from previous models in that it accounts for fractionation among the aqueous species in solution.

Our model development is based on the "React" computer code (Bethke, 1994), the LLNL thermodynamic dataset (Johnson, Oelkers, and Helgeson, 1991), and a database of isotope fractionation factors described later in this paper. We tested our model by simulating how stable isotopes fractionate during sediment diagenesis and hydrothermal alteration. The tests include (1) dolomitization of a limestone by a magnesium-rich groundwater, (2) diagenetic alteration caused by fluid mixing in the Lyons sandstone of the Denver basin, and (3) hydrothermal alteration by infiltrating meteoric waters of the Okanagan batholith in southern British Columbia. Comparing the results given by calculations in which minerals are segregated from isotopic exchange with those that

assume isotopic equilibrium, we find that the segregated models give markedly different results than the equilibrium calculations. In the last two cases, in which isotopic measurements are available for us to check the modeled results, calculations that segregate minerals from isotopic exchange predict the isotopic trends observed in nature, whereas those assuming isotopic equilibrium cannot. These results argue for the importance of accounting for isotopic disequilibrium in reaction modeling studies.

NOTATION*

α_{j-w}	Fractionation factor between aqueous species j and solvent water w
α_{k-w}	Fractionation factor between mineral k and solvent water w
α_{A-B}	Fractionation factor between phases or species A and B
δ_A	Isotopic composition of phases or species A, in permil deviation from a standard
$\delta^{18}O_w$	Oxygen isotopic composition of solvent water w
$\delta^{18}O_j$	Oxygen isotopic composition of aqueous species j
$\delta^{18}O_k$	Oxygen isotopic composition of unsegregated mineral k
$\delta^{18}O_{k'}$	Oxygen isotopic composition of segregated mineral k'
$\delta^{18}O_{k'-eq}$	Oxygen isotopic composition of a new increment of segregated mineral k' that precipitates over a step, which is set to equilibrium with fluid
$\delta^{18}O_r$	Oxygen isotopic composition of reactant r
$\delta^{18}O_T$	Bulk oxygen isotopic composition of the equilibrium system
n^w_O	Number of moles of oxygen in water in the isotopic equilibrium system
n^j_O	Number of moles of oxygen in aqueous species j in the isotopic equilibrium system
n^k_O	Number of moles of oxygen in unsegregated mineral k in the isotopic equilibrium system
$v^{k'}_O$	Stoichiometric oxygen content of segregated mineral k'
v^r_O	Stoichiometric oxygen content of reactant r
n^T_O	Number of moles of oxygen in the equilibrium system
$n_{k'}$	Number of moles of a previously existing, segregated mineral k'
Δn_r	Number of moles of reactant r added or removed over a reaction step
$\Delta n^{(-)}_{k'}$	Number of moles of segregated mineral k' that dissolves over the reaction step
$\Delta n^{(+)}_{k'}$	Number of moles in a newly formed increment of segregated mineral k'
T_K	Absolute temperature, in Kelvins
ξ	Reaction progress variable, varying from 0 to 1

* Showing ^{18}O isotope only, symbols for ^{2}H, ^{13}C, and ^{34}S are paralleled.

STABLE ISOTOPIC FRACTIONATION IN REACTION PATH MODELS

The numerical techniques of simulating isotopic fractionation in reacting systems are based on evaluating equations of mass balance, mass transfer, and mass distribution. In this section, we present a model that traces over the course of a reaction path the fractionation of stable isotopes under conditions of isotopic equilibrium and disequilibrium.

Fractionation Model for Oxygen

To track the oxygen isotopic composition of fluid and minerals over a course of a reaction path, we first set the initial compositions of water, aqueous species, and any minerals present in the system. From the initial compositions, we calculate the bulk isotopic composition of a part of the system to which we refer as the isotope equilibrium system. The isotope equilibrium system includes (1) the solvent and aqueous species, (2) any minerals held in isotopic equilibrium with the fluid (that is, those minerals not segregated from isotope exchange), (3) the masses of any segregated minerals that dissolve over a reaction step, and (4) the increments in mass of any segregated minerals that precipitate over a step.

Then at each step in the reaction path we recalculate the bulk composition and, from the updated composition, distribute isotopic mass among water, species, any unsegregated minerals, and the newly formed increments of any segregated minerals. In this way, the masses of any segregated minerals that neither dissolve nor precipitate over the reaction step are excluded from the calculation and retain their original isotopic compositions.

Initial isotopic composition.—The calculation begins with the isotopic composition of the initial water $\delta^{18}O_w$, provided by the modeler. From the initial water composition, the $\delta^{18}O$ of each dissolved species and fluid as well as any mineral in the system need to be determined. The composition of each species j is given by its fractionation factor α_{j-w}

$$\delta^{18}O_j = \alpha_{j-w}(1000 + \delta^{18}O_w) - 1000 \tag{1}$$

Here, we use the familiar δ notation

$$\delta^{18}O = \left[\frac{^{18}O/^{16}O_{Sample} - {}^{18}O/^{16}O_{Standard}}{^{18}O/^{16}O_{Standard}}\right] \times 1000 \tag{2}$$

which expresses deviation in permil from a fluid of standard composition.

Likewise, any mineral k in equilibrium with the initial system has a composition

$$\delta^{18}O_k = \alpha_{k-w}(1000 + \delta^{18}O_w) - 1000 \tag{3}$$

The initial isotopic composition of each isotopically segregated mineral k' can be provided by the modeler or simply set to the value given by eq (3) in equilibrium with the initial system.

Bulk isotopic composition.—A mass balance equation, similar to that presented by Bowers and Taylor (1985), gives the bulk composition $\delta^{18}O_T$ of the isotope equilibrium system

$$\delta^{18}O_T = \frac{1}{n_O^T}\left[n_O^w \delta^{18}O_w + \sum_j n_O^j \delta^{18}O_j + \sum_k n_O^k \delta^{18}O_k\right] \quad (4)$$

Here $\delta^{18}O_w$ and $\delta^{18}O_j$ are the compositions of solvent water and each aqueous species j, $\delta^{18}O_k$ is the composition of each unsegregated mineral, and n_O^w, n_O^j, and n_O^k are the number of moles of oxygen in water, each aqueous species, and each unsegregated mineral. The segregated minerals k', which are not held in equilibrium with the system, are excluded from the summation.

Mass transfer.—Over the course of a reaction path, the bulk composition of the isotope equilibrium system can change for two reasons. First, in defining the reaction path, the modeler is likely to specify that reactants be added to the chemical system. Each reactant has its own isotopic composition, so its addition affects bulk composition. Second, minerals segregated from isotope exchange may dissolve in response to the fluid's changing chemistry, altering bulk composition just as a reactant would.

In stepping forward in reaction progress from ξ_1 to ξ_2, where ξ is the reaction progress variable, the system's total isotopic composition will change according to

$$\delta^{18}O_T(\xi_2) = \frac{1}{n_O^T(\xi_2)}\left[n_O^T \delta^{18}O_T(\xi_1) + \sum_r \Delta n_r v_O^r \delta^{18}O_r - \sum_{k'} \Delta n_{k'}^{(-)} v_O^{k'} \delta^{18}O_{k'}\right] \quad (5)$$

where

$$n_O^T(\xi_2) = n_O^T(\xi_1) + \sum_r \Delta n_r v_O^r - \sum_{k'} \Delta n_{k'}^{(-)} v_O^{k'} \quad (6)$$

Here Δn_r is the number of moles of reactant r added or removed over the reaction step, v_O^r is the number of oxygen atoms in the reactant's stoichiometry, and $\delta^{18}O_r$ is the reactant's isotopic composition. For each segregated mineral k' that dissolves over the step, $\Delta n_{k'}^{(-)}$ is the change in its mass by dissolution, and $v_O^{k'}$ is its stoichiometric oxygen content. $\delta^{18}O_{k'}$ is the mineral's isotopic composition.

In general, the modeler sets the rate of mass transfer Δn_r explicitly. In the case of a gas reactant at fixed or sliding fugacity or of a reactant that precipitates or dissolves according to a kinetic rate law, Δn_r is implicit in the solution of the chemical equilibrium or kinetic equations. The modeler gives the isotopic composition $\delta^{18}O_r$ of each reactant added to the system as a boundary condition. In the case in which mass is removed from the system, however, the reactant's composition is the composition of this species, mineral, or gas in the equilibrium system at the beginning of the step.

The modeler does not set the transfer rate $\Delta n_{k'}^{(-)}$ for a dissolving segregated mineral. A segregated mineral dissolves according to thermodynamic equilibrium or reaction kinetics; therefore $\Delta n_{k'}^{(-)}$ is implicit in the solution of chemical model. The initial isotopic composition $\delta^{18}O_{k'}$ of each segregated mineral is set by the modeler as a boundary condition. As we show in the next section, however, the composition of a segregated mineral can change if more of it precipitates.

Distribution of isotopic mass.—Once the total isotopic composition $\delta^{18}O_T$ of the system is known at the end of a step along the reaction path, the new compositions of water, each aqueous species j, and each unsegregated mineral k and segregated mineral k' need to be calculated. Substituting the definition (in δ notation) of the fractionation factors for species and minerals (eqs 1 and 3) into the mass balance equation (4) gives the bulk composition

$$n_O^T\delta^{18}O_T = n_O^w\delta^{18}O_w + \sum_j n_O^j[\alpha_{j-w}(1000 + \delta^{18}O_w) - 1000] + \sum_k n_O^k[\alpha_{k-w}(1000 + \delta^{18}O_w) - 1000] \quad (7)$$

from the value of $\delta^{18}O_w$. In a polythermal calculation, the fractionation factors α correspond here to the temperature at ξ_2. Again, segregated minerals k' are excluded from the summation.

Rearranging eq (7), the composition of water as a function of the bulk composition is

$$\delta^{18}O_w = \frac{n_O^T\delta^{18}O_T - 1000\left[\sum_j n_O^j(\alpha_{j-w} - 1) + \sum_k n_O^k(\alpha_{k-w} - 1)\right]}{n_O^w + \sum_j n_O^j\alpha_{j-w} + \sum_k n_O^k\alpha_{k-w}} \quad (8)$$

This equation can be evaluated to give $\delta^{18}O_w$ directly from $\delta^{18}O_T$; then, the composition of each species and unsegregated mineral follows immediately from eqs (1) and (3).

If a segregated mineral k' precipitates in stepping from ξ_1 to ξ_2, its composition is recalculated as an average of the compositions of the previously existing and the newly formed mass

$$\delta^{18}O_{k'}(\xi_2) = \frac{n_{k'}\delta^{18}O_{k'}(\xi_1) + \Delta n_{k'}^{(+)}\delta^{18}O_{k'-eq}}{n_{k'} + \Delta n_{k'}^{(+)}} \quad (9)$$

Here $n_{k'}$ and $\Delta n_k^{(+)}$ are the number of moles of a previously existing mineral and its newly formed increment, respectively. $\delta^{18}O_{k'-eq}$ is the composition of the newly formed increment, which is set to equilibrium with the fluid. The isotopic composition of a segregated mineral remains unchanged if it dissolves over a reaction step.

Fractionation Models For Hydrogen, Carbon, and Sulfur

Like the oxygen model, the isotope models for hydrogen, carbon, and sulfur require that the mass balance, mass transfer, and fractionation equations be evaluated at each step along the reaction path. We express hydrogen fractionation relative to water, the fractionation of carbon with respect to aqueous or gaseous CO_2, and that of sulfur with respect to aqueous or gaseous H_2S.

The relevant equations for these elements are:

Bulk isotopic composition

$$\delta^2H_T = \frac{1}{n_H^T}\left[n_H^w\delta^2H_w + \sum_j n_H^j\delta^2H_j + \sum_k n_H^k\delta^2H_k\right] \tag{10}$$

$$\delta^{13}C_T = \frac{1}{n_C^T}\left[\sum_j n_C^j\delta^{13}C_j + \sum_k n_C^k\delta^{13}C_k\right] \tag{11}$$

$$\delta^{34}S_T = \frac{1}{n_S^T}\left[\sum_j n_S^j\delta^{34}S_j + \sum_k n_S^k\delta^{34}S_k\right] \tag{12}$$

Mass balance

$$\delta^2H_w = \frac{n_H^T\delta^2H_T - 1000\left[\sum_j n_H^j(\alpha_{j-w} - 1) + \sum_k n_H^k(\alpha_{k-w} - 1)\right]}{n_H^w + \sum_j n_H^j\alpha_{j-w} + \sum_k n_H^k\alpha_{k-w}} \tag{13}$$

$$\delta^{13}C_{CO_2} = \frac{n_C^T\delta^{13}C_T - 1000\left[\sum_j n_C^j(\alpha_{j-CO_2} - 1) + \sum_k n_C^k(\alpha_{k-CO_2} - 1)\right]}{\sum_j n_C^j\alpha_{j-CO_2} + \sum_k n_C^k\alpha_{k-CO_2}} \tag{14}$$

$$\delta^{34}S_{H_2S} = \frac{n_S^T\delta^{34}S_T - 1000\left[\sum_j n_S^j(\alpha_{j-H_2S} - 1) + \sum_k n_S^k(\alpha_{k-H_2S} - 1)\right]}{\sum_j n_S^j\alpha_{j-H_2S} + \sum_k n_S^k\alpha_{k-H_2S}} \tag{15}$$

Mass transfer

$$\delta^2H_T(\xi_2) = \frac{1}{n_H^T(\xi_2)}\left[n_H^T\delta^2H_T(\xi_1) + \sum_r \Delta n_r v_H^r\delta^2H_r - \sum_{k'} \Delta n_{k'}^{(-)} v_H^{k'}\delta^2H_{k'}\right] \tag{16}$$

$$n_H^T(\xi_2) = n_H^T(\xi_1) + \sum_r \Delta n_r v_H^r - \sum_{k'} \Delta n_{k'}^{(-)} v_H^{k'} \tag{17}$$

$$\delta^{13}C_T(\xi_2) = \frac{1}{n_C^T(\xi_2)}\left[n_C^T\delta^{13}C_T(\xi_1) + \sum_r \Delta n_r v_C^r\delta^{13}C_r - \sum_{k'} \Delta n_{k'}^{(-)} v_C^{k'}\delta^{13}C_{k'}\right] \tag{18}$$

$$n_C^T(\xi_2) = n_C^T(\xi_1) + \sum_r \Delta n_r v_C^r - \sum_{k'} \Delta n_{k'}^{(-)} v_C^{k'} \tag{19}$$

$$\delta^{34}S_T(\xi_2) = \frac{1}{n_S^T(\xi_2)}\left[n_S^T\delta^{34}S_T(\xi_1) + \sum_r \Delta n_r v_S^r \delta^{34}S_r - \sum_{k'} \Delta n_{k'}^{(-)} v_S^{k'} \delta^{34}S_{k'}\right] \quad (20)$$

$$n_S^T(\xi_2) = n_S^T(\xi_1) + \sum_r \Delta n_r v_S^r - \sum_{k'} \Delta n_{k'}^{(-)} v_S^{k'} \quad (21)$$

Isotope fractionation among aqueous species

$$\delta^2H_j = \alpha_{j-w}(1000 + \delta^2H_w) - 1000 \quad (22)$$

$$\delta^{13}C_j = \alpha_{j-CO_2}(1000 + \delta^{13}C_{CO_2}) - 1000 \quad (23)$$

$$\delta^{34}S_j = \alpha_{j-H_2S}(1000 + \delta^{34}S_{H_2S}) - 1000 \quad (24)$$

Isotope fractionation among minerals

$$\delta^2H_k = \alpha_{k-w}(1000 + \delta^2H_w) - 1000 \quad (25)$$

$$\delta^{13}C_k = \alpha_{k-CO_2}(1000 + \delta^{13}C_{CO_2}) - 1000 \quad (26)$$

$$\delta^{34}S_k = \alpha_{k-H_2S}(1000 + \delta^{34}S_{H_2S}) - 1000 \quad (27)$$

Database of Fractionation Factors

The fractionation factor between phases or species A and B is related to the difference in their δ values at equilibrium by the equation

$$1000 \ln \alpha_{A-B} \approx \delta_A - \delta_B \quad (28)$$

It is convenient to fit the fractionation factor 1000 ln α to a polynomial equation

$$1000 \ln \alpha = a + bT_K + c\left[\frac{10^3}{T_K}\right] + d\left[\frac{10^6}{T_K^2}\right] + e\left[\frac{10^9}{T_K^3}\right] \quad (29)$$

that gives α as a function of absolute temperature T_K and a set of coefficients a, b, c, d, and e. This equation works well over a broad temperature range of geological interest but can break down when applied to hydrogen isotopes in hydrated minerals or in those containing hydroxyl groups.

Predicting the distribution of isotopic mass in a reaction model requires an extensive database that describes the fractionation among solvent, aqueous species, minerals, and gases. The fractionation factors are derived largely from experimental measurements. In certain cases, the oxygen fractionation factors for silicate and aluminosilicate minerals can be estimated by summing the fractionation of cation-oxygen bonds in mineral's structure (Savin and Lee, 1988). The fractionation data in the database used in this paper were compiled from the literature (J. K. Bohlke, personal communication) or, in the absence of published experimental measurements, estimated by the bond-type model. For consistency, our database describes the fractionation relative to a reference species for each isotope: solvent H_2O for hydrogen and oxygen, aqueous

or gaseous CO_2 for carbon, and aqueous or gaseous H_2S for sulfur. The database appears in Lee (1993).

Calculation Overview

To integrate isotopic fractionation into a reaction model, we apply at each step in the calculation the equations developed in the previous section. In this section we discuss in detail the procedure for assigning isotopic compositions over the course of the reaction model; the procedure is summarized in table 1.

TABLE 1

How isotopic compositions are assigned in a reaction model

Constituent	Isotopic Composition
Initial system	
Water and dissolved species	In equilibrium w/each other, reflecting fluid's bulk composition
Unsegregated minerals and gases	In equilibrium w/fluid
Segregated minerals	In equilibrium w/fluid, or as set by modeler
Reactants being added to system	
Species, minerals, gases	Set by modeler
Buffered gases	In equilibrium w/initial system
Reactants being removed from system	
Species, minerals, gases, and buffered gases	In equilibrium w/system at start of current step
Equilibrium system, over course of reaction	
Water, species, unsegregated minerals	In equilibrium w/each other, reflecting system's bulk composition
Segregated minerals	Weighted average of composition of increments formed over reaction step and composition of pre-existing mass
	The composition remains unchanged if minerals dissolve
Gases	In equilibrium w/current system

Assigning initial compositions.—To begin a calculation, the modeler provides the value for the isotopic composition of solvent water, in the cases of oxygen and hydrogen, and the compositions of CO_2 and H_2S, in the cases of carbon and sulfur. These values reflect the compositions that would be measured with a mass spectrometer. From the composition of reference species (H_2O, CO_2, and H_2S), the model assigns isotopic compositions to the dissolved species and unsegregated minerals according to their fractionation factors using eqs (1), (3), and (22) to (27).

If a mineral is assumed to be segregated isotopically, its composition can be given by the modeler or set to equilibrium with the initial fluid. The model determines the initial total composition of the isotopic equilibrium system by summing over the fluid and unsegregated minerals.

Tracing isotopic evolution.—The remaining task is to trace the system's isotopic evolution over the course of the reaction path. The simplest case is one in which no mass transfer occurs, such as the heating or cooling of a

closed system. At each point along the reaction path the model evaluates the fractionation factors α as functions of temperature. The total isotopic composition of the system is unchanged, so the reference composition and the compositions of species and minerals can be determined using eqs (1), (3), and (22) to (27).

More generally, the modeler specifies that one or more reactants, each of which has a known isotopic composition, be added to the system. A reactant may be added at a fixed rate or according to a kinetic rate law. At each point in the reaction path, the model evaluates how the increments of reactants added over the past step have altered the system's total composition. The model then recalculates the reference composition (eqs 8, 13-15) and from it the compositions of species and minerals (eqs 1, 3, 22-27).

In reaction modeling, reactants are sometimes removed from the system, rather than added to it. A model of evaporation, for example, may be accomplished by removing water vapor (steam) from a fluid. In this case, the model uses the isotopic composition of the entity being removed to update the system's composition. Here a reactant's entity could affect the calculation: we would get a different result if we were to remove liquid water rather than isotopically lighter water vapor from the fluid.

It should be noted that the model presented here does not consider kinetic processes that may affect isotopic fractionation. Stable isotopes in natural waters, for example, may fractionate kinetically during evaporation. Experimental studies by Lloyd (1966), Sofer and Gat (1975), and Holser (1979) indicate that the enrichment of heavy isotopes in the residual fluid does not continue indefinitely; during evaporation to the point of gypsum saturation, the fluid becomes progressively depleted in ^{18}O and ^{2}H and forms a hook-shaped trajectory, which would not be predicted by our modeling techniques.

Regardless of the types of mass transfer considered, the results will reflect whether minerals remain within the equilibrium system or are segregated isotopically from it. In the first case, all the mineral mass is considered when distributing isotopic mass at the end of a reaction step. The model treats minerals as if they had undergone complete isotopic exchange. A segregated model allows one or more minerals to be isolated from isotopic exchange. Isotopic mass is distributed just over the mass of the segregated minerals that formed over the course of a step. Only the mineral mass precipitated over a reaction step has an equilibrium composition; any mass present at the beginning of the step maintains its past composition. In contrast, when a mineral dissolves it alters the fluid's isotopic composition, but any mass remaining at the end of the step is unchanged.

EXAMPLE 1: DOLOMITIZATION

The small CO_2 contents of many groundwaters led many investigators to believe that the carbon isotopic composition of a carbonate cement simply reflects the $\delta^{13}C$ of its precursor mineral (Mattes and Mountjoy,

1980; Meyers and Lohmann, 1985). The reasoning here is that there is a much larger carbon reservoir in the precursor minerals than dissolved in groundwater. Whether this argument is valid in the presence of a CO_2-charged groundwater, however, is not clear.

As an example, we consider a simple case in which a migrating groundwater of a certain CO_2 fugacity drives the reaction of calcite in a limestone to form dolomite. We use the modeling technique described above to calculate how the carbon isotopic composition of the product dolomite evolves over the reaction. The initial fluid, in which calcite is stable, is a solution of *p*H 6 that contains 0.1 molal NaCl and 0.02 molal $CaCl_2$. The dolomitizing fluid is a 0.1 molal NaCl solution that has equilibrated with dolomite. The Ca^{2+} and Mg^{2+} concentrations are 0.01 molal. We arbitrarily fix *p*H by setting the CO_2 fugacity to different values, as we will discuss later.

The extent of the initial system is 1 kg fluid and 4000 cm^3 calcite. To convert calcite to dolomite, we gradually pass 4000 kg of a dolomitizing fluid through the rock displacing the existing fluid. We consider an open system ("flush" model) in which the dolomitizing fluid with a constant chemical and isotopic composition continuously displaces the existing fluid and its dissolved load. Each increment of the fluid fills the pore space and re-equilibrates chemically with the limestone. For a fluid in equilibrium with calcite and dolomite, the $a_{Mg^{2+}}/a_{Ca^{2+}}$ ratio is fixed by the reaction

$$\underset{\textit{calcite}}{2CaCO_3} + Mg^{2+} \Leftrightarrow \underset{\textit{dolomite}}{CaMg(CO_3)_2} + Ca^{2+}$$

At 60°C, the equilibrium $a_{Mg^{2+}}/a_{Ca^{2+}}$ ratio is about 0.08. The dolomitizing fluid has a $a_{Mg^{2+}}/a_{Ca^{2+}}$ ratio = 1.3, thereby favoring dolomitization. The model predicts that reaction with each kilogram of fluid dissolves about 0.68 cm^3 of calcite and precipitates 0.56 cm^3 of dolomite.

We trace the fractionation of carbon isotopes for two cases. First, we assume that calcite and dolomite re-equilibrate isotopically with the fluid. In the second case, we leave the minerals segregated from isotopic exchange with the fluid. Table 2 shows the fractionation factors used in the calculation. We arbitrarily set the initial $\delta^{13}C$ composition of CO_2 in fluid to −10 permil on the PDB scale. By isotopic equilibrium, calcite has a $\delta^{13}C$ value of about −6 permil. We set the $\delta^{13}C$ of the dolomitizing fluid to 0 permil.

In the first case, in which calcite and dolomite are in isotopic equilibrium with the fluid, we predict the isotopic composition of the dolomite, assuming CO_2 fugacities for the dolomitization fluid of 0.01, 0.1, 1, 10, and 100. The results show that the isotopic composition of dolomite is determined by the CO_2 fugacity and the volume of dolomitizing fluid that has reacted (fig 1). As the isotopically heavier fluid continuously displaces the existing fluid, the $\delta^{13}C$ values of the system increase

TABLE 2

*Isotope fractionation factors assumed in the calculations of dolomitization and diagenesis of Lyons sandstone, expressed as 1000 ln α. Factors describe fractionation at 60°C of ^{13}C relative to CO_2, and at 100°C of ^{13}C relative to CO_2 and ^{18}O relative to water**

	^{13}C (60°C)	^{13}C (100°C)	^{18}O (100°C)
Anhydrite	—	—	18.3
Calcite	6.37	3.38	17.1
Dolomite	4.58	1.91	21.5
Quartz	—	—	21.4
CO_2(aq)	0	0	28.0
HCO_3^-	5.7	3.5	0**
CO_3^{2-}	5.7	3.5	0**
SO_4^{2-}	—	—	17.1

* Fractionation factors calculated from regression curves compiled by J. K. Bohlke from the following sources: Bottinga (1968), Chiba and others (1981), Clayton, O'Neil, and Mayeda (1972), Malinin, Kropotova, and Grinenko (1967), Northrop & Clayton (1966), O'Neil, Clayton, and Mayeda (1969), Richet, Bottinga, and Javoy (1977), Sheppard and Schwarcz (1970).

** Assumed.

gradually and finally approach a composition reflecting equilibrium with the dolomitizing fluid. The process continues regardless of the CO_2 fugacity. The rates at which the system approaches isotopic equilibrium with the fluid, however, is determined by the CO_2 fugacity. The lower the CO_2 fugacity, the larger the volume of the fluid required to flush through the system for the rock to become isotopically heavy. Similar models of stable isotope transport with fluid flow have been used in studying metamorphism (Baumgartner and Rumble, 1988; Bickle and Baker, 1990; Bowman, Willett, and Cook, 1994) and diagenesis of carbonate rocks (Banner, Hanson, and Meyers, 1988).

In the second set of calculations, calcite and dolomite are segregated from isotopic exchange. We assume the same CO_2 fugacities (0.01, 0.1, 1, 10, and 100) for the dolomitizing fluid as before. The results show that the composition of dolomite is determined by the CO_2 fugacity and the composition of original calcite, rather than by the volume of dolomitizing fluid. At each reaction step, the carbon composition depends on the ratio of increments derived from two sources: the fluid that flushes the system and the calcite that dissolves. After several volumes of pore fluid are displaced, the system reaches a steady state and the dolomite composition remains as a constant over the reaction path (fig 2). The system reaches a steady state when carbon entering the system is balanced by that which precipitates in dolomite and that which is lost in the displaced fluid. At low CO_2 fugacities, the light carbon derived from dissolving calcite is the dominant source. The dolomite formed from the fluid, therefore, has a light isotopic composition. As the CO_2 fugacity increases, the heavy carbon derived from the dolomitizing fluid becomes more important, and the resulting dolomite is isotopically heavier.

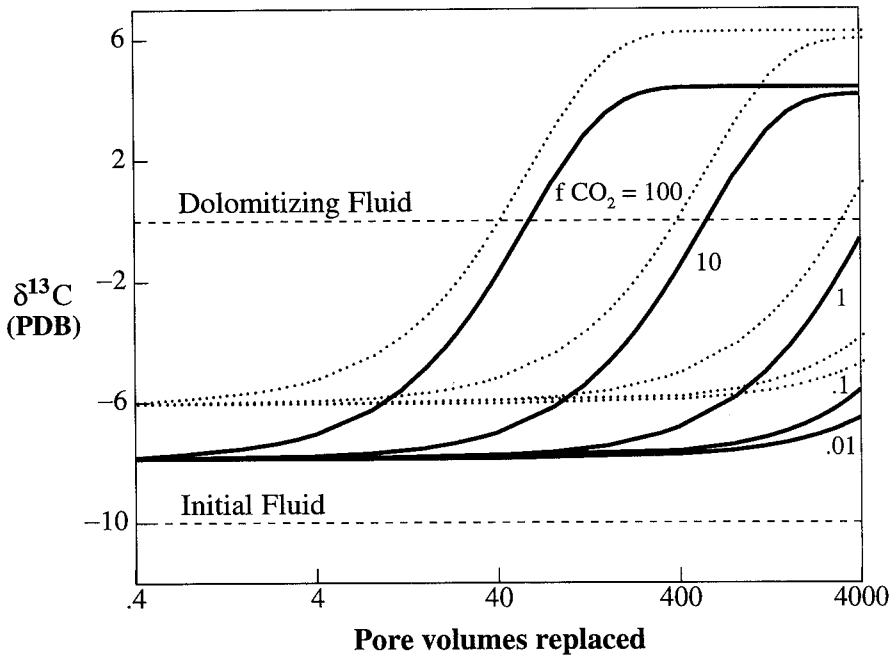


Fig. 1. Results of tracing a dolomitization reaction in which fluid and minerals maintain isotopic equilibrium. Carbon isotopic compositions of dolomite (solid lines) and precursor calcite (dotted lines) were calculated assuming different CO_2 fugacities for the dolomitizing fluid. $\delta^{13}C$ of CO_2 in the initial fluid is −10 permil on the PDB scale (dashed line). The dolomitizing fluid has a $\delta^{13}C$ value of 0 permil.

These results demonstrate that CO_2-charged groundwaters can comprise an important component of the carbon reservoir during dolomitization, and that authigenic dolomite can differ sharply in carbon isotope composition from its precursor minerals. The results also argue for the importance of holding minerals segregated from isotope exchange when modeling even simple diagenetic reactions.

EXAMPLE 2: DIAGENESIS OF LYONS SANDSTONE

As a second example, we consider the origin and isotopic composition of dolomite and anhydrite cements in the Permian Lyons sandstone of the Denver basin, which lies to the east of the Front Range in Colorado and Wyoming. The cements are of special interest because the distribution of a gray diagenetic facies in the Lyons, a sandstone composed dominantly of a red facies, mirrors the occurrence of petroleum reservoirs in the formation (Levandowski and others, 1973).

Lee and Bethke (1994) concluded that the gray Lyons facies formed in a zone of dispersive mixing when brine upwelling from underlying formations reacted with sediment and groundwater of the red Lyons.

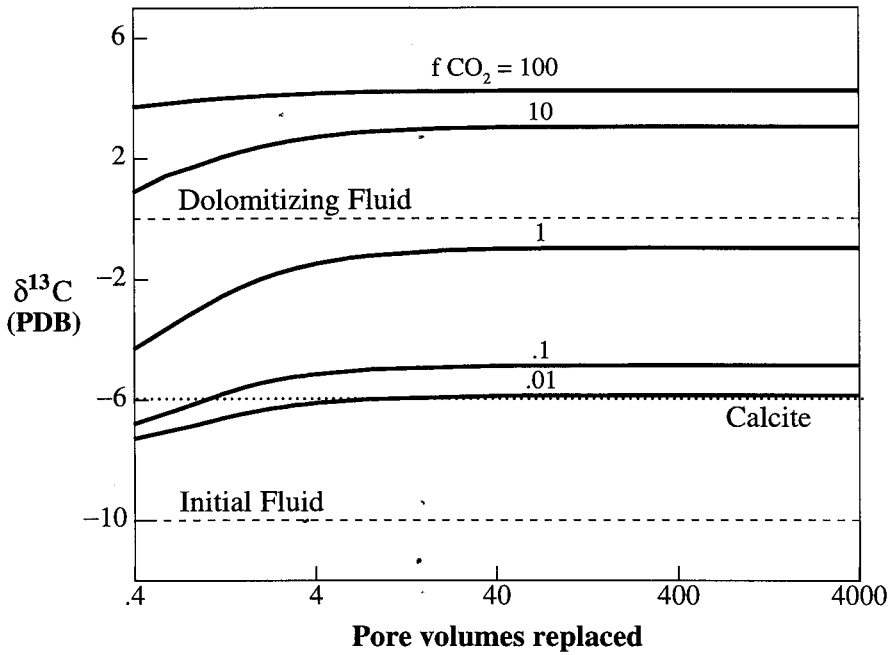


Fig. 2. Results of tracing a dolomitization reaction in which minerals are segregated from isotopic exchange. Carbon isotopic compositions of the resulting dolomite (solid lines) are shown for calculations made assuming various CO_2 fugacities for the dolomitizing fluid. The carbon isotopic compositions of the initial and the dolomitizing fluid are the same as shown in figure 1. The $\delta^{13}C$ value of the calcite, which dissolves over the reaction, is unchanged (−6 permil, dotted line).

The mixing reaction occurred when Eocene uplift of the western basin during the Laramide orogeny drove groundwater flow eastward. Flow was relatively rapid in the Lyons, but in the Pennsylvanian Fountain formation, a sandstone aquifer that underlies the Lyons and is separated from it by an aquitard complex, flow was more restricted because the formation grades into less permeable dolomite and shale in the deep basin. As brines in the Fountain encountered less permeable sediments near the basin's axis, they migrated upward along faults and fractures into the Lyons aquifer, where they mixed with less saline groundwater. As fluids mixed, calcite dissolved, and the Ca^{2+} and HCO_3^- added to solution drove precipitation of anhydrite and dolomite by a common-ion effect. The overall reaction was

$$\underset{\textit{calcite}}{5\ CaCO_3} + 2\ SO_4^{2-} + \tfrac{5}{2}\ Mg^{2+} \longrightarrow \underset{\textit{anhydrite}}{2\ CaSO_4} + \tfrac{5}{2}\ \underset{\textit{dolomite}}{CaMg(CO_3)_2} + \tfrac{1}{2}\ Ca^{2+}$$

The isotopic composition of dolomite cements (fig. 3) is compatible with an origin by fluid mixing. The dolomite cements range in $\delta^{18}O$ from

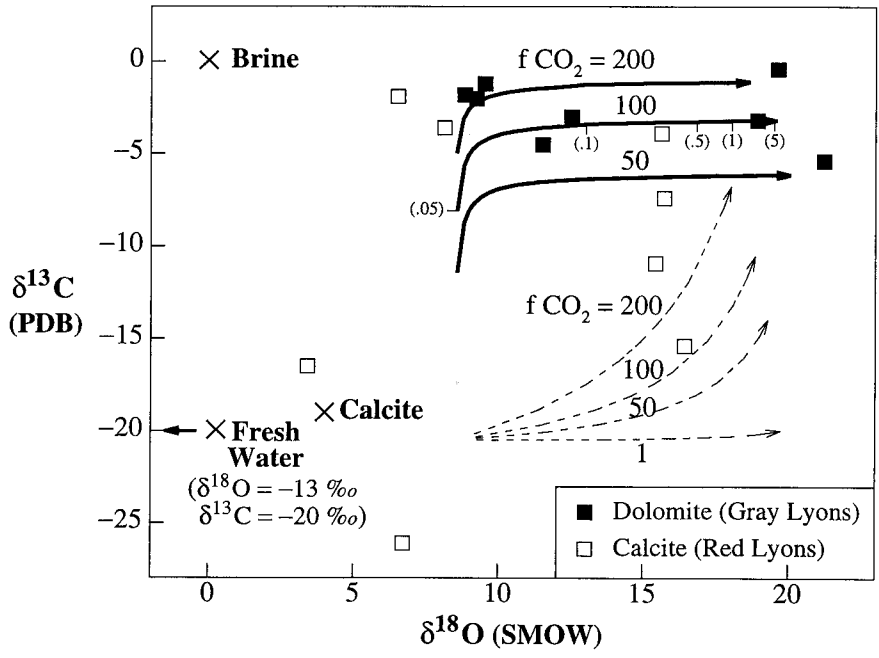


Fig. 3. Calculated isotopic composition of dolomite resulting from the reaction of upwelling brine with fluid and sediment of the Lyons sandstone. The initial ^{18}O composition of the Lyons groundwater is −13 permil, which matches estimates for Tertiary rainfall in the Rocky Mountains (Taylor, 1974; Lander and Anderson, 1989). The brine has $\delta^{18}O$ = 0 permil and $\delta^{13}C$ = 0 permil (cross), as might be expected in a sedimentary basin. The $\delta^{13}C$ of the initial Lyons fluid is −20 permil, reflecting the light isotopic composition of calcite cement (−19 permil) found in the red diagenetic facies. Assuming that minerals are isotopically segregated, each solid curve shows for a given CO_2 fugacity of the brine (on an atmosphere scale) how the isotopic composition of dolomite evolves over the course of the reaction. Numbers on tick marks along the isotope curves are water-rock ratios (mass ratio of water to minerals). Dashed lines are results calculated assuming isotopic equilibrium. Observed calcite and dolomite compositions (boxes) are from Levandowski and others (1973).

+8.8 to +21.2 permil (relative to SMOW). The scatter in the $\delta^{18}O$ data likely reflects mixing in varying proportions of meteoric water in the Lyons with the Fountain brine. The dolomite cements are enriched in ^{13}C compared to many of the calcite samples. The carbon data can be interpreted to reflect the influence of a deep CO_2-charged brine that has $\delta^{13}C$ values similar to that of seawater.

We modeled how the stable isotopes ^{13}C and ^{18}O fractionate during the mixing reaction, which we assume occurred at 100°C, for two cases. We consider that (1) minerals reequilibrate isotopically with the fluid mixture, and (2) minerals are segregated from isotopic exchange. For each case, assuming different CO_2 fugacities for the Fountain brine, we calculate how the isotopic composition of dolomite cements evolved as

the Fountain brine mixed into the Lyons (fig 3). The fractionation factors used in the calculation are shown in table 2.

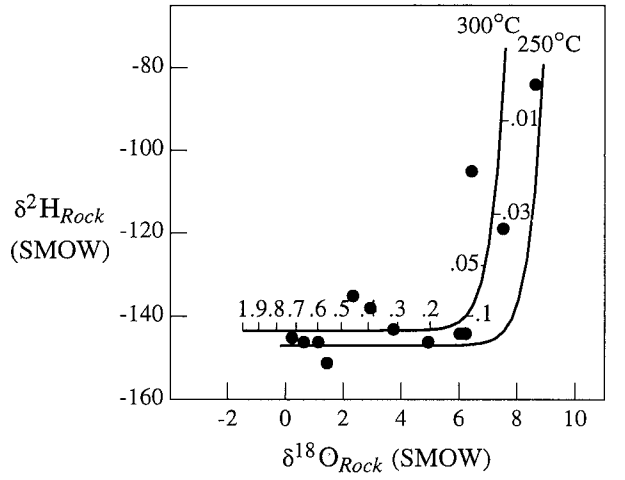
The $\delta^{13}C$ values predicted by the model depend on the CO_2 fugacity assumed for the Fountain brine and whether minerals maintain isotopic equilibrium with the fluid or are segregated from isotopic exchange. When we assume isotopic equilibrium and a relatively low CO_2 fugacity of 1, the calculation predicts dolomite compositions similar to the $\delta^{13}C$ of the precursor calcite because the carbon derived from calcite overwhelms that from the fluid. Even when we assume high CO_2 fugacities (50-200) under the equilibrium condition, the compositions predicted by the model differ markedly from the isotopic trends observed in the sandstone. When minerals and fluid are segregated from isotopic exchange and CO_2 fugacities are in the range of about 50 to 200, however, the model predicts dolomite compositions that span the observed range. In this case, the dolomite $\delta^{13}C$ more closely reflects the isotopic composition of carbonate species in the brine than that of the precursor calcite.

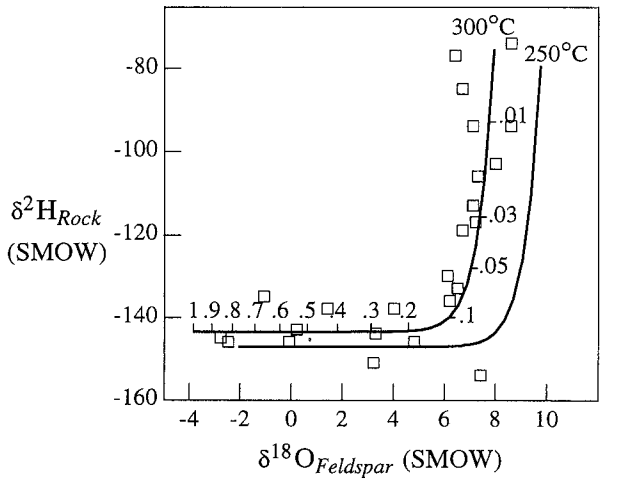
EXAMPLE 3: ALTERATION OF OKANAGAN GRANITE

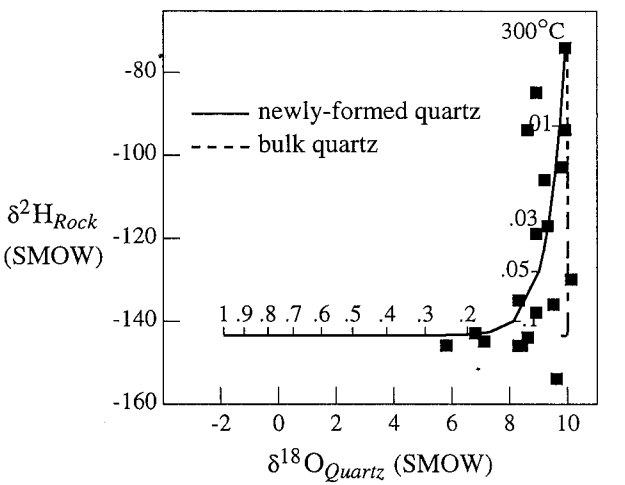
In a third example, we model the interaction of meteoric waters with granite of the Okanagan batholith in southern British Columbia. The batholith consists of Jurassic granodiorite and quartz monzonites (Peto, 1973; Peto and Armstrong, 1976). Since it was emplaced, the batholith has been silicified, chloritized, and carbonatized to varying extents by hydrothermal fluids. Heavily altered granite is associated with volcanic rocks having K-Ar ages of about 50 my (Parkinson, 1985), suggesting that igneous intrusion and a period of hydrothermal alteration occurred during the Eocene.

The Okanagan granite is strongly depleted in ^{18}O (+0.2 to +9.1 permil, SMOW) and deuterium (−84 to −154 permil, SMOW) relative to those of unaltered granitic rocks (Magaritz and Taylor, 1986). Like many igneous intrusions, the isotopic composition is characterized by an "inverted-L" pattern (fig. 4A). In fluid inclusion and stable isotope study of quartz veins in the area, Zhang, Nesbitt, and Muehlenbachs (1989) recognized two distinct hydrothermal fluids: (1) a shallow fluid that formed epithermal deposits which is characterized by relatively low temperatures (230°-250°C), low salinities (<1 wt percent NaCl), and

Fig. 4(A) Predicted whole-rock $\delta^{18}O$ and $\delta^{2}H$ values of the hydrothermally altered Okanagan granite at varying W/R ratios. W/R ratios, ranging from 0.01 to 1, are labeled on the curve calculated for 300°C. Data points are whole-rock compositions measured by Magaritz and Taylor (1986). Quartz is segregated from isotopic exchange in this model. (B) Predicted and measured $\delta^{18}O$ of feldspar and whole-rock $\delta^{2}H$ values. Open squares indicate the $\delta^{2}H$ composition of whole rocks and $\delta^{18}O$ values of feldspar within them (Magaritz and Taylor, 1986). (C) Predicted $\delta^{18}O$ of quartz and $\delta^{2}H$ values of rocks that would be obtained during the hydrothermal alteration of the Okanagan granite at 300°C. The solid line indicates the equilibrium ^{18}O composition of the newly precipitated quartz at varying W/R ratios. The bulk $\delta^{18}O$ values of quartz, an average composition of the newly formed "rims" and segregated cores, are shown as the dashed line. Boxes indicate the $\delta^{18}O$ values of quartz observed in the granite (Magaritz and Taylor, 1986).


A.
300°C
250°C
.01
.03
.05
.1
1.9.8.7.6.5.4.3.2
-80
-100
-120
-140
-160
-2
0
2
4
6
8
10
δ²H_Rock (SMOW)
δ¹⁸O_Rock (SMOW)


B.
300°C
250°C
.01
.03
.05
.1
1.9.8.7.6.5.4.3.2
-80
-100
-120
-140
-160
-4
-2
0
2
4
6
8
10
δ²H_Rock (SMOW)
δ¹⁸O_Feldspar (SMOW)


C.
300°C
newly-formed quartz
bulk quartz
.01
.03
.05
1.9.8.7.6.5.4.3.2
-80
-100
-120
-140
-160
-2
0
2
4
6
8
10
δ²H_Rock (SMOW)
δ¹⁸O_Quartz (SMOW)

depleted values of ^{18}O (−7 to −9 permil) and ^{2}H (−133 permil); and (2) a deep fluid at higher temperature (280°-330°C) with higher salinities (3-6 wt percent NaCl), low $\delta^{2}H$ values (−121 to −148 permil), but high $\delta^{18}O$ compositions (+4 to +6 permil). The hydrothermal fluids contained CO_2 in varying proportions (0.5-20 wt percent), indicating that the fluids might have exsolved CO_2 during migration. Zhang, Nesbitt, and Muehlenbachs (1989) interpreted that the low salinities and depleted isotopic compositions of the shallow fluids reflect their origin as meteoric water, whereas the more saline and isotopically heavier fluids arose at depth from mixing magmatic water in varying proportions with meteoric water.

Lee (1993) used React to model at 250° and 300°C the chemical interaction between the deeply circulating meteoric water and the Okanagan granite. In his model, the initial system includes granodiorite in equilibrium with a modeled fluid. The Cl^- concentration of the modeled fluid is set to reflect the salinity of deep hydrothermal fluids (36000 ppm Cl or 6 wt percent NaCl); the concentrations of H^+, Na^+, K^+, Mg^{2+}, Fe^{2+}, Al^{3+}, HCO_3^-, and SiO_2(aq) in the fluid are calculated by assuming equilibrium with prehnite, albite, K-feldspar, tremolite, minnesotaite (an Fe mica in the LLNL dataset), chlorite, calcite, and quartz. The Ca^{2+} concentration is set by charge balance. The meteoric water contains 1 wt percent CO_2, in accord with fluid inclusion studies. The chemical model traces the chemical consequences of flushing the initial system with meteoric water. In the model results, chlorite, quartz, and calcite precipitate at the expense of tremolite, minnesotaite, and zeolite. Small amounts of albite and K-feldspar dissolve. The overall reaction is

$$\underset{\textit{minnesotaite}}{Fe_3Si_4O_{10}(OH)_2} + 0.5613\ \underset{\textit{tremolite}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + 2.623\ \underset{\textit{prehnite}}{Ca_2Al_2Si_3O_{10}(OH)_2}$$

$$+ 0.1742\ \underset{\textit{K-feldspar}}{KAlSi_3O_8} + 0.06774\ \underset{\textit{albite}}{NaAlSi_3O_8} + 6.358\ CO_2(aq) + 3.558\ H_2O$$

$$\rightarrow 6.358\ \underset{\textit{calcite}}{CaCO_3} + 10.62\ \underset{\textit{quartz}}{SiO_2}$$

$$+ 1.936\ \underset{\textit{chlorite}}{Ca_{.005}Na_{.035}K_{.09}Fe_{1.55}Mg_{1.45}\ Al_{2.835}Si_{3.34}O_{10}(OH)_8}$$

According to this reaction, chlorite replaces biotite, hornblende, and prehnite as the meteoric water displaces the original pore fluid. Calcite precipitates by reaction between Ca^{2+} derived from dissolving hornblende and zeolite and CO_2 carried by meteoric water. Excess silica in the reaction precipitates as quartz. The predicted reaction explains the

petrographic observations of chloritization, silicification, and carbonization.

We trace fractionation of ^{18}O and ^{2}H in the predicted reaction. We consider an open system in which meteoric water continuously displaces the existing fluid and its dissolved load. In this model configuration, we envision a hydrologic system in which meteoric waters, once they have reacted, are lost to the intermediate system, perhaps by discharge to the surface.

We calculate the isotopic composition of whole rock and minerals at 250° and 300°C as a function of the water-rock (W/R) ratio (defined here as the molar ratio of oxygen in meteoric water to oxygen in the unsegregated minerals). In the calculation, the initial fluid is assumed to have a $\delta^2H = -50$ and $\delta^{18}O = +2.5$ permil; the meteoric water has $\delta^2H = -120$ and $\delta^{18}O = -16$ permil. These values were chosen to represent Eocene meteoric waters in southern British Columbia and the original fluids in granite. We assume that all minerals except quartz maintain isotopic equilibrium with the reacting fluid. We set the initial $\delta^{18}O$ value of segregated quartz to +10 permil, the approximate composition of unaltered quartz cores in the granite. The oxygen isotopic fractionation factors between minerals and water used in the model are shown in table 3. The ^{2}H fractionation factors for chlorite-H_2O, biotite-H_2O, hornblende-H_2O, and zeolite-H_2O are taken to be the same as those for serpentine (Wenner and Taylor, 1973; Suzuoki and Epstein, 1976): about −31 at 250°C and −27 at 300°C, expressed as 1000 ln α.

TABLE 3

Oxygen isotopic fractionation factors (1000 ln α) of minerals used in the calculation of alteration of Okanagan granite. The factors describe fractionation relative to solvent H_2O*

Minerals	250°C	300°C
Quartz	9.45	7.39
Calcite	7.27	5.57
K-feldspar	7.22	5.45
Albite	7.22	5.45
Tremolite	1.00	0.05
Prehnite	3.75	2.64
Minnesotaite	4.17	2.48
Chlorite	3.19	1.38

* Fractionation factors calculated from regression curves compiled by J. K. Bohlke from the following sources: Clayton, O'Neil, and Mayeda (1972), O'Neil, Clayton, and Mayeda (1969), O'Neil and Taylor (1967), Wenner and Taylor (1973), and Matthews, Goldsmith, and Clayton (1983). Factors for minnesotaite and chlorite are calculated using the bond-type model of Savin and Lee (1988).

The calculation results (fig. 4A) show that, as the W/R ratio increases from 0 to 0.1, the δ^2H values of the bulk rock drop by as much as 60 permil with little depletion in the ^{18}O content. As the W/R ratio continues to increase, the $\delta^{18}O$ values become progressively depleted, while the δ^2H

values of rocks remain about −140 to −150 permil. The δ^2H values of bulk rocks drop quickly with the addition of meteoric water because the ^2H derived from this source overwhelms that available from OH-bearing minerals, which comprise only a small fraction of the granite. The δ^2H values of the rock finally approach a composition reflecting isotopic equilibrium with meteoric water. In contrast, the $\delta^{18}O$ values of the rock decrease gradually as the W/R ratio increases, because minerals in the granite comprise a significant component of the oxygen reservoir.

The predicted composition of ^{18}O in feldspar and ^2H in the whole rock also show a inverted L-shaped pattern on a δ^2H-$\delta^{18}O$ plot (fig. 4B). The results compare favorably with isotopic measurements by Magaritz and Taylor (1986). The depleted isotopic compositions of feldspar thus indicate that there has been considerable isotopic exchange among feldspar minerals and meteoric waters. In a contrast to feldspar, quartz has undergone no appreciable depletion in ^{18}O (fig. 4C).

Quartz is set to be isotopically segregated in our model; therefore, only the newly precipitated mass is in isotopic equilibrium with the fluid, while the previously formed cores are segregated. We calculate at each reaction step the instantaneous $\delta^{18}O$ values of additional quartz increment. The model shows that, as the W/R ratio gradually increases, the $\delta^{18}O$ values of newly formed quartz become progressively depleted (fig. 4C). This result explains why the outer rims of quartz grains are more depleted in ^{18}O than are their inner cores, as observed by Magaritz and Taylor (1986). Because the mass of precipitated quartz is so small with respect to primary quartz, however, the bulk composition of quartz decreases only slightly, from its initial value +10 to about +9.5 permil (fig. 4C). Because of the development of the stable isotope laser probe techniques for measuring fine-scale variations in the $\delta^{18}O$ of silicate minerals (Sharp, 1990), studies have found both zoned (Conrad and Chamberlain, 1992; Chamberlain and Conrad, 1991, 1993) and unzoned mineral samples (Kohn and Valley, 1994). The isotopic patterns have significant implications for isotope transfer processes in geochemical reacting systems.

CONCLUSIONS

In this study, we present a numerical model that traces the fractionation of stable isotopes among solvent, aqueous species, minerals, and gases over the course of a reaction path. Using the model, we demonstrate how isotopes fractionate under conditions of isotopic equilibrium and disequilibrium during sediment diagenesis and hydrothermal alteration. In each of the examples presented, results of calculations in which minerals are segregated from isotopic exchange differ markedly from those that assume isotopic equilibrium.

1. When isotopic equilibrium is assumed, the dolomite composition is determined by the CO_2 fugacity and the volume of dolomitizing fluid. The lower the CO_2 fugacity, the larger the volume of the fluid required to make the dolomite isotopically heavier. As the

W/R ratio increases, the dolomite composition finally approaches a constant reflecting equilibrium with the dolomitizing fluid. When we assume isotopic disequilibrium, the dolomite composition depends on the ratio of increments derived from the dolomitizing fluid and the dissolving calcite. At low CO_2 fugacities, the dissolving calcite is the dominant reservoir, and dolomite has a light composition. As CO_2 fugacity increases, the dolomitizing fluid becomes more important, and dolomite is heavier.

2. In the Lyons sandstone the mixing of brine in differing proportions with meteoric water accounts for the broad range of $\delta^{18}O$ values observed for dolomite cements in the formation. When we assume isotopic equilibrium, the predicted carbon compositions differed markedly from the observed ^{13}C trend of the dolomite regardless of the CO_2 fugacity assumed. When we segregate minerals from isotopic exchange and take a value for the CO_2 fugacity of the brine in the range of about 50 to 200, however, the dolomite ^{13}C compositions predicted span the observed range.
3. In a model of the hydrothermal reaction of meteoric water with the Okanagan granite, chlorite, quartz, and calcite form at the expense of hornblende, biotite, and zeolite. The model shows that the depleted compositions of clay and feldspar likely reflect an isotopic equilibrium with infiltrating freshwaters. In contrast, the bulk composition of quartz decreases only slightly from the ^{18}O composition of its unaltered cores, suggesting that quartz is segregated from isotopic exchange with isotopically lighter fluids during hydrothermal alteration.

In our second and third examples, which are based on field observations, only calculations that segregate minerals from isotopic exchange can predict the isotopic trends observed in nature. In the third example, the isotopic compositions of feldspar and clay likely reflect isotopic equilibrium with meteoric waters. In contrast, the composition of quartz indicates clearly that dissolution and precipitation reactions rather than isotopic exchange provide the dominant control on the distribution of isotopic mass. This result argues for the necessity of accounting for isotopic disequilibrium when using reaction path modeling to study the fractionation of stable isotopes during natural reaction processes.

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