

Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis

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ABSTRACT

Carbonate rocks and natural waters exhibit a wide range in the concentration and isotopic composition of strontium. This wide range and the quantifiable covariation of these parameters can provide diagnostic tools for understanding processes of fluid-rock interaction. Careful consideration of the uncertainties associated with trace element partitioning, sample heterogeneity and fluid-rock interaction mechanisms is required to advance the application of the trace element and isotope geochemistry of strontium to studies of diagenesis, groundwater evolution, ancient seawater chemistry and isotope stratigraphy.

A principal uncertainty involved in the application of Sr concentration variations to carbonate systems is the large range of experimental and empirical results for trace element partitioning of Sr between mineral and solution. This variation may be a function of precipitation rate, mineral stoichiometry, crystal growth mechanism, fluid composition and temperature. Calcite and dolomite in ancient limestones commonly have significantly lower Sr concentrations (20–70 p.p.m.) than would be expected from published trace element distribution coefficient values and Sr/Ca ratios of most modern sedimentary pore waters. This discrepancy probably reflects the uncertainties associated with determining distribution coefficient values.

As techniques improve for the analytical measurement and theoretical modelling of Sr concentration and isotopic variations, the petrological analysis of carbonate samples becomes increasingly important. The presence of even small percentages of non-carbonate phases with high Rb concentrations and high $^{87}\text{Sr}/^{86}\text{Sr}$ values, such as clay minerals, can have significant effects on the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values of carbonate rocks, due to the decay of ^{87}Rb to ^{87}Sr . For example, a Permian marine limestone with 50 p.p.m. Sr and 1 p.p.m. Rb will have a present-day $^{87}\text{Sr}/^{86}\text{Sr}$ value that is $>2 \times 10^{-4}$ higher than its original value. This difference is an order of magnitude greater than the analytical uncertainty, and illustrates the importance of assessing the need for and accuracy of such corrections.

A quantitative evaluation of the effects of water-rock interaction on Sr concentrations and isotope compositions in carbonates strengthens the application of these geochemical tracers. Geochemical modelling that combines the use of trace elements and isotopes can be used to distinguish between different mechanisms of water-rock interaction, including diffusive and advective transport of diagenetic constituents in meteoric pore fluids during the recrystallization of carbonate minerals. Quantitative modelling may also be used to construct diagnostic fluid-rock interaction trends that are independent of distribution coefficient values, and to distinguish between mixing of mineral end-members and fluid-rock interaction.

INTRODUCTION

The trace element and isotope geochemistry of strontium have emerged as powerful tools in studies of the hydrological cycle and the diagenesis of carbonate sediments. The special utility of strontium, compared with other elemental and isotopic systems, lies in (1) substantial variations in its concentration and isotopic composition in sedimentary rocks and waters, which can provide important clues to such parameters as mineralogy, fluid salinity, fluid source and extent of fluid-rock interaction, and (2) the linked trace element partitioning and isotopic mixing behaviour of this element. Several avenues of research have led to a better understanding of the behaviour of Sr in sedimentary systems.

Early studies established the applicability of Sr as a trace element in the analysis of carbonate diagenetic systems (Holland *et al.*, 1964; Kinsman, 1969). Subsequent application of Sr isotopes to ancient marine carbonates illustrated significant variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through time (Brass, 1976; Burke *et al.*, 1982). Recent advances established Sr isotope variations in Cenozoic marine carbonates as a high-resolution stratigraphic tool and as a potential climatic indicator (DePaolo & Ingram, 1985; Hess *et al.*, 1986; Raymo *et al.*, 1988; Capo & DePaolo, 1990; Hodell *et al.*, 1990; Blum & Erel, 1995). Similar applications to Palaeozoic and older strata appear feasible (e.g. Popp *et al.*, 1986). These efforts require a detailed understanding of the isotope and trace element behaviour of Sr during carbonate diagenesis. The analysis of Sr isotopes in groundwater and surface water from a variety of environments (Chaudhuri, 1978; McNutt *et al.*, 1984; Stueber *et al.*, 1984; Goldstein & Jacobsen, 1987; Banner *et al.*, 1989, 1994; Müller *et al.*, 1991; Blum *et al.*, 1994) has led to the application of Sr isotopes to the study of fluid migration in sedimentary basins and diagenetic processes in carbonate rocks (e.g. Moore, 1985; Banner *et al.*, 1988a). As a result, the application of Sr isotope and trace element studies to low-temperature carbonate systems has become widespread. The use of multiple isotopic and elemental variables will probably provide the maximum petrogenetic constraints for any study. This study focuses on Sr by reviewing, critically assessing and offering new perspectives into the application of strontium's trace element and isotope geochemistry to sedimentary carbonate rocks and minerals.

TRACE ELEMENT BEHAVIOUR OF STRONTIUM IN CARBONATE MINERALS

Trace metals may be incorporated into minerals via (1) impurities such as fluid or mineral inclusions, (2) occlusion in lattice defects, (3) sorption onto growing crystal surfaces and (4) solid-solution substitution for a major element that is an essential structural constituent (i.e. a lattice component) of the mineral (McIntire, 1964; Sun & Hanson, 1975). Theoretical and experimental approaches to modelling the trace element behaviour of Sr in carbonate-fluid systems assume that solid-solution substitution of Sr^{2+} into Ca^{2+} structural sites (no. 4, above) is the only significant mechanism. This assumption is based on the similar size and charge of these ions, and is consistent with experimental studies of other mechanisms. Ion-exchange studies show that less than 1% of the Sr in aragonitic corals resides in exchangeable, non-lattice sites (Amiel *et al.*, 1973). The results of sorption experiments indicate that less than 3% of Sr in solution (pH < 8.5) is sorbed onto calcite (Zachara *et al.*, 1991). X-ray absorption spectroscopic measurements indicate that Sr is incorporated into calcite by substitution at Ca structural sites, in a dilute solid solution, with only minimal incorporation by sorption, occlusion or in undetected trace phases (Pingitore *et al.*, 1992). This apparent restriction of Sr to Ca structural sites simplifies a quantitative approach to Sr trace element behaviour in carbonate-fluid systems. A number of complicating factors are discussed below.

Aragonite and calcite precipitated from identical solutions will have markedly different Sr concentrations due to differences in their crystal structures. The Ca site is larger in the ninefold coordination of the orthorhombic aragonite structure compared with sixfold coordination in the rhombohedral calcite structure (see reviews by Reeder, 1983; Speer, 1983). Comparisons between CaCO_3 minerals and dolomite are complicated by the different and variable number of Ca sites in dolomite. The presence of Sr-rich impurities such as gypsum, anhydrite, celestite, strontianite and saline fluid inclusions must be evaluated prior to consideration of the trace element behaviour of Sr in a suite of carbonate samples.

Trace element distribution coefficient values quantitatively represent how a trace element is partitioned between mineral and fluid phases. Sverjensky (1984) outlines a theoretical basis for the use of mineral-fluid distribution coefficients between cation pairs with similar ionic radii,

such as $\text{Sr}^{2+}/\text{Pb}^{2+}$ and $\text{Mg}^{2+}/\text{Zn}^{2+}$. Considering the important role that fluid composition plays in determining carbonate mineral trace element contents, this study is concerned with Sr–Ca exchange and use of the large amount of published Sr and Ca analyses of natural and synthetic carbonates and fluids. The distribution coefficient K_D , is used to quantify the extent of ideal substitution of Sr^{2+} in Ca^{2+} structural sites during precipitation of a carbonate mineral in homogeneous equilibrium with a solution of a given composition. The K_D value is a measure of the difference in the Sr/Ca ratio between the carbonate mineral and precipitating solution:

$$K_D^{\text{Sr-Ca}} = (\text{Sr/Ca})_{\text{mineral}} / (\text{Sr/Ca})_{\text{solution}} = D_{\text{Sr}} / D_{\text{Ca}} \quad (1)$$

where $K_D^{\text{Sr-Ca}}$ refers to the Sr–Ca exchange distribution coefficient of Banner & Hanson (1990; 'distribution coefficient' hereafter), and Sr/Ca concentration ratios are for the mineral and solution, expressed on either a weight or molar basis. The terms D_{Sr} ($=\text{Sr}_{\text{mineral}}/\text{Sr}_{\text{solution}}$) and D_{Ca} refer to the single element distribution coefficient of Sr and Ca, respectively. The concentration of Sr in calcite, aragonite or dolomite is therefore a function of the $K_D^{\text{Sr-Ca}}$ value for each mineral and the Sr and Ca concentrations of the solution from which it forms. Trace element distribution coefficient values of less than 1 indicate that the mineral phase discriminates against incorporation of the trace element relative to the major element compared with the (trace element)/(major element) ratio in the solution phase. Values of greater than 1 indicate preferential trace element incorporation into the mineral. The use of the abundance and isotopic composition of a trace element for quantitative modelling of diagenetic processes warrants a careful consideration of K_D values.

Experimental and empirical determinations of $K_D^{\text{Sr-Ca}}$ values

Quantification of Sr–Ca substitution in carbonates is achieved by two methods: (1) growing carbonate minerals in synthetic solutions under controlled laboratory conditions, with the solution and mineral being analysed for Sr and Ca concentrations; and (2) empirical analysis of natural systems where contemporaneous carbonate minerals and fluids are accessible. Empirical determinations offer the application to complex natural environments that are difficult to simulate in the laboratory. Experiments offer potential

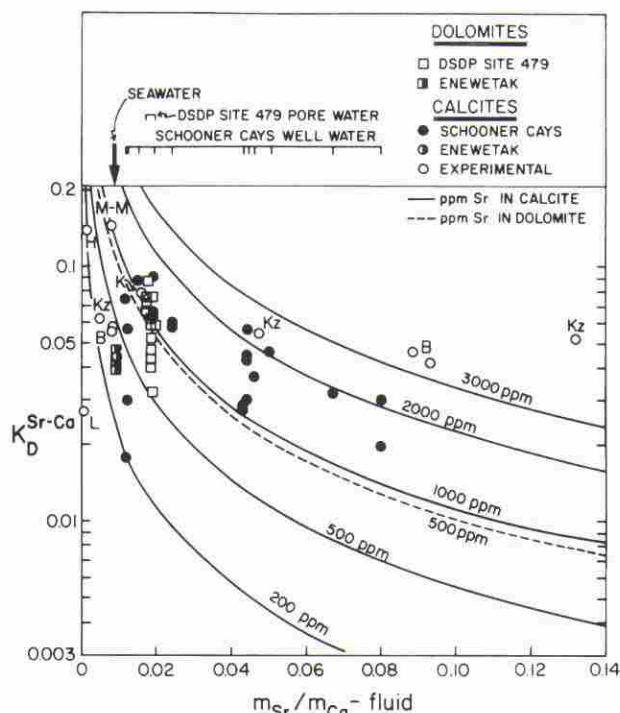


Fig. 1. $K_D^{\text{Sr-Ca}}$ value vs. molar Sr/Ca ratio in fluid. Contours are for calcite and dolomite Sr concentrations in p.p.m. and are determined using Eq. (1). Given any two of the three values ($K_D^{\text{Sr-Ca}}$, Sr/Ca ratio in fluid or carbonate mineral Sr concentration), the third value can be calculated using Eq. (1) and estimated by inspection from this diagram. Reported $K_D^{\text{Sr-Ca}}$ -fluid Sr/Ca pairs are plotted for studies of experimental and natural systems. $K_D^{\text{Sr-Ca}}$ values for natural systems determined from analysis of (1) dolomites and pore waters from cores at DSDP site 479 (Baker & Burns, 1985), (2) calcites and well waters from Schooner Cays, Bahamas (Budd, 1984) and (3) dolomites and calcites from Enewetak Atoll and seawater (Saller, 1984a,b; Quinby-Hunt & Turekian, 1983). Natural fluid compositions (seawater, DSDP pore waters and Schooner Cays well water) are plotted relative to abscissa only. Experimental values (\circ) are determined by the following studies: B=Baker *et al.* (1982): two determinations each at 60 and 80°C; H=Holland *et al.* (1964) and L=Lorens (1981): 25°C value for lowest precipitation rate, equilibrium fluid compositions not reported; K=Kitano *et al.* (1971): average $K_D^{\text{Sr-Ca}}$ value at 20°C; Kz=Katz *et al.* (1972): average $K_D^{\text{Sr-Ca}}$ value for selected experiments at high and low fluid Sr/Ca ratios, all at 40°C; M-M=Mucci & Morse (1983): average $K_D^{\text{Sr-Ca}}$ value using synthetic fluid with seawater composition.

control on the establishment of equilibrium as well as the flexibility of testing the effects of variables such as temperature, pressure, precipitation rate and solution composition. Both approaches have yielded a wide range of $K_D^{\text{Sr-Ca}}$ values (Fig. 1).

Aragonite

Empirical determinations of $K_D^{\text{Sr-Ca}}$ values are least ambiguous when using analyses of seawater and unaltered marine minerals, such as aragonite marine cements and skeletal material. Experimental results and empirical observations on modern and fossil aragonite skeletons (Kinsman, 1969; Kinsman & Holland, 1969; Amiel *et al.*, 1973; Veizer, 1983) indicate an aragonite-solution $K_D^{\text{Sr-Ca}}$ value of approximately 1. Skeletal secretion mechanisms and metabolic fluid compositions vary between species, however, and these biological effects can affect the trace metal partitioning behaviour (and effective $K_D^{\text{Sr-Ca}}$ values) of biogenic carbonates. Studies of natural and experimentally grown scleractinian corals show a temperature dependence of the $K_D^{\text{Sr-Ca}}$ value for skeletal aragonite that varies with species (Smith *et al.*, 1979; Beck *et al.*, 1992). For example, the temperature dependence for *Porites lobata* is expressed as

$$T (^{\circ}\text{C}) = 171.6 - 16013 \times (\text{Sr}/\text{Ca})_{\text{molar}} \quad (2)$$

This relationship can be used, along with high-precision determinations of Sr/Ca ratios in well-preserved fossil aragonite corals, to construct a record of seawater palaeotemperatures to within $\pm 0.5^{\circ}\text{C}$ (Beck *et al.*, 1992).

Calcite

Strontium partitioning between calcite and aqueous solutions has been determined in the laboratory by several methods. The direct precipitation of calcite overgrowths on high-Mg calcite seeds from seawater solutions yielded a $K_D^{\text{Sr-Ca}}$ value of 0.146 (Mucci & Morse, 1983), while the direct precipitation of low-Mg calcite from ammoniacal CaCl_2 - SrCl_2 solutions yielded a value of 0.14 (Holland *et al.*, 1964). Two independent experimental studies of the recrystallization of aragonite to calcite in a synthetic fluid of seawater composition give an average $K_D^{\text{Sr-Ca}}$ value of 0.045 when the results are extrapolated to 25°C (Katz *et al.*, 1972; Baker *et al.*, 1982). The direct precipitation study determined an inverse correlation between $K_D^{\text{Sr-Ca}}$ values and temperature (Holland *et al.*, 1964), while the aragonite-calcite recrystallization experiments yielded only a minor direct correlation between these parameters (Katz *et al.*, 1972; Baker *et al.*, 1982).

Experimental studies demonstrate that precipitation rate has an important effect on K_D values. Calcite was precipitated at controlled rates as overgrowths on calcite seed crystals from CaCl_2 -

NaCl - NaHCO_3 solutions at 25°C (Lorens, 1981) and as direct precipitates from $\text{Ca}(\text{HCO}_3)_2$ - SrCl_2 solutions (Kitano *et al.*, 1971). For high rates of precipitation, K_D values for Sr, Mn, Co and Cd approach unity due to the diminished ability of the more rapidly forming calcite lattice to distinguish trace divalent cations from Ca^{2+} in solution. The distribution coefficient for Sr-Ca partitioning varied from 0.03 for the slowest precipitation rates to 0.1 for rates that are two orders of magnitude higher (Lorens, 1981; Kitano *et al.*, 1971). Experiments using high-Mg calcite overgrowths yielded (1) a precipitation rate control on $K_D^{\text{Sr-Ca}}$ value for a given solution Mg^{2+} concentration, (2) a direct correlation between the MgCO_3 content (2.7–11.2 mol% MgCO_3) of the overgrowths and $K_D^{\text{Sr-Ca}}$ and (3) high $K_D^{\text{Sr-Ca}}$ values of 0.20–0.44 compared with other experimental studies that use low-Mg calcite (Mucci & Morse, 1983; Morse & Bender, 1990). The incorporation of the relatively small Mg^{2+} ion apparently results in expansion of the Ca sites in the calcite lattice, which in turn results in increased Sr substitution (Mucci & Morse, 1983). A dependence of $K_D^{\text{Sr-Ca}}$ values on Mg content was also noted for Holocene marine calcites by Carpenter & Lohmann (1992). The results of the experimental studies of Sr-Ca partitioning are presented in Fig. 1, which shows the variation in $K_D^{\text{Sr-Ca}}$ and fluid Sr/Ca ratios. This type of diagram may be used to illustrate the factors that may account for the variability of trace element K_D values in carbonate minerals (Dickson, 1990).

Several problems exist with applying these experimental results to studies of diagenetic carbonates, including (1) the applicability of high-temperature results to low-temperature diagenesis, (2) evidence for growth mechanism control on varying K_D values during crystal growth (discussed below), (3) the high precipitation rates of most experiments relative to calcite growth rates in natural systems (e.g. Budd, 1984) and (4) the simplicity of the experimental systems with respect to their organic and inorganic compositions (e.g. Morse & Bender, 1990; Burton, 1991). In addition, Sr concentrations have been determined on experimental run products by bulk sample analysis in most studies. The potential contamination of calcite by small percentages of aragonite can have pronounced effects on the determination of calcite Sr contents (Holland *et al.*, 1964).

In contrast to mineral-melt distribution coefficients based on mineral-matrix pairs in volcanic rocks (e.g. Schnetzler & Philpotts, 1970), K_D

values based on groundwater-carbonate and fluid-inclusion-carbonate pairs in ancient strata are not as straightforward. This is due to difficulties associated with extracting the waters and determining whether they are representative of the waters which precipitated the diagenetic phases considered. In light of this, the most useful information on trace element partitioning in natural samples is obtained from modern carbonates and their coexisting pore fluids, and from well-preserved marine carbonates and modern seawater data.

Electron microprobe analyses of Sr concentrations in Holocene calcite cements from shallow boreholes on Schooner Cays in the Bahamas, and Sr and Ca analyses on waters from the same boreholes, are used to calculate K_D^{Sr-Ca} values, assuming equilibrium between water and cement (Budd, 1984). Uncertainties associated with this assumption are differences in age between the modern waters and the cements, which are up to 700 years old, and seasonal fluctuations in groundwater compositions (Budd, 1984). Strontium contents were measured by electron microprobe and atomic absorption in upper Eocene to Miocene calcite cements and dolomites from Enewetak Atoll (Fig. 1; Saller, 1986). Geochemical and petrological data indicate that these phases formed from seawater at 13–22°C (Saller, 1986). Using these data and the Sr/Ca ratio of seawater, K_D^{Sr-Ca} values for calcite may be calculated. Calcite K_D^{Sr-Ca} values based on the Schooner Cays and Enewetak data are shown as a function of solution composition in Fig. 1. The K_D^{Sr-Ca} values for these natural calcites range from 0.019–0.089 and give an average value of 0.05 ± 0.02 . Holocene marine calcite cements from Little Bahama Bank, Jamaica and Enewetak Atoll have Sr concentrations that range from 200 to 1900 p.p.m. (as compiled in Carpenter & Lohmann, 1992), which correspond to a range of K_D^{Sr-Ca} values of 0.026–0.247 for a seawater Sr/Ca value.

The lower limit of the K_D^{Sr-Ca} values determined from natural calcites is similar to the lower limit of experimental values (Fig. 1). The consistency of these results suggests that a K_D^{Sr-Ca} value of 0.03 ± 0.02 may be applicable to low-temperature diagenetic calcites that form at slow growth rates (see also Carpenter & Lohmann, 1992).

Compared to inorganic marine calcite cements, Holocene biogenic marine calcites contain approximately 1250 p.p.m. more Sr, for equivalent Mg contents, and a similar covariation between Sr and Mg concentrations (Carpenter &

Lohmann, 1992). These results suggest that biogenic calcite precipitates at a faster rate than inorganic calcite, resulting in a higher K_D^{Sr-Ca} value. Trace element partitioning in biogenic calcite is also complicated by biological fractionation, as discussed earlier for aragonite. In addition, the role of bacteria in mediating presumed inorganic carbonate mineral precipitation (Folk, 1994) may also affect trace element partitioning.

Analysis of some natural and synthetic calcite and dolomite crystals reveals complex, non-concentric trace element distributions that vary within and between time-equivalent growth sectors. These variations appear to be a complex function of crystal growth mechanism and indicate that K_D values can vary spatially and temporally within a crystal during growth (Reeder & Prosky, 1986; Reeder & Grams, 1987; Reeder & Paquette, 1989; Paquette & Reeder, 1990, 1995; Hendry & Marshall, 1991; Paquette *et al.*, 1993).

Dolomite

The difficulty in synthesizing dolomite in the laboratory at Earth surface conditions (McKenzie *et al.*, 1995, is a recent exception) has led to a dearth of experimental studies of trace element partitioning between dolomite and solution. Two high-temperature (>150°C) experimental studies on dolomite-water Sr partitioning yield a single element distribution coefficient value (D_{Sr} ; Eq. 1) of 0.048 (Jacobson & Usdowski, 1976) and a K_D^{Sr-Ca} value of 0.023–0.028 (Katz & Matthews, 1977). Empirical, low-temperature K_D^{Sr-Ca} values for dolomite are calculated from analyses of dolomites and pore waters from DSDP site 479 (Baker & Burns, 1985). These calculations assume steady-state conditions for the pore water geochemistry at this site since the time of dolomitization of these late Quaternary diatomaceous oozes. The results for 19 dolomite-fluid pairs give a mean value of 0.060 ± 0.014 (1σ , Fig. 1). Using data for dolomites of marine origin from Enewetak Atoll (Saller, 1984a,b), a K_D^{Sr-Ca} value for dolomite of 0.039–0.048 is determined (Fig. 1). The DSDP and Enewetak data yield K_D^{Sr-Ca} values for dolomite that are similar to the values derived for experimental and natural calcites.

Sr-Ca variations in Bahamian dolomites of proposed marine origin are used to determine the following empirical relationship between dolomite stoichiometry and K_D^{Sr-Ca} , using a seawater Sr/Ca ratio:

$$K_D^{Sr-Ca} = [(50+20X)/Ca_{dolo}]/(Sr/Ca)_{fluid} \quad (3)$$

where X is excess mol% CaCO_3 and concentrations are expressed in p.p.m. (Vahrenkamp & Swart, 1990). This equation is used to calculate (1) a $K_D^{\text{Sr-Ca}}$ value of 0.0118 for stoichiometric dolomite, which is considerably lower than the values discussed above (Fig. 1), and (2) a $K_D^{\text{Sr-Ca}}$ value of 0.051 for dolomite with 60 mol% CaCO_3 , which is consistent with the $K_D^{\text{Sr-Ca}}$ values derived above from recent dolomites and the calcian compositions of the recent dolomites. This relationship between dolomite stoichiometry and $K_D^{\text{Sr-Ca}}$ may be due to kinetic effects, whereby rapid precipitation rates increase both the effective $K_D^{\text{Sr-Ca}}$ value, as discussed earlier for calcite, and the incorporation of Ca into Mg sites in dolomite (Vahrenkamp & Swart, 1990). As with all empirical determinations of $K_D^{\text{Sr-Ca}}$ values that are based on data for marine carbonates and sea-water, this relationship between distribution coefficient and stoichiometry is based on the assumption that the dolomites precipitated from a fluid with the same Sr/Ca ratio as seawater. Diagenetic reactions mediated by marine pore waters or mixed meteoric-marine pore waters, however, may alter the Sr/Ca and Mg/Ca ratios of the fluids involved in dolomitization (e.g. Baker & Burns, 1985; Swart & Ginsburg, 1991; Cander, 1994; Kimbell & Humphrey, 1994). The wide range of Sr contents found for the Bahamian marine dolomites and the susceptibility of dolomite to recrystallization underscore the difficulty in using Sr contents to constrain dolomitization models for ancient occurrences.

Some modern dolomites of proposed marine (Baker & Burns, 1985; Carballo *et al.*, 1987; Dawans & Swart, 1988) and evaporative-marine (Butler, 1969; Behrens & Land, 1972) origin have high Sr contents, in excess of 600 p.p.m., and Ca-rich compositions. Precipitation kinetics may play an important role in determining dolomite Sr contents. Dawans & Swart (1988) suggest that both high- and low-Sr dolomites can form during early diagenesis, dependent upon rates of fluid flow and crystal growth. Bein & Land (1983) argue that such high Sr dolomites (500–700 p.p.m.) form during early diagenesis under relatively high growth rates, and therefore higher effective $K_D^{\text{Sr-Ca}}$ values may be applicable. These high-Sr dolomites may then be more slowly transformed by multiple recrystallization events to a more stoichiometric dolomite, whereby a lower effective distribution coefficient may be applicable. This would lead to lower Sr contents (100–200 p.p.m.) in these later dolomites. Other factors that

may lead to the high Sr content of some early diagenetic dolomite samples include:

1 Many high-Sr dolomite suites were analysed by whole-rock methods. As discussed earlier in the section on calcite, small percentages of aragonite, high-Mg calcite or celestite can also significantly affect dolomite Sr abundances (Bein & Land, 1983). A sample consisting of 3% aragonite with 10 000 p.p.m. Sr and 97% dolomite with 200 p.p.m. Sr, for example, will give a whole-rock Sr concentration of 500 p.p.m. These potential effects can be evaluated by petrographic, X-ray diffraction, and electron microprobe analysis.

2 As discussed above, pore waters that migrate through carbonate sediments during or subsequent to dolomite formation may have Sr/Ca ratios as much as an order of magnitude higher than seawater, as observed in groundwaters from settings such as Barbados and Schooner Cays that have metastable mineral assemblages (Harris & Matthews, 1968; Budd, 1984; Banner *et al.*, 1994). Strontium contents of up to 3000 p.p.m. in dolomites from the Falmouth Formation of Jamaica are attributed to formation from groundwaters enriched in Sr due to aragonite dissolution and calcite precipitation (Land, 1973).

3 Strontium contents in DSDP dolomites are proposed to vary as a function of the stoichiometry of the dolomitization reaction (Baker & Burns, 1985). In calcareous sediments, for example, the stoichiometry may involve 2 moles of calcite dissolving to produce 1 mole of dolomite, thereby elevating pore water Ca contents. Dolomite formed from seawater will have 250 p.p.m. Sr for a $K_D^{\text{Sr-Ca}}$ value of 0.06, and continued dolomitization via this reaction stoichiometry will lower the pore water Sr/Ca ratio and produce dolomites with <250 p.p.m. Sr. An alternative reaction is the mole for mole replacement of calcite by dolomite. In this case, pore fluid Ca contents will remain constant, and fluid Sr/Ca ratios will rise to 2–5 times the seawater value as dolomitization proceeds. This reaction stoichiometry will produce dolomites with 500–1300 p.p.m. Sr.

Note from the curves in Fig. 1 that for equal $K_D^{\text{Sr-Ca}}$ values for dolomite and calcite, the dolomite will incorporate approximately half as much Sr as the calcite. This difference is based on dolomite having approximately half as much Ca (217 000 p.p.m.) as calcite (400 000 p.p.m.). From the correlation between metal-oxygen bond lengths and ionic radii for various cations in dolomite (Reeder, 1983), it is expected that the large Sr^{2+} ion should substitute almost exclusively for Ca in the A site in dolomite. This is

consistent with the substitution of Sr for Mg in magnesite at concentrations of only 2 or 3 p.p.m. (Patterson, 1972; Bein & Land, 1983). An experimentally determined, single-element D_{Sr} value for dolomite is approximately half the value determined for calcite (Jacobson & Usdowski, 1976), and is consistent with the ionic radii inferences and the magnesite data.

Strontium in natural waters

Strontium concentrations in natural waters vary widely, from part per billion levels in river waters to up to 2000 p.p.m. in subsurface brines (Goldstein & Jacobsen, 1987; Land, 1987), and broadly correlated with salinity. Fluid Sr/Ca ratios exert a fundamental control on the Sr concentration of diagenetic carbonates. This parameter varies widely in natural fluids (Fig. 2), and it may be diagnostic of a given type or source of fluid when used in conjunction with other parameters, such as $^{87}Sr/^{86}Sr$ (Banner *et al.*, 1994). The Sr/Ca ratio will be dependent on the Sr/Ca ratios of minerals being dissolved and precipitated during fluid-rock interaction. For example, the albitization of K-feldspar and the aragonite-calcite conversion both involve substantial changes in the Sr/Ca ratio of the minerals that are destroyed and of the minerals that are formed, and therefore the Sr/Ca ratio of the fluids that control these reactions are also affected.

Strontium in diagenetic carbonates

Strontium concentrations in diagenetic carbonates range from 20 p.p.m. (Gregg & Shelton, 1989; Kaufman *et al.*, 1991) to greater than 10 000 p.p.m. (Land, 1973; Kimbell & Humphrey, 1994). As discussed in earlier sections, samples at the high end of this range typically reflect formation from a diagenetic fluid whose composition has been modified by the aragonite to calcite transformation. In ancient marine limestones, low Sr contents of 20–70 p.p.m. are common in diagenetically altered components, including recrystallized allochems, micrite and pore-filling cements. These low Sr concentrations are difficult to explain in the context of Sr/Ca data for natural fluids and K_D^{Sr-Ca} values. Figure 2 illustrates the variations in Sr concentrations in calcite and dolomite as a function of K_D^{Sr-Ca} and fluid composition, and the range of Sr/Ca data reported for fluids from surficial and burial environments. Note that most saline fluids in burial environments have significantly higher Sr/Ca ratios than

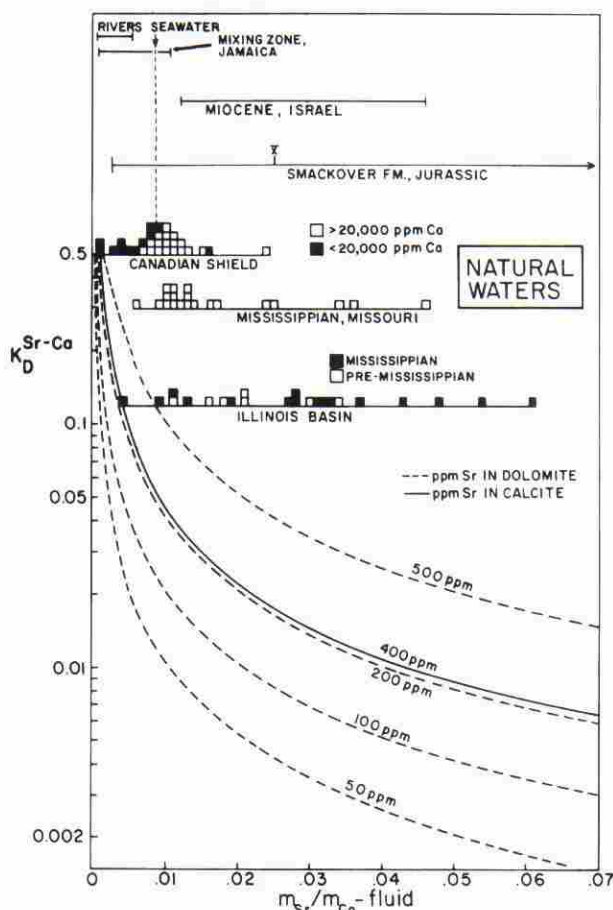


Fig. 2. K_D^{Sr-Ca} value vs. molar Sr/Ca ratio in fluid, contoured for calcite and dolomite Sr concentrations as in Fig. 1. Natural water compositions, represented by histograms and ranges of m_{Sr}/m_{Ca} values, are plotted relative to abscissa only. Note that over the range of reported K_D^{Sr-Ca} values of 0.01–0.2 (Fig. 1), calcite and dolomite formed from nearly all subsurface fluid compositions will have much greater than 50 p.p.m. Sr. Data sources as follows: seawater, Quinby-Hunt & Turekian (1983); rivers from Wadleigh *et al.* (1985); mixing zone of Jamaica, O'Neil (1974); brines from Mavqii clastics and evaporites, Upper Miocene, Israel coastal plain, from Starinsky *et al.* (1983); brines from Jurassic Smackover Fm. from Trout (1974); brines from Precambrian Sheild of Canada from Frapet *et al.* (1984); saline groundwaters from Ordovician and Mississippian carbonates and sandstones from Missouri from Carpenter & Miller (1969); Illinois Basin brines from Stueber *et al.* (1987).

seawater. The formation of diagenetic carbonates with 20–70 p.p.m. Sr from such fluids requires low K_D^{Sr-Ca} values of less than 0.01 (Fig. 2). These low values may reflect either or both of the following: (1) the experimentally and empirically determined K_D^{Sr-Ca} values discussed in preceding sections (Fig. 1) are not representative of values pertinent to natural burial environments; and (2)

the high-Sr/Ca pore waters that have been sampled from sedimentary basins are not representative of fluids that formed the diagenetic carbonates. If the low Sr concentrations of many ancient carbonates reflect lower effective K_D^{Sr-Ca} values at higher temperatures associated with burial, then a possible explanation for this lower effective K_D^{Sr-Ca} value may be the sixfold increase in the value of the association constant of the $SrHCO_3^+$ ion pair at 80°C relative to 25°C, compared with the near-constant value of the association constant of the $CaHCO_3^+$ ion pair over the same temperature range (Plummer & Busenburg, 1982; Busenburg *et al.*, 1984). These differences would create a lower thermodynamically effective Sr concentration in diagenetic fluids in burial environments. Low Sr contents observed in diagenetic carbonates from near-surface (low-temperature) environments, on the other hand, may simply reflect low fluid Sr/Ca ratios (e.g. Vahrenkamp & Swart, 1990).

In summary, studies using trace element distribution coefficients are subject to a number of uncertainties involved in the determination of K_D values, and K_D values used for trace element modelling should be considered as effective distribution coefficients, rather than as equilibrium distribution coefficients. This discussion has shown that the Sr concentration of a diagenetic carbonate sample may be a consequence of any combination of a variety of factors, including diagenetic fluid composition, temperature, biological effects, precipitation rate, extent of recrystallization, type of mineral-solution reaction and crystal growth mechanism. Given the uncertainties associated with these multiple controlling factors, the following sections discuss how useful constraints on diagenetic processes and fluid compositions may be obtained through (1) the combined use of trace element and isotopic variations, and (2) application of quantitative models for fluid-rock interactions.

STRONTIUM ISOTOPE GEOCHEMISTRY OF CARBONATES

Variations in the Sr isotopic composition of ancient limestones and dolostones can be used as a stratigraphic correlation tool and as an indicator of fluid compositions and mechanisms of diagenesis. Unlike trace elements and stable C and O isotopes, Sr isotope compositions of carbonate minerals directly record fluid isotope compositions. The effects of mass-dependent Sr isotopic

fractionation during crystal growth from solution are negligible owing to mass spectrometric data reduction procedures that correct measured isotope ratios for fractionation (Banner & Kaufman, 1994). High-precision Sr isotope studies of Pleistocene foraminifera show no interspecies $^{87}Sr/^{86}Sr$ variation (Henderson *et al.*, 1994).

Natural waters have a wide range of Sr isotope compositions. Pore waters from siliciclastic sections of sedimentary basins commonly have $^{87}Sr/^{86}Sr$ values that are significantly greater than estimates for Phanerozoic seawater (i.e. >0.7095), and are indicative of interaction with Rb-rich clay minerals and feldspars that are common constituents in these sediments (e.g. Stueber *et al.*, 1984, 1987). K-feldspars and micas in crystalline basement rocks also impart high $^{87}Sr/^{86}Sr$ values to groundwaters derived from these environments (e.g. McNutt *et al.*, 1984, 1990), whereas interaction with plagioclase feldspar may produce relatively low $^{87}Sr/^{86}Sr$ values (Franklyn *et al.*, 1991). Fluids that have mantle-derived volcanic rocks as a source of dissolved Sr will have $^{87}Sr/^{86}Sr$ values that are significantly lower than Phanerozoic marine sediments (i.e. <0.7068; Goldstein & Jacobsen, 1987). Meteoric waters and brines that interact with marine carbonates may inherit Sr isotope compositions that are diagnostic of the age of the carbonates (e.g. Müller *et al.*, 1991; Banner *et al.*, 1994). Variations in mineral weathering rates and soil development may also control groundwater and surface water $^{87}Sr/^{86}Sr$ values (Blum *et al.*, 1994). The $^{87}Sr/^{86}Sr$ values of these natural fluids may be preserved in recrystallized carbonates and carbonate cements that form during fluid-rock interaction, providing important clues to the source of diagenetic fluids and the nature of the interaction process.

Analytical methods

Recent advances in thermal ionization mass spectrometry have been applied to the analysis of marine carbonates. Multiple-collector instruments have reduced analysis time and analytical uncertainties associated with unstable ion beams such that $^{87}Sr/^{86}Sr$ ratios are routinely measured with an internal precision of $< \pm 2 \times 10^{-5}$ ($2\sigma_{\text{mean}}$). Analytical resolution has been further improved through measurement of multiple replicate samples (e.g. Capo & DePaolo, 1990). These techniques have been used to enhance the potential resolution of Sr isotope stratigraphy. Continued advances in ionization and detection methods will allow submilligram-sized carbonate

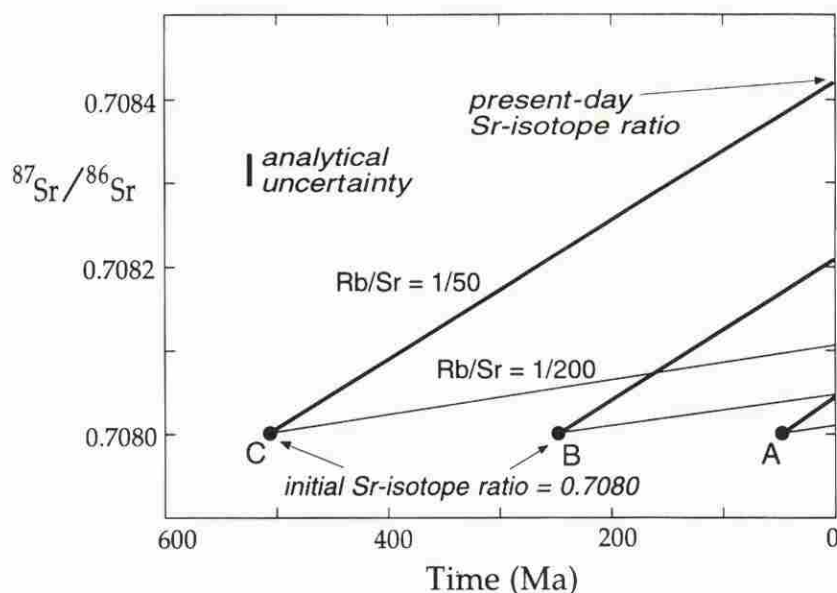


Fig. 3. Sr isotope evolution diagram for three hypothetical carbonate rocks. Sample ages are A, 60 Ma; B, 250 Ma; and C, 510 Ma. All samples had $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7080 at the time of their formation (i.e. initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$). For each sample, two Sr isotope evolution pathways are shown, one for a Rb/Sr ratio of 1:50 (bold line) and one for a Rb/Sr ratio of 1:200 (light line). Note that for nearly all sample ages and Rb/Sr ratios illustrated, present-day $^{87}\text{Sr}/^{86}\text{Sr}$ values are significantly greater than the initial $^{87}\text{Sr}/^{86}\text{Sr}$ values. A typical analytical uncertainty of $\pm 2 \times 10^{-5}$ is shown. This illustrates the importance of determining the concentrations of, and sites for, Rb and Sr in applying Sr isotope studies to ancient carbonates.

samples with low Sr concentrations, such as micro-sampled cement zones in limestones, to be analysed for $^{87}\text{Sr}/^{86}\text{Sr}$.

As technical advances allow us to address new questions and refine geological models using the Sr isotope geochemistry of sedimentary carbonates, some fundamental considerations regarding the purity of the samples to be analysed should be undertaken. Inclusions of Sr-rich minerals such as aragonite, celestite, strontianite and secondary fluid inclusions can have different Sr isotope compositions than the carbonate phase of interest and therefore will significantly affect whole-rock analyses. Some whole-rock carbonate samples may be shown to contain a single diagenetic phase using petrographic and electron microprobe analyses. On the other hand, the same techniques may demonstrate that a single 50- μm cement crystal in another sample has numerous growth zones that record precipitation from multiple diagenetic fluids. Individual samples that are each recovered from two or more diagenetic zones will have compositions that lie along mixing curves on isotope and trace element covariation diagrams. As will be discussed below, appropriate models can be constructed to discriminate between samples related by such mixing of different end-member diagenetic phases

and samples of single diagenetic phases that are related by processes of fluid-rock interaction.

The *in situ* decay of ^{87}Rb to produce ^{87}Sr also requires careful evaluation in ancient sedimentary carbonates. As carbonate minerals do not readily incorporate Rb^+ into Ca^{2+} structural sites, pure carbonates should contain negligible ^{87}Sr from *in situ* decay of ^{87}Rb , even after several hundred million years. Significant amounts of Rb, however, may reside in non-carbonate inclusions such as clay minerals, K-feldspar, mica (McNutt *et al.*, 1990), oxides (Baturin, 1987) and fluid inclusions (Shepherd & Darbyshire, 1981). Small percentages of these contaminants, especially clay minerals, may significantly affect the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of carbonate samples, even when ion exchange and gentle leaching procedures are used (e.g. Banner *et al.*, 1988b; Cander, 1994; I. P. Montañez *et al.*, unpublished observation). To illustrate the effects of such contaminants on Sr isotope analyses, the Sr isotope evolution of carbonate samples of three different ages (60, 250 and 510 Ma) are shown in Fig. 3. Strontium isotope evolution lines and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are calculated using the following equation:

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{today}} = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{initial}} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \times (e^{\lambda t} - 1), \quad (4)$$

where $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{today}}$ is the value that is measured, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{initial}}$ refers to the Sr isotope composition at the time of formation (t) of the sample, and λ is the decay constant for ^{87}Rb ($1.42 \times 10^{-11} \text{ yr}^{-1}$; see review in Faure, 1986). For each age considered, evolution lines are shown for samples having Rb/Sr ratios of 1:50 and 1:200. These ratios are equivalent to samples having 50 and 200 p.p.m. Sr, which is a range that encompasses many ancient diagenetic carbonates, and a Rb content of 1 p.p.m., which can be contributed by less than 1% clay minerals in a whole-rock sample. Significant differences exist between the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a given sample, which is the value of interest, and the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the same sample, which is the value that is measured (Fig. 3). These differences are larger than the analytical uncertainty for samples of all ages shown. Therefore, Sr isotope analysis of carbonate rocks with as little as 1 p.p.m. Rb may produce inaccurate results unless a proper correction for the ^{87}Sr produced from the decay of ^{87}Rb can be made. Rubidium and Sr concentration measurements, made via a method such as isotope dilution mass spectrometry or inductively coupled plasma mass spectrometry, are required to determine whether this correction is significant relative to the analytical uncertainty of the $^{87}\text{Sr}/^{86}\text{Sr}$ measurement.

If a significant correction to the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is required, then the validity of the correction must be evaluated. Uncertainties involved in this correction may be considerable, and are dependent on knowledge of the following factors regarding the non-carbonate contaminants in the sample: time of formation, depositional and diagenetic history, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Banner *et al.*, 1988b). Given the fine-grained nature of siliciclastic components in carbonates, it is insufficient to dismiss the necessity for such a correction based on the lack of Rb-rich phases observed in thin section. Significant advances have been made in the establishment of a high-resolution $^{87}\text{Sr}/^{86}\text{Sr}$ record of Cenozoic seawater using marine carbonates, and in interpreting links between this record and climatic, tectonic and eustatic variations (e.g. DePaolo & Ingram, 1985; Raymo *et al.*, 1988; Capo & DePaolo, 1990; Hodell *et al.*, 1990; Edmond, 1992; Blum & Erel 1995). The analytical considerations discussed here merit scrutiny if similar advances are to be made for Palaeozoic and Precambrian marine carbonates. The magnitude of Rb corrections, as well as the uncertainties associated with them, are magnified compared with Cenozoic studies because

Palaeozoic and Precambrian limestones have (1) a longer history of *in situ* decay of ^{87}Rb , (2) lower Sr contents and higher Rb/Sr ratios and (3) more extensive diagenetic mobilization of Sr and alteration of primary marine isotopic signatures. Failure to account for these 'Rb effects' may result in a number of incorrect conclusions, including (1) interpreting a non-marine origin for a well-preserved marine limestone, (2) misinterpreting the composition of diagenetic fluids and (3) constructing an inaccurate Sr-isotope stratigraphy.

APPLICATIONS TO STUDIES OF FLUID-ROCK INTERACTION

Mechanisms of fluid-rock interaction

Carbonate sediments are modified during and subsequent to deposition by processes that include: (1) replacement involving no change in mineralogy (recrystallization), (2) mineralogical transformation via dissolution-precipitation reactions and (3) cementation, or growth, of diagenetic carbonate minerals in pre-existing pore spaces. Our knowledge of these processes, which involve advective and diffusive transport, surface-solution interaction, sorption, exchange between micropore and macropore environments, etc., is incomplete. A quantitative approach, however, may be used in some cases to distinguish between these processes.

Quantification of trace element and isotope variations in water-rock systems

Through the use of mass-balance relationships and distribution coefficients, the variations that occur in the concentration and isotopic composition of Sr during fluid-rock interaction can be quantified. Equations can be developed that quantify elemental and isotopic mass balance in a closed system represented by a fluid weight fraction, F , and a solid weight fraction, $1 - F$ (as outlined in Banner & Hanson, 1990). Upon homogeneous equilibration of the solid and fluid, a new solid composition is calculated, and the process is repeated by introduction of a new, unreacted fluid phase. This repetition, or iteration, of the closed system represents open-system fluid-rock interaction (Land, 1980). The closed-system equations are as follows.

Upon infiltration of a fluid into a given volume of rock, and prior to any interaction, the

concentration of Sr in the composite fluid–rock system, C_0^{Sr} , is given by a mass-balance equation:

$$C_0^{Sr} = F \times C_{f,0}^{Sr} + (1 - F) \times C_{s,0}^{Sr} \quad (5)$$

$C_{f,0}^{Sr}$ is the Sr concentration in the fluid before interaction, and $C_{s,0}^{Sr}$ is the Sr concentration in the solid before interaction. Through substitution of the K_D^{Sr-Ca} and D^{Sr} expressions from Eq. (1) in Eq. (5) and rearrangement, the Sr concentration of the solid at equilibrium may be expressed as (see Banner & Hanson, 1990)

$$C_s^{Sr} = C_0^{Sr} / [F/D^{Sr} + (1 - F)] \quad (6)$$

For homogeneous equilibrium, the Sr isotope ratio in the solid phase, fluid phase and in the entire system will be the same. A mass-balance expression for the Sr isotopic composition of the solid–fluid system ($^{87}Sr/^{86}Sr)_0$, will therefore also give the $^{87}Sr/^{86}Sr$ value of the solid upon equilibration:

$$\begin{aligned} (^{87}Sr/^{86}Sr)_0 = \\ \frac{(^{87}Sr/^{86}Sr)_{f,0}(C_{f,0}^{Sr})F + (^{87}Sr/^{86}Sr)_{s,0}(C_{s,0}^{Sr})(1 - F)}{(C_{f,0}^{Sr})F + (C_{s,0}^{Sr})(1 - F)} \quad (7) \end{aligned}$$

where $(^{87}Sr/^{86}Sr)_0$ is the Sr isotopic composition of the entire fluid–rock system considered, and $(^{87}Sr/^{86}Sr)_{f,0}$ and $(^{87}Sr/^{86}Sr)_{s,0}$ are the Sr isotopic compositions of the fluid and solid phase, respectively, prior to any interaction. Equations (6) and (7) are used iteratively to calculate changes in the trace element and isotopic composition of a carbonate rock during progressive water–rock interaction. Analogous equations may be derived for modelling other isotopic and trace element systems (Banner & Hanson, 1990).

The mass-balance approach outlined above simulates a sequence of recrystallization steps. During each step, the pore fluid attains isotopic equilibrium with the rock before it is displaced by the next pore volume of fluid. This approach has been applied to modelling recrystallization processes in dolostones (Banner *et al.*, 1988a; Montañez & Read, 1989; Gao, 1990; Kaufman *et al.*, 1991; Winter *et al.*, 1995), foraminifera grainstones (Budd & Hiatt, 1993) and marine calcite cements (Douthit *et al.*, 1993). Uncertainties involved in these models arise from limits on our understanding of the nature of diagenetic processes in natural carbonate aquifers, in terms of (1) pertinent values for parameters such as distribution coefficients, porosity, water-to-rock ratios and fluid fluxes, (2) the extent of conduit vs. matrix flow and diffusive vs. advective ion transport, (3) the efficiency of water–rock interaction

processes (Cander, 1995), (4) the scale of transport of calcium carbonate (Morse & McKenzie, 1991) and trace metal constituents in solution, (5) the extent to which diagenesis proceeds by cementation vs. replacement and (6) the manner in which diagenetic fluids evolve during alteration of carbonates. Through a quantitative consideration of trace element and isotope data, however, model pathways can be constructed that minimize the effects of these variables. The model calculations may also be adapted to simulate the effects of some of these uncertainties pertinent to real systems, an example of which is discussed below. The evolution of groundwater compositions during processes of dissolution, recrystallization, mineralogical transformation and fluid mixing may also be simulated by the same mass-balance approach (e.g. Banner *et al.*, 1989, 1994; Cander, 1994; Kimbell & Humphrey, 1994).

Thin-film microenvironment vs. bulk recrystallization mechanisms

Two models have been proposed for the mechanism of exchange of ions between aquifer pore fluids and marine carbonate grains during diagenesis. In the bulk recrystallization model of Morrow & Mayers (1978), ions (e.g. Sr^{2+}) in the bulk solution of the carbonate aquifer are advectively exchanged with ions at reaction sites in the carbonate grains during dissolution–precipitation or recrystallization reactions. The diagenesis of Sr-rich marine carbonate sediments by this mechanism requires 10^5 pore volumes of meteoric water to produce the low Sr contents of ancient limestones. The alternative ‘thin-film’ model involves the diffusion of dissolved Sr from semi-isolated, thin-film ‘micropore’ environments, which are adjacent to reaction sites in the carbonate grains, to ‘macropore’ environments that are in advective communication with the bulk aquifer solution. This model has been applied to ancient carbonates through theoretical and case studies by Pingitore (1976, 1982), Veizer (1978, 1983), Given & Lohmann (1984) and Saller & Koepnick (1990). This model stemmed in part from an attempt to reconcile the large number of fluid pore volumes and bulk recrystallization events involved in the bulk recrystallization model with the fine-scale textures preserved in carbonate rocks (Veizer, 1978). An Sr concentration gradient is established between the micropore (Sr-rich, thin-film fluid) and macropore (Sr-poor, dilute meteoric water of bulk aquifer) environments. The gradient dictates that the newly dissolved Sr

will diffuse away from the micropore environment surrounding the Sr-rich carbonate grains. This 'one-way street' for Sr in the thin-film model serves to produce successively lower Sr contents in the diagenetic products, and does not require large numbers of pore volumes of fluid to pass

through the micropore environments. As discussed by Drever (1988) and Veizer (1983), the relative rates of dissolution-precipitation reactions, aqueous diffusion and advective transport of trace element species in the aquifer will determine the importance of each model process in governing the trace element concentration of a diagenetic carbonate.

The quantification of the simultaneous variations in trace element and isotopic compositions that occur during fluid-rock interaction can be used to discriminate between these rate-controlling mechanisms for a given suite of diagenetic carbonates. Figure 4(a) compares the results of calculations that simulate changes in the Sr concentration and isotopic composition of a marine limestone for the two fluid-mineral

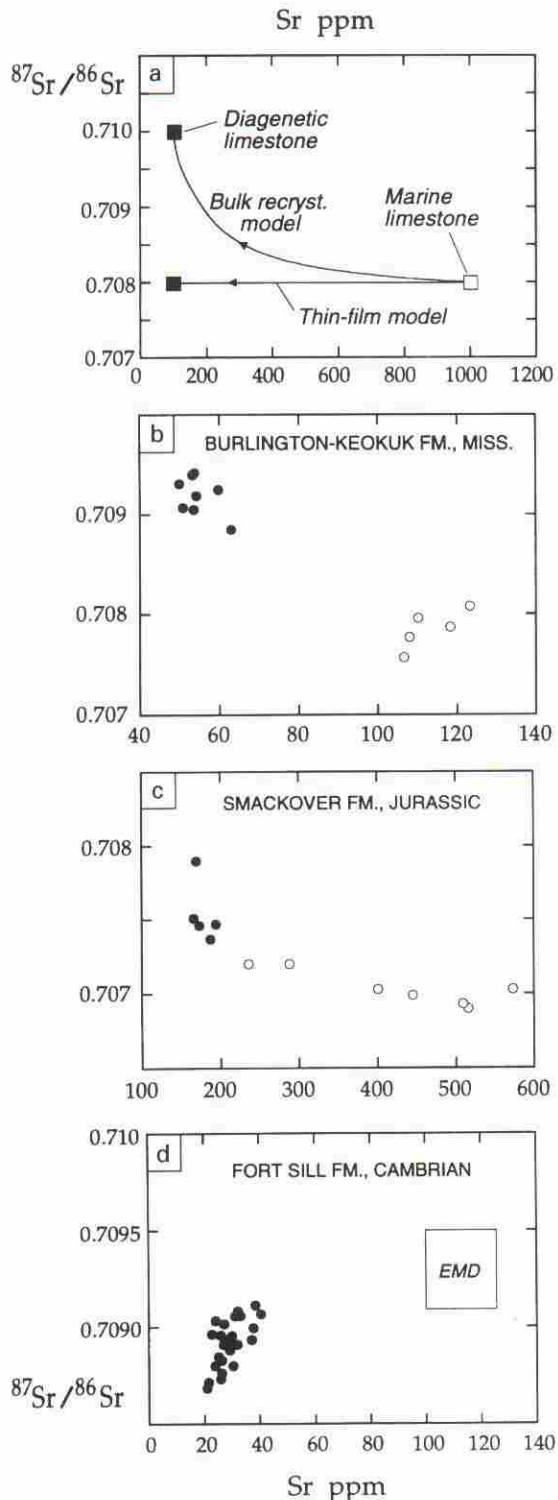


Fig. 4. Covariation in Sr isotopic composition and Sr concentration in diagenetic carbonates. (a) Results of model calculations; (b-d) data for three case studies. In all diagrams, open symbols are compositions of initial rock or early diagenetic phases and solid symbols are late diagenetic phases. Method of curve calculation discussed in text. (a) Simultaneous variations in Sr isotopic composition and Sr concentration for two fluid-rock interaction mechanisms discussed in text: the thin-film microenvironment model and the bulk recrystallization model. Initial marine limestone (open square) and fluid ($^{87}\text{Sr}/^{86}\text{Sr}=0.710$, 0.2 p.p.m. Sr, 40 p.p.m. Ca) compositions are the same in each model. Mixing curve between marine and diagenetic end-member calcites are equivalent to the fluid-rock interaction pathways shown for each model when the end-members are fixed (see fig. 2 in Banner & Hanson, 1990). These model results indicate that an extraformational source of Sr and a concomitant decrease in Sr content would be reflected by diagenetic carbonates that formed by the bulk recrystallization mechanism. (b) Sr isotope and trace element data for Mississippian Burlington-Keokuk dolomites from Iowa, Illinois and Missouri. Open symbols represent early dolomite generation (dolomite I) and solid symbols represent late dolomite generation (dolomite II) that formed via the recrystallization of dolomite I (data from Banner *et al.*, 1988a). (c) Sr data for allochems (ooids, bivalves - open symbols) and pore-filling calcite cements (solid symbols) from Jurassic Smackover Fm., southern Arkansas (data from Stueber *et al.*, 1984). The cement data record precipitation from a diagenetic fluid with high $^{87}\text{Sr}/^{86}\text{Sr}$. The allochem compositions with relatively low Sr and high $^{87}\text{Sr}/^{86}\text{Sr}$ may be accounted for by recrystallization of original high-Sr, low- $^{87}\text{Sr}/^{86}\text{Sr}$ allochems by diagenetic fluids similar to those that precipitated the cements. (d) Sr data for Cambrian Royer Dolomite of the Fort Sill Fm., Oklahoma (data from Gao, 1990). EMD represents composition of estimated marine dolomite that was a precursor to recrystallized dolomite samples (solid symbols).

exchange mechanisms. The fluid has the same major and trace element and isotopic composition in each case. In the bulk recrystallization mode, the diagenetic products record the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ and low Sr/Ca values of the fluid because this process involves the *exchange* of Sr ions via advection between the bulk solution and the reactive surfaces of the carbonate grains in the aquifer. This recrystallization pathway is calculated as described in the previous section. In the thin-film microenvironment model, the transport of Sr ions away from carbonate grains by diffusion leaves the diagenetic products with lower concentrations of Sr. However, this new Sr concentration of the diagenetic carbonate is composed of a portion of the original population of Sr ions in the carbonate grains and therefore has an unchanged Sr isotopic composition. This diagenetic process can be graphically illustrated as a linear pathway of decreasing Sr contents and constant isotopic composition (Fig. 4a). This linear pathway will apply for this model as long as the bulk solution has a lower Sr concentration than that produced in the thin-film environment via reaction with carbonate grains.

The operation of both mechanisms in an aquifer will produce fluid-rock interaction pathways intermediate between the two end-member models shown. These theoretical isotope-trace element trends may be compared with data from natural systems. An inverse correlation between Sr isotopic composition and Sr concentration is commonly observed in suites of ancient marine platform carbonates from continental settings (e.g. Fig. 4b,c). In many cases, this trend is accounted for by extraformational basinal fluids that bear elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values derived from siliciclastic components. Positive correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr concentrations in recrystallized carbonates are less common (Fig. 4d). Such trends are attributed to diagenetic fluids that derived extraformational Sr from older carbonates with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g. Gao, 1990). Note that significant departures in $^{87}\text{Sr}/^{86}\text{Sr}$ values from estimated original marine $^{87}\text{Sr}/^{86}\text{Sr}$ values in all of these carbonate suites require that a significant fraction of the Sr in these rocks was derived by exchange of Sr with the bulk solution in the aquifer. Therefore, the thin-film mechanism played either a subordinate or early role in the diagenetic history of such a carbonate sequence.

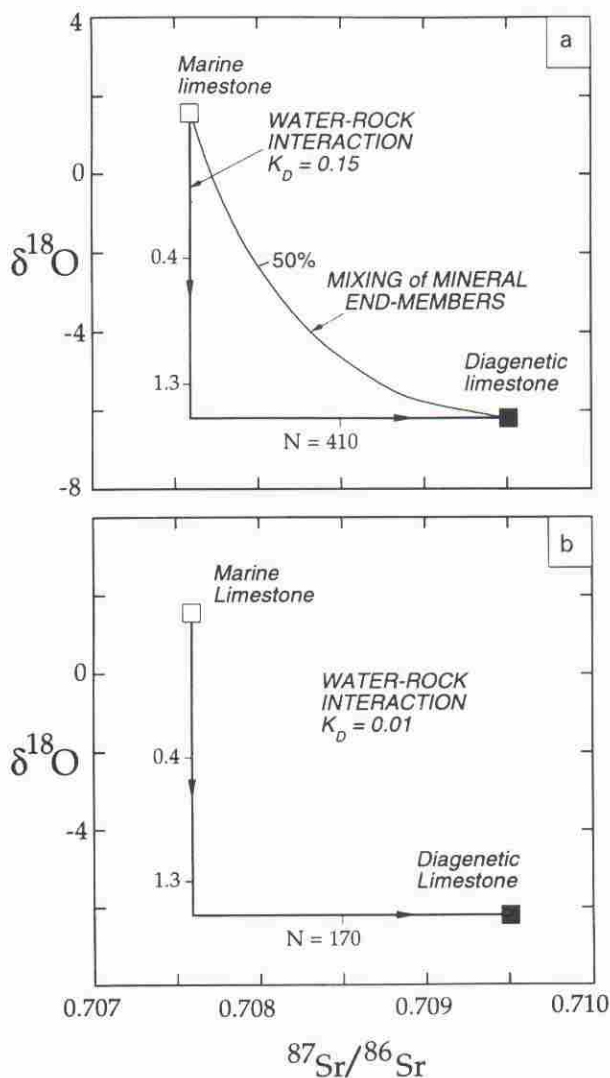
In spite of uncertainties introduced by the range of values reported for $K_D^{\text{Sr-Ca}}$, one can construct water-rock interaction pathways that

are independent of these values over the range illustrated in Fig. 1 (Banner & Hanson, 1990). For the case of freshwater-limestone interaction, large differences in the proportions of Sr and O in the fluid and rock phases results in an L-shaped pathway that does not vary in shape over an order of magnitude change in $K_D^{\text{Sr-Ca}}$ (Fig. 5). The only differences in the model results are the water-to-rock ratio values (expressed as N =water-to-rock mass ratio) required to attain a given isotopic composition of Sr along the pathway. Considering the uncertainties associated with determining the K_D values that are pertinent to natural systems, these model results underscore the difficulties involved in using the isotopic composition of an ancient diagenetic carbonate to infer an absolute value of N . The model results also illustrate the advantage in considering the simultaneous variations in multiple isotopic and trace element systems, and the *relative* values of N , in order to evaluate different processes (e.g. fluid-rock interaction vs. mineral end-member mixing) for the origin of a suite of diagenetic carbonates. The effects of these parameters must be considered for each bivariate modelling diagram.

Fluid-rock interaction vs. mixing of mineral end-members

In many case studies of diagenetic carbonates, petrographic analysis may be of limited use for identifying and sampling end-member phases in a paragenetic sequence because of a number of factors, including replacement processes that partially overprint precursor phases, and fine cement intergrowths that are not resolved with micro-sampling methods. The samples analysed in a geochemical study may thus comprise physical mixtures of two or more end-member mineral phases of depositional and/or diagenetic origin. It is important to be able to distinguish between the effects of such end-member mixing and fluid-rock interaction. An example of applying quantitative isotopic variations to make this distinction is illustrated in Fig. 6(a), which shows the simultaneous variations of C and Sr isotopes that occur during fluid-rock interaction and mineral end-member mixing. Due to the differences in the concentrations in C and Sr between a brine and an initial limestone composition, fluid-rock interaction will reset the Sr isotopic composition of the diagenetic products at relatively low N values, while the C isotopic composition will change

only at relatively high N values (Fig. 6a). On the other hand, the similar C concentrations and different Sr concentrations of original marine and altered end-member carbonate minerals will produce a mineral end-member mixing curve that is distinct from the fluid–rock interaction curve (Fig. 6a). This mixing curve represents a model for cementation of a limestone in which original components are progressively dissolved and cements are precipitated from an end-member diagenetic fluid. The model curves show that if end-member rock compositions are known, then the recrystallization (i.e. fluid–rock interaction) and cementation (i.e. mineral end-member mixing) processes are readily distinguishable. In addition, if the actual process that relates a suite of diagenetic carbonate samples is intermediate between these model processes, then the samples' compositions would lie between the two path-



ways shown. Similar distinctions between these kinds of processes also can be made based on the model pathways illustrated in Fig. 5(a).

Carbon and Sr isotopic variations in two major generations of replacement dolomite and two minor generations of vug-filling carbonate cement in the Burlington–Keokuk Fm. of mid-continent North America are illustrated in Fig. 6(b). Comparison of the dolomite data with the model curves in Fig. 6(a) suggests that the recrystallization of early dolomite I to produce dolomite II was effected by a saline fluid (i.e. relatively high dissolved Sr content) at moderate N values. This process would reset the Sr isotope compositions of the dolomites to higher values and have little effect on the C isotope compositions. The high $^{87}\text{Sr}/^{86}\text{Sr}$ values and low $\delta^{13}\text{C}$ values in the late-stage carbonate cements can be accounted for by fluids similar to those that produced dolomite II, but the fluid–rock interaction process must have occurred at significantly higher N values. Higher N values are consistent with a system in which late-stage fluids experience minimal interaction with their previously recrystallized carbonate host rocks prior to precipitation of pore-filling cements.

Carbon and Sr isotope compositions are linearly correlated in dolomites and ankerite

Fig. 5. Modelled O vs. Sr isotopic variations resulting from the recrystallization of a limestone by freshwater, illustrating the effect of $K_D^{\text{Sr-Ca}}$ values ($=0.15$ in a, and 0.01 in b) on model pathways. Water-to-rock ratios by mass ($=N$) during recrystallization are shown at given stages along the water–rock interaction paths. For each model, the original limestone has $\delta^{18}\text{O}=1.5$ ‰ (PDB), $^{87}\text{Sr}/^{86}\text{Sr}=0.7076$, and 300 p.p.m. Sr; the freshwater composition is $\delta^{18}\text{O}=-1$ ‰ (SMOW), $^{87}\text{Sr}/^{86}\text{Sr}=0.7095$, 0.6 p.p.m. Sr and 30 p.p.m. Ca; $T=40^\circ\text{C}$; porosity=20%. The diagenetic limestone composition shown will result from large extents of recrystallization (i.e. large N values) by the freshwater. 'Mixing of mineral end-members' model curve shows the distinct trend that would result if a suite of carbonate samples was related by different extents of cementation of an original marine limestone by an end-member cement having a composition represented by the diagenetic limestone. The shape of the mixing trend is controlled by the difference in Sr concentrations between the marine and diagenetic calcite end-members. For equal Sr contents in these end-members, a straight line mixing relationship would result. The water–rock interaction relationship paths in (a) and (b) demonstrate the negligible effect of variations in $K_D^{\text{Sr-Ca}}$ on the reaction pathways, and the significant effect of variations in this parameter on the absolute value of the water-to-rock ratio that would be estimated from a given Sr isotopic composition of a diagenetic carbonate.

cements in the Rotliegend Fm. of the North Sea (Fig. 6c). The model curves in Fig. 6(a) indicate that the dolomites and ankerites are not related by varying extents of brine-rock interaction. The linear relationship in the ankerite data may be interpreted to reflect either (1) precipitation from a series of mixtures between two fluids, a brine and seawater, having similar Sr/C ratios, or (2) mixing between two mineral end-members with similar Sr concentrations. Petrographic observations indicate that the ankerites are all of the same

generation of cement, which leads to the conclusion that fluid mixing is the operative process (Sullivan *et al.*, 1990). These case study examples have shown that the multiple processes that may have controlled the geochemistry of a suite of diagenetic carbonate samples can be best evaluated through a quantitative approach.

CONCLUSIONS

Strontium trace element and isotope studies provide fundamental information regarding the evolution of marine carbonates during diagenesis. Quantification of Sr trace element behaviour in natural low-temperature systems is limited by considerable variation in experimental and empirical values for the Sr–Ca distribution coefficient. An example of the uncertainty that results from this variation is the lack of reconciliation between the relatively low Sr concentrations in ancient diagenetic carbonates and the high Sr/Ca ratios of most present-day subsurface fluids. However, a quantitative approach towards evaluating the simultaneous variations in Sr concentrations, Sr isotopic compositions, and other trace element and isotopic parameters can be used to distinguish between different diagenetic fluids, different mineral–solution reaction mechanisms, and between the varied processes of fluid–rock interaction, fluid mixing and mineral end-member mixing.

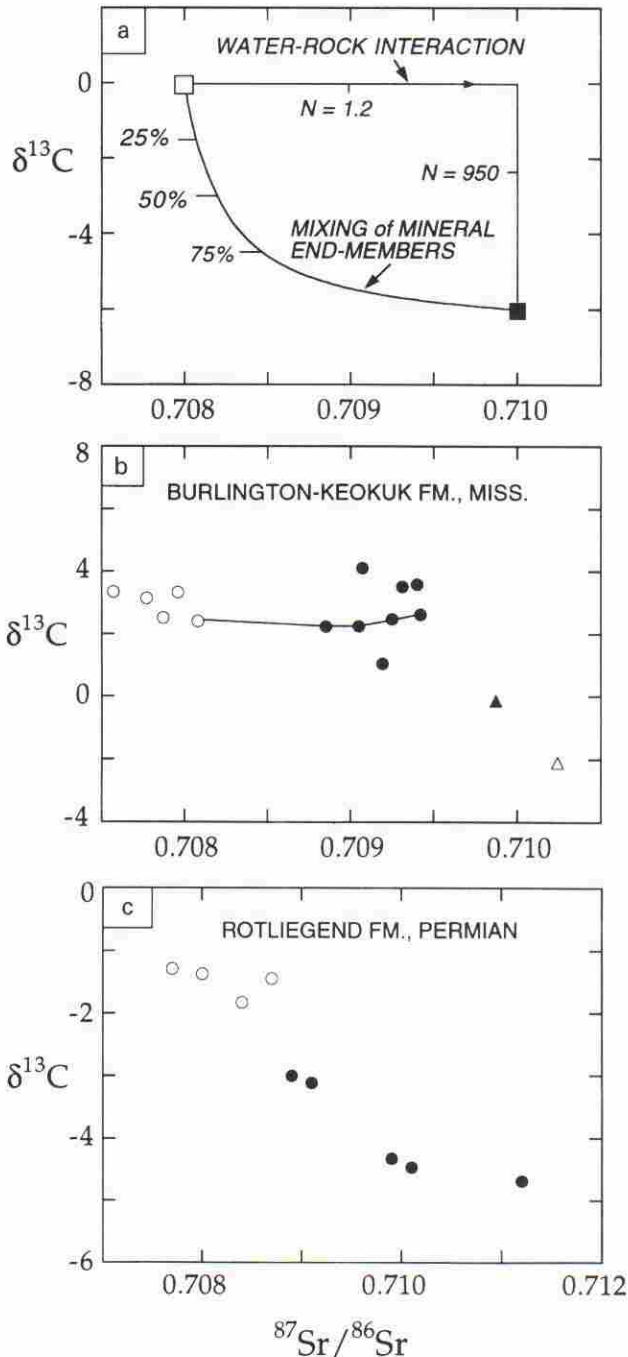


Fig. 6. (a) Modelled simultaneous variations of C and Sr isotopes in carbonates related by: (1) recrystallization of an initial marine limestone or calcite (\square : $\delta^{13}\text{C} = 0\text{‰}$ PDB; $^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$; 1000 p.p.m. Sr) by a brine having the following composition: $\delta^{13}\text{C} = -6\text{‰}$; $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$; 200 p.p.m. Sr; 300 p.p.m. HCO_3^- ; Sr/Ca = 0.005, and (2) mixing between two mineral end-members, one having the marine calcite composition given in (1), and the other representing a diagenetic calcite composition, having $\delta^{13}\text{C} = -6\text{‰}$; $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$, and 100 p.p.m. Sr (\blacksquare). N values as in Fig. 5. Percentages of diagenetic calcite in mixtures are shown along mineral end-member mixing curve. As discussed in Fig. 5, a straight line mixing relationship would result from equal Sr contents in the end-member calcites. (b) Carbon vs. Sr isotopic composition for dolomite I (\circ) and dolomite II (\bullet) from Burlington–Keokuk Fm. (see Fig. 4 for paragenesis). Line connects samples from a single locality; \triangle = vug-filling dolomite cement; \blacktriangle = vug-filling calcite cement. Vug-filling phases post-date dolomites I and II (data from Banner *et al.*, 1988a). (c) Carbon vs. Sr isotopic compositions for early dolomites (open symbols) and late ankerite cements (solid symbols) from Rotliegend Fm. sandstones, North Sea (data from Sullivan *et al.*, 1990).

As applications of Sr-isotope studies to ancient carbonates are advanced, our ability to apply these methods relies on petrological analysis and an understanding of the distribution of Rb and Sr in a given sample. Failure to assess these analytical factors accurately may introduce uncertainties on a sample's $^{87}\text{Sr}/^{86}\text{Sr}$ value that are considerably larger than the uncertainties associated with mass spectrometry, Sr isotope stratigraphy and calculated diagenetic models.

Calculations that model variations in Sr isotope and trace element concentrations during water-rock interaction are used to discriminate between diffusion-controlled vs. reaction- or advection-controlled mechanisms for the alteration of marine carbonate sediments. Significant deviations in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of ancient limestones and dolostones from their original marine values suggest that their low Sr contents result from fluid-rock interaction processes that involve predominantly advective rather than diffusive transport of Sr between reactive carbonate mineral surfaces and the aquifer solution. Calculations that model variations in Sr and C isotopes in a suite of diagenetic carbonate samples may be used to determine the extent to which the isotopic data reflect (1) natural processes of fluid-rock interaction vs. (2) the resolution of sampling techniques.

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