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FLUID FLOW IN THE CRUST: AN EXAMPLE FROM A PYRENEAN THRUST RAMP

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ABSTRACT. En-echelon calcite filled vein arrays and accompanying stylolites are developed in the carbonate units of a ramp section in the upper plate of the Pineta Thrust Complex in the Cinca Valley of the Spanish Pyrenees. Many of the individual veins are sigmoidal and filled with fibrous calcite. Non-fibrous euhedral calcite infillings often crosscut the pre-existing fiber patterns in discrete zones of late dilation. Late fractures that run sub-parallel to the late calcite infillings also cut some of the sigmoidal vein cores. Stylolites form a continuous network across the vein system, usually do not truncate vein limbs, and have been rotated in the same sense as the sigmoidal veins. The attitudes of the veins and stylolites are compatible with the expected principle stress trajectories for parts of the upper plate of a ramp section. In addition, a consistent chronology of vein and stylolite development can be established from the external and internal geometries of the vein-stylolite system. This chronology allows us to document changes in the fluid-rock exchange history before and during ramp development using carbon and oxygen isotopic values recorded in the veins and wall rocks.

Carbon and oxygen isotope data were obtained from chronologically placed micro-samples of calcite (dental drill samples of individual fibers) both from rock matrix and sigmoidal veins. The matrix carbonates have $\delta^{18}O$ values of between 20.7 and 22.6 permil (SMOW) and $\delta^{13}C$ values of between 0.9 and 1.2 permil (PDB). There is no relationship between proximity to stylolites and the observed isotopic ratios in the matrix cycle. The $\delta^{18}O$ values are depleted relative to other marine carbonates in the Pyrenees of comparable age by about 6 permil. The vein limbs have $\delta^{18}O$ values between 16.6 and 21.6 permil and $\delta^{13}C$ values between 0.1 and 1.2 permil. The late calcite infillings have $\delta^{18}O$ values between 16.3 and 17.7 and $\delta^{13}C$ values of between -0.6 and 0.9 permil. These data taken together form what can be interpreted as a typical exchange path between a fluid and the local wall rocks on a $\delta^{18}O$ versus $\delta^{13}C$ plot.

We interpret these data to indicate that the matrix calcite was massively exchanged with an externally derived fluid during an early porous flow regime prior to the development of the vein-stylolite system. Once the vein-stylolite system began to develop in the ramp,

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fluid flow became restricted to stylolites and vein openings. As stylolites represent dissolution sites little or no exchange of the matrix calcite took place. However, the calcite fibers record the varying degrees that the fluid exchanged with rocks along the entire channelized flow path prior to entering the vein opening. Finally, as fractures developed fluid flow became more channelized and less exchange with the wall rocks was possible. This process resulted in the calcite infillings recording the isotopic composition of the externally derived fluids.

The externally derived fluid had a $\delta^{18}O$ value between 10.6 and 12.1 permil. If the fluids were derived from a carbonate terrain they must have been descending fluids. Alternatively, fluids could have been derived from underlying silicate rocks. In either case, fluid transport must have occurred on the order of at least several kilometers

INTRODUCTION

Fluid-rock interaction petrochemistry is a field of scientific and economic importance. At present, techniques that can be applied to investigate the origin of fluids in ancient rocks, or the mechanisms and pathways used during escape from their site of origin, are still at the forefront of their development.

There are three direct approaches that can be used to examine the history of fluids in rocks. The approaches include studies of the phase relationships among hydrous minerals and carbonates (Skippen and Trommsdorff, 1975; Rice, 1977), fluid inclusion studies (Touret, 1974a, b), and stable isotope studies of silicates, hydrous phases, carbonates, and fluid inclusions (Rye and others, 1976; Kreulan, 1980; Lattanzi and others, 1980; Rumble, 1982; Tracy and others, 1983). A fourth, indirect method is an experimental-thermodynamic approach such as that described by Kerrick and Slaughter (1976) and Ohmoto and Kerrick (1977). In this paper, stable isotopic techniques are used to study fluid rock interactions in carbonates during deformation and fluid flow through a thrust sheet.

The major aim of this paper is to characterize the fluid-wall rock interactions that occurred in carbonates during fluid flow through parts of the Pineta Thrust Complex in the Spanish Pyrenees. Three components of the fluid-wall rock system will be described: (1) The nature of the fluid circulation system, (2) the extent to which the fluids reacted with the rocks, both in time and space, and (3) the source of the fluids.

Fluids in any specific volume of low grade metasediments at any given time may be: (1) Inherited basinal pore fluids, (2) internally generated by dehydration and/or decarbonation reactions with the fluid composition being controlled by such reactions, (3) introduced from another volume of rock with or without the fluid composition being controlled by internal reactions, or (4) a function of some combination of the above. In a broad sense these possibilities can be looked at as representing rock systems that were either open or closed

systems with respect to fluids. One way to determine if a system was open or closed with respect to fluid is to determine if the whole rocks have behaved as an isotopically open or closed system. If the whole rock oxygen isotopic values are identical to the original values then it is posssible that the system was never open to external fluids. On the other hand, if the whole rock oxygen isotopic values are different from the original rock plus pore fluid values than it follows that the system had to have been open with respect to fluids.

Fluid flow through a rock may be either through connected pore spaces or along specific channels such as bedding planes, stylolites, or fractures. During porous flow the possibility exists for whole-rock isotopic exchange to take place. Whereas, during channelized fluid flow exchange can only take place along the "walls" of the channel. For calcite, exchange with fluid occurs effectively only by a mechanism of dissolution and precipitation (Chai, 1975). Therefore the only places that exchange can be observed in a limestone is where both dissolution and precipitation took place. The consequence of this behavior is that, during porous flow in a limestone, significant exchange may only be recorded if recrystallization took place in the presence of a fluid phase. A further consequence is that stylolites may not record any exchange history if they were strictly dissolution sites. Finally, the carbon and oxygen isotopic composition of carbonate veins in carbonate host rocks will record the integrated amount of carbonate that was dissolved and reprecipitated along the fluid pathways through the rocks.

By establishing chronologies based on vein geometries and the growth history of their internal mineral fibers, it is possible to study changes in the integrated fluid-rock exchange history through time using the carbon and oxygen isotopic values recorded in the veins.

GEOLOGY

Rock System

The host rock and vein system studied is contained in a series of homogeneous biomicritic limestones of Maastrichtian to Selandian age that comprise part of the Pineta Thrust Complex. The Pineta Thrust Complex is a 5 km thick sequence dominated by selected Cretaceous and Tertiary lithologies. The area of study was in the Cinca Valley of the Spanish Pyrenees. Within the Cinca Valley extensively developed vein arrays are confined to the basal 50 m of the carbonate section and are associated with a well developed stylolite network. These stylolites are physically traceable outside the zone of vein formation into slaty and spaced cleavages within the Permo-Triassic basement and Tertiary cover respectively. Preliminary mineralogical and microchemical data from the Permo-Triassic rocks indicate phengite-forming reactions during cleavage development, possibly a transformation from illite-chlorite to phengite-chlorite (compare Knipe, 1981, reaction 3). The relationship between the stylolite and cleavages suggests that the stylo-

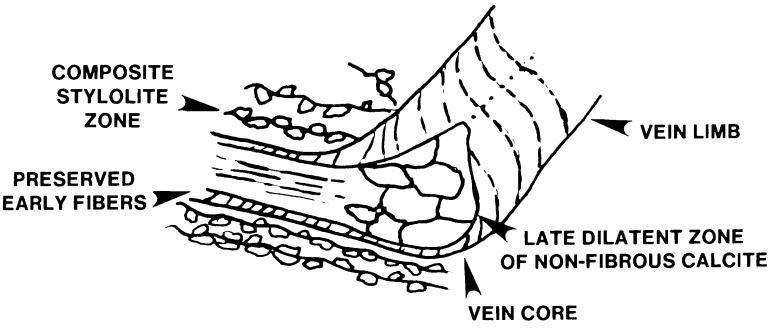


Fig. 1. Enlarged drawing of sigmoidal vein core illustrating the relationships between non-fibrous and fibrous calcite. The fibers are orthogonal to the median suture and oblique to the vein edge suggesting antitaxial vein growth. The non-fibrous calcite cross cuts the curved fibrous calcite indicating that the non-fibrous calcite was precipitated as a late event in the evolution of the vein.

lites formed during thrusting. Relationships between veins and the stylolites indicate that the veins and the stylolites formed at the same time. Therefore, the fluid history that we deduce for the stylolite-vein system should be reflective of the fluid history during the thrusting event.

Veins

Although their host is a quartz-bearing carbonate, only calcite forms vein infillings. Individual veins may be planar or sigmoidal. Many of the vein fillings are fibrous. In general, the fibers in the cores of sigmoidal veins are extremely curved and become progressively less curved as the tips of the veins are approached. The individual fibers are orthogonal to the median suture within a given vein. Often non-fibrous euhedral calcite, formed by cavity filling, crosscuts the pre-existing fiber patterns in discrete zones of late dilation. Usually these zones are spatially restricted to the cores of strongly sigmoidal veins and represent extremely limited volumes of calcite precipitation. (See fig. 1 for a typical vein geometry.) Some of the veins are crosscut by late fractures that run through the sigmoidal cores sub-parallel to the late calcite infillings. Individual veins occur in en-echlon vein arrays. Boundaries of arrays are generally sharp, but no significant differences exist between deformation in the matrix immediately adjoining vein material and that elsewhere within the host carbonates. The stylolite network of the matrix is continuous across the margins of arrays, although its attitude is variable. Arrays are commonly observed to die out along their length. Conjugate arrays are ubiquitous. Their attitudes are compatible with expected principal stress trajectories for parts of the upper plate of ramp sections (for example Wiltschko, 1979). Most common variants of vein geometry sub-types have been observed (compare Beach, 1980, p. 433).

Vein growth.—A significant number of studies has been carried out on the geometry of en-echelon vein arrays. Beach (1975), for example, extended the strain compatibility arguments of Ramsay and Graham (1970) for sigmoidal vein geometries established under progressive simple shear, illustrating the relationships between vein dilation and orientation for various brittle-ductile deformation zones. The theoretical basis necessary to explain the sigmoidal form common to many veins from such zones has been outlined and reviewed by Ramsay (1967,1980).

Durney and Ramsay (1973) pioneered the use of mineral fibers to study the incremental dilation history of syntectonic veins and pressure shadow zones. During a non-coaxial strain history, syntaxial and antitaxial mineral growth respectively toward and away from the median surface of veins lead to characteristically different patterns of curved fibers (fig. 2; see also Durney and Ramsay, 1973 figs. 1 and 12). A corollary of these growth habits is that, for any one section through a vein, young fibers are to be found farthest from the vein walls for syntaxial growth and at the walls for antitaxial growth. Additionally, the simplest modes of dilation cause syntaxial fibers first to form orthogonal to vein margins, whereas antitaxial fibers may form orthogonal to median sutures. More complex vein fiber histories can exist especially in the case of fibers developed by crack-seal mechanisms (Ramsay, 1980), the incremental growth of which has been considered by Cox and Etheridge (1983).

The fact that fibers in sigmoidal veins are curved, become less curved toward vein tips, and tend to be orthogonal to the median suture suggests that the veins studied were not developed by crack-seal mechanisms but by an accretionary process similar to that envisaged for antitaxial vein growth by Durney and Ramsay (1973). The external geometry of sigmoidal veins and the incremental growth history of antitaxial fibers can be combined to establish the relative times at which different parts of veins were formed during the history of the shear zones in which they formed. This procedure provides a relative time frame for mineral precipitation resulting from fluid-rock interactions. Two broad generalizations from this analysis are noted. The first is that vein dilation close to evolving sigmoidal cores persisted during much of the vein propagation history, to leave a simple transition from exaggeratedly curved to non-curved fibers as vein tips are approached. Secondly, as a consequence, individual fibers become progressively younger toward vein margins, and the fiber package becomes systematically younger toward vein tip terminations.

The late vein dilation and filling complicate the simple growth history described above in a number of shear zones examined. The fact that these infillings crosscut strongly curved fibers in the cores of the sigmoidal veins clearly demonstrates that sigmoidal veins had already undergone a rotational incremental strain history before this late precipitation event (fig. 1). We interpret these textural relationships to

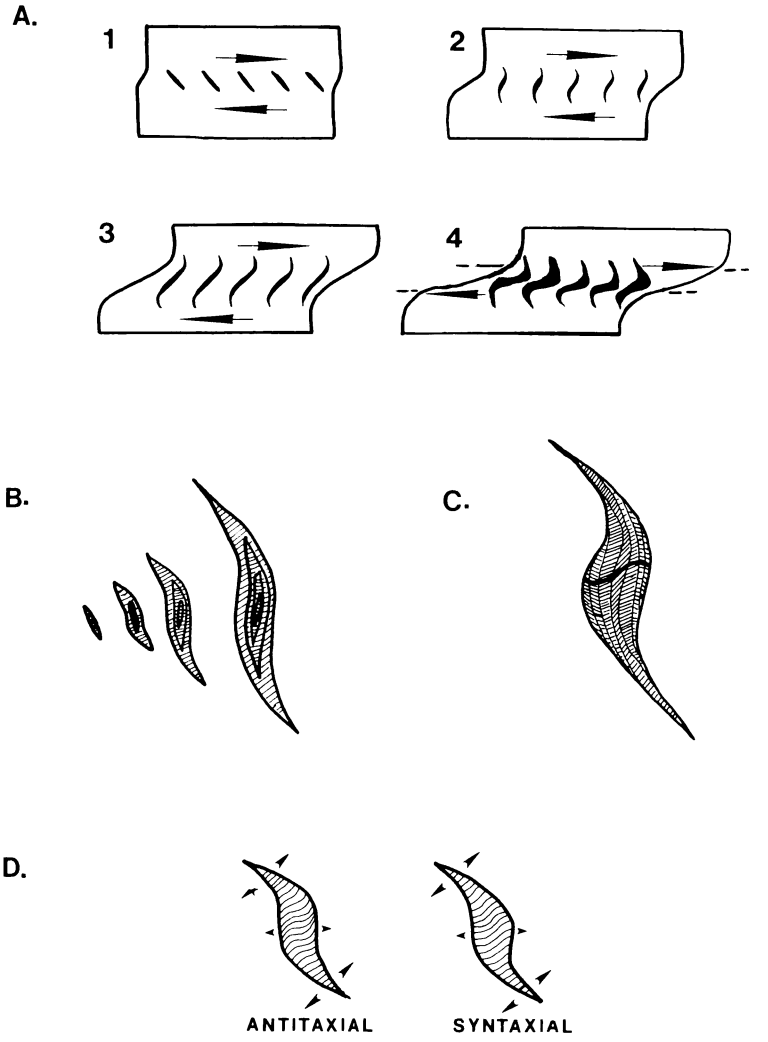


Fig. 2. Aspects of vein and mineral fiber growth. (A) illustrates incremental extension and dilation of an increasingly sigmoidal en echelon vein array under progressive simple shear. (A1) to (A3) show characteristic asymmetry and elongation of initially planer veins with increased shear strain. (A4) illustrates final strain hardening of shear zone with preferential additional increment of vein dilation within established vein cores. (B) illustrates progressive elongation and dilation of an individual vein in simple shear. Dilation competes with elongation leading to what is diagramatically shown as a simple internal shell structure for each incremental external morphology Antitaxial mineral fibers schematically shown for each increment of growth. (C) shows example of syntaxial growth of mineral fibers for a case in which vein elongation does not compete with dilation, leading to complexities in patterns of time-lines (not shown) for isochronous growth of different fibers in different parts of veins. (D) illustrates differences in the sense of asymmetry of internal habits; small arrows represent earlier direction of maximum incremental extension, large arrows represent latest direction of maximum incremental extension with respect to shear zone margins (compare to A).

represent strain hardening within the shear zone as a whole, premonitory to brittle failure, which is evident in some zones.

Stylolites

The host rock to the vein system is predominantly composed of calcite but with a significant component of quartz (approx 21 percent of modes). Equant grains of quartz (diam 0.05 mm) are often twice the dimensions of calcite grains, show little variation in grain size, and have an isotropic distribution as separate grains supported by a fine calcite matrix. Set in this calcite-quartz rock is a network of extremely low amplitude stylolites. Adjacent to vein material the distribution of stylolites is commonly related to their location with respect to vein walls. The orientations and changes in orientations of stylolites are consistent with the strain history recorded by fibers within the adjacent veins. Veins are only rarely truncated by individual stylolites. Normally, stylolites approach and are connected to vein walls. Their distributional patterns are commonly different on opposite walls of a vein (for example fig. 3). This fact clearly demonstrates that they did not form some pre-existing planar fabric system through which the veins subsequently propagated. These relationships suggest a close association between the geometry and timing of stylolite and vein formation.

Quartz grains are clustered within stylolite zones without modification of their size or shape and without the formation of internal deformation sub-structures or the development of a preferred arrangement of crystallographic orientations different from that outside stylolite zones. These textural observations along with the fact that no zoning of quartz grains was observed in cathodoluminescence (indicating homogeneity of transition metal contents) suggest that quartz grains are concentrated by calcite volume loss and residue occlusion at stylolites without taking part in dissolution and reprecipitation during the fluid history of the rock. Similarly, opaque grains are passively concentrated at stylolites. In addition to these textural criteria, there is no evidence for quartz dissolution and precipitation anywhere within the entire carbonate section of the thrust system we have looked at.

Stylolites form a continuous network across the vein system and are not strictly confined to the vicinity of conjugate vein arrays. Their attitudes and spacing varies across vein boundaries by differing amounts dependent on the magnitude of shear strain. The only notable exception to their reasonably regular spacing within the biomicrite occurs close to the zones of late development of sigmoidal vein cores discussed above, where stylolite density is significantly increased. Compared to the system as a whole, such regions are volumetrically insignificant.

VOLUME GAINS AND LOSSES

Volume Loss at Stylolites

Within individual stylolites, estimates of volume loss of calcite have been made using three methods in thin sections cut orthogonal to the

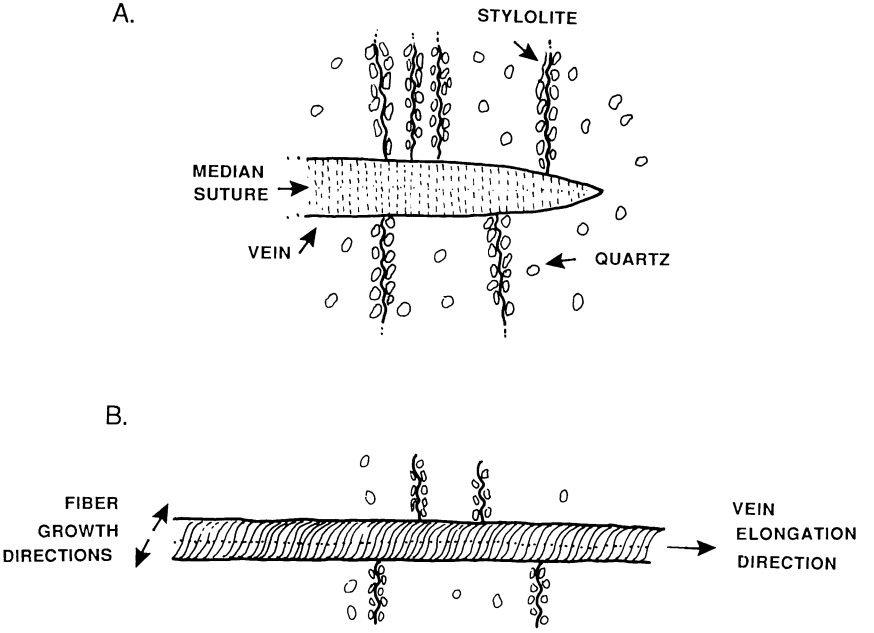


Fig. 3. Sketches of typical sigmoidal vein limb and vein tip. (A) shows the relationship between the fibers within the vein and the stylolite network near a vein tip. Note that stylolites do not match up on opposite sides of the vein, nor do they truncate the vein. Note also that the fibers are not strongly curved near the vein tip. (B) illustrates a typical vein limb. The stylolites do not match up on opposite sides of the vein nor do they cross cut the vein. The individual fibers are strongly curved and are orthogonal to the median suture of the vein.

stylolitic surfaces. The first of these was a comparison of modes within the rock matrix and within the planar segments of stylolite zones, using a close-spaced line transect technique on enlarged photographs of thin sections studied under cross-polars with an inserted gypsum plate. Volume loss of calcite was gauged from the relative proportions of calcite to quartz and calcite to opaque minerals inside and outside the stylolite zones. Within the accuracy of the technique the results obtained using quartz were the same as those obtained using opaque minerals. The second method directly calculated volume loss from the offset relationships of foramanifera cut by stylolites, assuming volume loss without seam parallel shear (compare Delair and Leroux, 1978). The third method used the density distribution of quartz grain centers inside and outside stylolite zones (autocovariance method of Hanna and Fry, 1979). All three methods gave generally consistent results for calcite volume loss. However, because of statistical problems with the second and third methods these could not be universally applied, and reliance was placed on detailed modal analysis.

The mean values of line transects for matrix, stylolites, and stylolites adjacent to cores of sigmoidal veins can be summarized as follows. The carbonate matrix has a mode of 74 percent calcite, 21 percent quartz, and 5 percent opaque minerals. Individual stylolites consistently indicate 42 percent calcite loss except where they are found close to late vein material, where 57 percent calcite loss is observed. Little variation was found in calcite volume loss along the length of any stylolite or from one stylolite to the next.

Volume Gain in Veins

The volume percent of calcite veins within the carbonate in the Cinca section was calculated from randomly oriented band transects across overlapping photographs of the vein-matrix system. In 25 transects vein material consistently comprised 6 percent of the rock volume.

Thin-section studies indicate an average width of stylolite seams of 0.3 mm and a mean spacing between seams of approx 4 mm. For any given total volume of carbonate (in the present case calculated for 500 m long rock cuts), taking a 50 percent calcite loss at each stylolite and a 6 percent vein volume (each vein having 100 percent calcite gain), it follows that approx 40 percent of the calcite volume of vein material can be derived from the immediate stylolite network. This estimate requires that some calcite was carried as solute from outside the observed boundaries of the stylolite-vein system. The scale of this transport may only be on the order of meters or it may be on the order of kilometers. Below we try to address the problem of scale in the isotopic study. Before going on to the isotopic studies we attempt to estimate the temperature attained in the carbonate sequence.

Importantly, it appears that veins formed at the same time that major dissolution took place in the host rocks. It therefore appears appropriate to equate the temperatures reached in the host rocks with the temperatures at which fluid flow occurred.

TEMPERATURE

Calcite-Dolomite Solvus

Accurate thermometry in the micrite and veins is not possible. The fine grained nature of the vein fibers precludes the use of fluid inclusion thermometry in the fibrous veins. The monomineralic nature of vein material and the likelihood of significant isotopic disequilibrium effects in the matrix minerals resulting from the selective nature of the exchange process (quartz apparently did not exchange) prohibits use of oxygen isotopic thermometry in the micrites. X-ray diffraction measurements confirm that it is not possible either in the host rocks or the veins to use element partitioning thermometry because there are no appropriate mineral pairs.

In order to estimate temperatures that these rocks achieved it was necessary to use mineral compositional data from rocks immediately outside the vein-matrix system in which we did the isotopic studies. Specifically, calcite-dolomite solvus thermometry was applied to samples of a brecciated carbonate unit collected immediately within the hanging wall sequence above the basal thrust. This approach presents a number of difficulties. The extent to which temperatures from the rock matrix in dolomitic units directly indicate the temperature of interest depends firstly on the relative position of these units and that of the vein system and, secondly, on the degree of thermal disequilibrium between fluid and its surroundings. We have tried to minimize the spatial problem through our sample selection. We imply in our isotopic studies that the fluid history operated over a significant period of time. If this implication is correct we would expect any thermal disequilibrium between fluid and its host rock to be only transient and not significant over most if not all the vein growth history.

Other equally significant problems in the application of mineral compositional thermometry to calcite-dolomite pairs are that of chemical equilibration in rocks of such relatively low grade and that of successful extrapolation of the experimental data to low temperatures. The failure of coexisting calcite-dolomite pairs to reach chemical equilibrium under the highest temperatures achieved by a rock mass, together with the potential for continued re-equilibration during temperature decrease, are inherent problems of the thermometer which can only be resolved on the somewhat ad hoc basis of finding an appropriately homogeneous set of microprobe analyses. The microprobe data for calcite-dolomite pairs are presented in table 1. The tabulated calcite values represent average values of about 12 analyses per calcite grain.

For temperatures above 400 degrees C, Richardson and Powell (1976) have derived expressions for the solubility of $MgCO_3$ in calcite at equilibrium with dolomite, fitting the experimental data of Goldsmith and Newton (1969). Below 600 degrees C their expression is: mole percent$MgCO_3$ = $100 \exp (0.847 - 3090/T) + P(0.00017T - 0.033)$ where T is in degrees K and P is in kb. In this study, we assume that the Richardson and Powell equation can be extrapolated well below 400 degrees C. Because of this large extrapolation and the other problems outlined above, the mineral thermometry cannot be considered rigorous. However, we do not believe that the temperature we calculate is in serious enough error to alter any of the conclusions that we reach regarding the fluid history.

For present purposes, we have used a 2.25 kb pressure appropriate to a minimum 9 km thickness of the carbonate overburden (using ρ of 2500 kgm^{-3}) determined from palinspasitic restoration of the Pineta and Cortiella-Montsec thrust masses. (An estimate that takes account of internal shortening in the Pineta Sheet calculated from finite strain

TABLE 1

*Microprobe analyses of calcite-dolomite pairs**

Mineral	% $FeCO_3$	% $MnCO_3$	% $MgCO_3$	% $CaCO_3$
Dolomite	0.96	0.21	48.32	50.51
Calcite	0.09	0.07	1.38	98.45
Dolomite	1.25	0.00	48.42	50.32
Calcite	0.25	0.07	1.44	98.16
Dolomite	0.73	0.00	49.27	49.99
Calcite	0.00	0.16	1.46	98.39

*Average recalculated carbonate analyses for specimen HB/82-TB-9 selected from 15 calcite-dolomite pairs with approx 12 analyses per calcite grain.

data.) Given all the other uncertainties in the method we have not made a correction for the small amounts of iron in the calcite. Using the estimated pressure of 2.25 kb and the mean mole percent $MgCO_3$ value of 1.43 for calcites coexisting with dolomite the Richardson and Powell equation yields a temperature of 320 degrees C. Within the limits of accuracy of estimating the initial thickness of the nappe pile, this would conform to a geotherm approximating 30 degrees C/km.

The development of phengite in the slaty cleavage immediately below the carbonate section is consistent with the assumption that the temperature obtained from the calcite-dolomite pairs is representative of the temperature reached during the deformation that produced stylolites and vein array.

ISOTOPIC STUDY

Sampling

Carbon and oxygen isotopic compositions of calcite were measured from both the rock matrix and the veins. In order to make full use of both the external geometry of the veins and the history of dilation recorded by internal mineral fibers attention was focussed on samples of strongly sigmoidal veins collected from a vein array within the Cinca Valley near Beilsa. Three 2 cm thick slabs were cut from a large specimen containing the vein array. Suites of thin sections were then made from the slab faces, whereas opposing faces were used for isotopic analysis. Fifty-four samples for this analysis were collected along and across individual veins and into the adjoining matrix using a high speed dental drill. Ten additional samples were collected in the same manner from two traverses made perpendicular to stylolites. The location of these dental drill samples on each of the three slab faces is illustrated in figure 4. In addition timed extractions were made on two samples of the washed -80 $+120$ mesh size fraction collected from a brecciated calcite-dolomite bearing carbonate located near the basal thrust. The data are listed in tables 2 and 3.

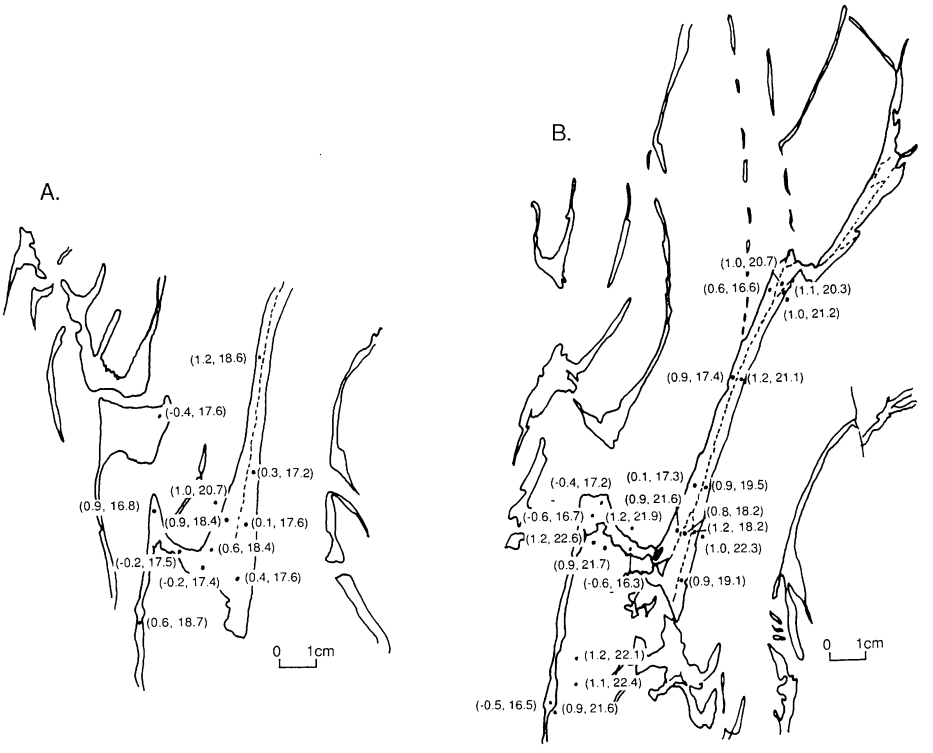


Fig. 4. Scetch of typical vein array showing isotopic data. The three drawings (A,B, and C) are of parallel slab faces that were cut every 2 cm. The first number in each bracket is the carbon isotopic value, the second number is the oxygen isotopic value.

Isotopic Techniques

Carbon and oxygen isotopic analyses were performed using standard techniques. Carbon dioxide was liberated from calcite using H_3PO_4 following the method of McCrea (1950). Following extraction CO_2 samples were analyzed using a Nuclide 6-60 ratio mass spectrometer. Results are generally reproducible to ±0.1 permil or better for carbon and ±0.2 permil or better for oxygen. For calcite-dolomite thermometry we used a method of timed extractions following the procedures similar to those reported by Epstein, Graf, and Degens (1964). It was found essential to use periods of 3, 10, 30 min, 1, 3, 10, 30, and 48 hrs. Sharp plateaus in the isotopic composition of the evolved gas occurred between the 3 and 30 min interval and between the 30 and 48 hr intervals. This kind of behavior can be taken as good evidence that complete separation of the gas from calcite and from dolomite was achieved. The various fractionate factors used were $\alpha = 1.0412$ for CO_2/H_2O at 25 degrees C, $\alpha = 1.01025$ for H_3PO_4-liberated $CO_2/CaCO_3$ at 25 degrees C, $\alpha = 1.01109$ for H_3PO_4-liberated

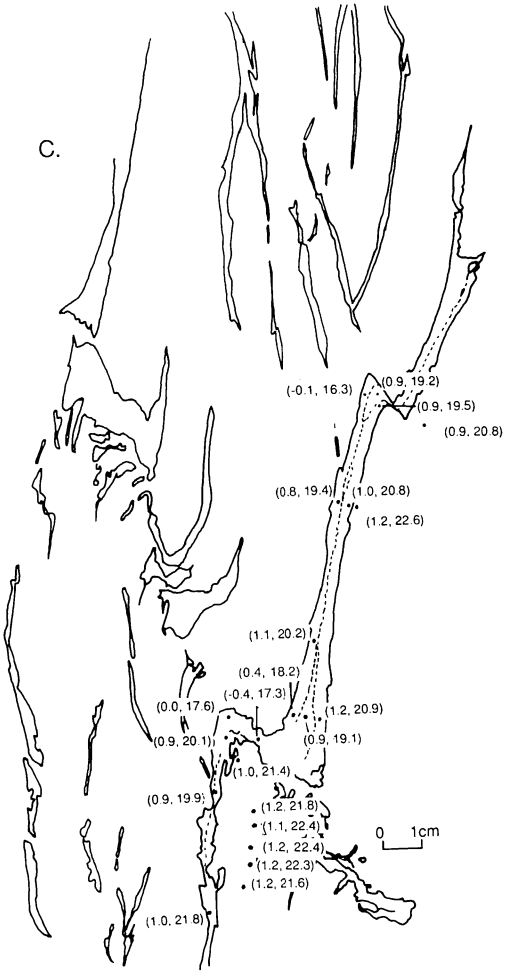


Fig. 4. (continued)

$CO_2/CaMg(CO_3)_2$ at 25 degrees C, and $\alpha = 1.00022$ for H_3PO_4-liberated CO_2 from PDB/CO_2 in equilibrium with SMOW at 25 degrees C. All data are reported in standard δ notation [permil values], according to the following:

$$\delta^{18}O = 10^3 \left[\frac{(^{18}O/^{16}O)\ \text{Sample}}{(^{18}O/^{16}O)\ \text{Standard}} - 1 \right]$$

$$\delta^{13}C = 10^3 \left[\frac{(^{13}C/^{12}C)\ \text{Sample}}{(^{13}C/^{12}C)\ \text{Standard}} - 1 \right]$$

TABLE 2

Matrix-vein calcite isotopic data

Sample	Setting	$\delta^{13}C$	$\delta^{18}O$	Sample	Setting	$\delta^{13}C$	$\delta^{18}O$
202-B0.13	M	1.0	20.7	205-B1.26	VL	0.1	17.3
205-B1.23	M	1.0	21.2	205-B1.32	VL	0.9	19.1
205-B1.31	M	1.0	22.3	206-B2.21	VL	0.9	19.2
206-B1.40	M	0.9	21.6	206-B2.22	VL	0.9	19.5
207-B2M	M	1.2	22.6	206-B2.24	VL	0.8	19.4
208-B2.36	M	1.0	21.4	206-B2.25	VL	1.0	20.8
209-B2.23C	M	0.9	20.8	207-B2.26	VL	1.1	20.2
209-B2-T-9	M	1.2	22.4	208-B2.28	VL	0.4	18.2
209-B2-T-11	M	1.2	21.6	208-B2.29	VL	0.9	19.1
210-B1-T-2	M	1.2	21.9	208-B2.30	VL	1.2	20.9
210-B1-T-4	M	1.2	22.6	208-B2.35	VL	0.9	20.1
210-B1-T-5	M	0.9	21.7	208-B2.37	VL	0.9	19.9
210-B2-T-6	M	1.2	21.8	209-B2.40	VL	1.0	21.8
210-B2-T-7	M	1.1	22.4	201-B0.11	VC	−0.2	17.5
210-B2-T-10	M	1.2	22.3	202-B0.1	VC	−0.2	17.4
221-B1-T-11	M	1.2	22.1	202-B0.12	VC	0.9	16.9
221-B1-T-12	M	1.1	22.4	202-B0.14	VC	−0.4	17.6
201-B0.2	VL	0.6	18.4	203-B0.18	VC	−0.3	17.7
201-B0.5	VL	1.2	18.6	203-B1.20	VC	0.6	16.6
202-B0.3	VL	0.9	18.4	205-B1.33	VC	−0.6	16.3
202-B0.7	VL	0.4	17.6	205-B1.34	VC	−0.4	17.2
202-B0.9	VL	0.1	17.6	206-B1.35	VC	−0.6	16.7
202-B0.10	VL	0.3	17.2	206-B1.39	VC	−0.5	16.5
203-B0.17	VL	0.6	18.7	206-B2.20	VC	−0.1	16.3
203-B1.22	VL	1.1	20.3	208-B2.32	VC	−0.4	17.5
203-B1.24	VL	0.9	17.4	208-B2.33	VC	−0.4	17.3
203-B1.25	VL	1.2	21.1	208-B2.34	VC	−0.4	17.2
204-B1.21	VL	0.6	16.6	221-B2.69	SV	1.1	18.8
204-B1.27	VL	0.9	19.5	221-B2.70	SV	1.0	18.7
204-B1.28	VL	0.9	21.6	221-B2.71	SV	1.1	18.5
204-B1.29	VL	0.8	18.2	221-B2.72	SV	1.1	19.2
204-B1.30	VL	1.2	18.2	221-B2.73	SV	1.2	19.5

M—Biomicrite matrix calcite
VL—Sigmoidal vein limb calcite
VC—Sigmoidal vein core calcite
SV—Small vein limb calcite

TABLE 3

Timed extraction data

Time	Sample Number					
	TB-8 (Gas)	TB-9 (Gas)	TB-8 (CC)	TB-8 (Dol)	TB-9 (CC)	TB-9 (Dol)
3 min		23.65			23.65	
10 min	23.60	23.61	23.60		23.61	
30 min	23.65	24.73	23.65			
1 hr	24.36	24.81				
3 hrs	25.73	25.03				
10 hrs	26.21	25.41				
30 hrs	26.49	26.59		25.66		25.76
48 hrs	26.39	26.52		25.56		25.69

where the oxygen standard is Vienna-Standard Mean Ocean Water (SMOW) and the carbon standard is the Cretaceous Pee Dee Belemnite (PDB) standard.

Isotopic Data

The data from the detailed vein array study are listed in table 2 and plotted in figure 5 on a $\delta^{18}O$ versus $\delta^{13}C$ plot. Distinction is made between values for the host rock, for the limbs of sigmoidal veins, and for the non-fibrous late cores of sigmoidal veins as defined in figure 1. Comparison of the data collected from other veins indicates that the data-set for the vein array shown in figure 5 is typical of an individual vein and its surrounding host rock.

Host-rock, vein limb, and vein core isotopic values fall within distinct populations. Calcite from the host-rock has the heaviest oxygen

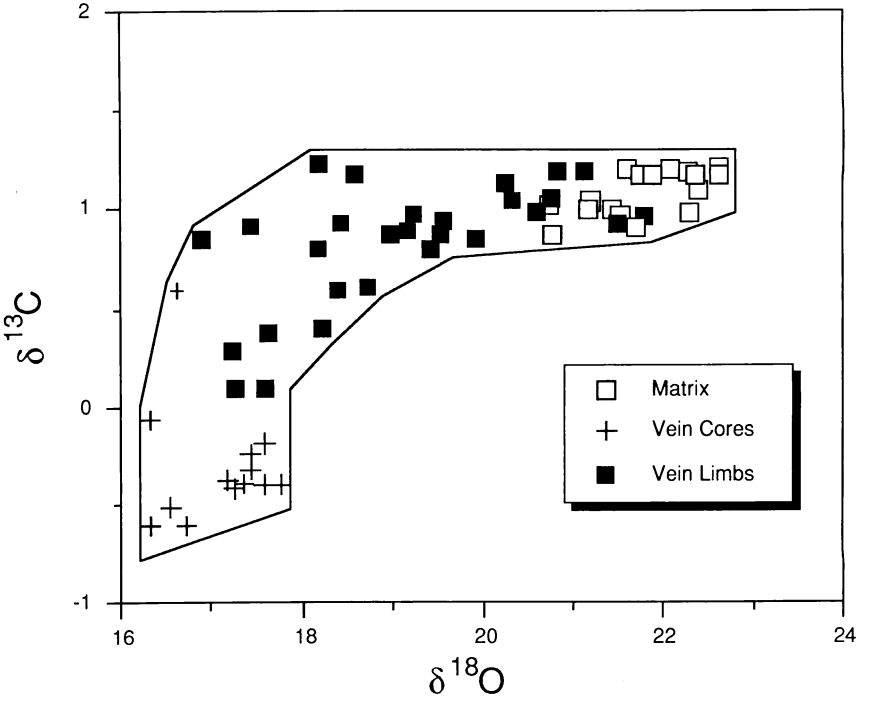


Fig. 5. Data from figure 4 and table 2 shown on a $\delta^{18}O$ versus $\delta^{13}C$ plot. Open squares represent data collected from the matrix, filled squares represent data collected from fibrous vein material along the length of the vein, and crosses represent data from the late non fibrous calcite. Carbon and oxygen isotopic values are on PDB and SMOW scales respectively. Note there is a sharp bend in the data envelope that delineates a region of almost pure oxygen isotopic variations from a region of almost pure carbon isotopic variations.

isotopic values, with values ranging from 20.7 to 22.6 permil. By contrast, vein limbs are less restricted in their range of $\delta^{18}O$ values, varying between 16.6 and 21.6 permil, with all but two of the thirty-three samples measured having values between 17.4 and 21.6 permil. In general, the lightest oxygen isotopic compositions are found within the non-fibrous vein cores with $\delta^{18}O$ values of 16.3 to 17.7 permil, with all but two of the fourteen samples measured having values betwen 16.3 and 17.5 permil. The carbon isotopic composition of the host-rock carbonates is restricted to a narrow range of 0.9 to 1.2 permil. The vein limbs have $\delta^{13}C$ values of 0.1 to 1.2 permil, with all but four of the thirty-three samples analyzed having values between 0.6 and 1.2 permil. Sigmoidal vein cores have $\delta^{13}C$ values between -0.6 and 0.9 permil, with all but one of the fourteen samples analyzed having values between -0.6 and 0.0 permil. Although host-rock, vein limb, and vein core oxygen isotopic data fall in distinctive groups, there is overlap from one population to the next. Indeed, the vein-host-rock data set as a whole appears to define a continuous array. The profile defined by the data on a $\delta^{18}O$ versus $\delta^{13}C$ plot comprises two extreme isotopic regions, one a region of almost pure $\delta^{18}O$ variations (host rock and vein limb data), the other a region of almost pure $\delta^{13}C$ variations (vein core data). We will show below that this type of array closely approximates that expected for a continuous isotopic exchange profile between a water rich fluid and the host rock.

Two sample traverses were taken perpendicular to stylolites. The data are listed in table 2 and designated with a T (for example, 209-B2-T-9). The observed $\delta^{18}O$ values in traverse B1-T vary from 21.7 to 22.6 permil, and the observed $\delta^{13}C$ values vary from 0.9 to 1.2 permil. In traverse B2-T the $\delta^{18}O$ values vary from 21.6 to 22.4 permil, and the $\delta^{13}C$ values vary from 1.1 to 1.2 permil. In both traverses the observed variations apparently are not related to the distance from any stylolite.

The timed extraction data on mixed calcite and dolomite samples are listed in table 3. The measured $\Delta^{18}O$ values for the two calcite dolomite are 2.0 and 2.1 permil.

In order satisfactorily to interpret vein-host rock isotopic data in general, and that of figure 5 in particular, it is necessary to introduce some aspects of isotopic equilibrium and exchange theory before proceeding with modeling.

Isotopic Exchange Theory

The isotopic exchange between H_2O and $CaCO_3$ can be written as follows:

$$1/3(CaC^{16}O_3) + H_2{}^{18}O = 1/3(CaC^{18}O_3) + H_2{}^{16}O$$

The equilibrium constant for the reaction is given by:

$$K = \frac{[CaC^{18}O_3]^{1/3}[H_2{}^{16}O]}{[CaC^{16}O_3]^{1/3}[H_2{}^{18}O]}$$

For one exchangable atom, the equilibrium constant is equal to the fractionation factor α where:

$$\alpha = \frac{[{}^{18}O/{}^{16}O]_{CaCO_3}}{[{}^{18}O/{}^{16}O]_{H_2O}}$$

Defined in terms of standard isotopic measurements:

$$\alpha_{CaCO_3-H_2O} = \frac{1 + [\delta^{18}O_{CaCO_3}]/10^3}{1 + [\delta^{18}O_{H_2O}]/10^3}$$

Because δ values are small:

$$10^3 \ln \alpha \sim \delta^{18}O_{CaCO_3} - \delta^{18}O_{H_2O} = \Delta^{18}O_{CC-H_2O}; \quad \text{Where CC} = CaCO_3$$

The experimentally determined calcite-H_2O oxygen isotopic fractionation curve can be used to calculate the temperature of isotopic exchange from the measured oxygen isotopic compositions. Alternatively if the temperature is determined independently the isotopic composition of H_2O can be calculated from the measured isotopic composition of calcite using the fractionation curve. The oxygen isotopic fractionation curve for calcite-water we will use is:

$$\Delta^{18}O_{CC-H_2O} \sim 1000 \ln \alpha_{CC-H_2O} = [2.78(10^6/T^2)] - 3.06$$

O'Neil and others (1969)

where T is in degrees K.
A similar curve can be used for the isotopic fractionation between carbon in solution and calcite. However, this treatment requires that the carbon species in solution are known. For instance, an acceptable fractionation curve for H_2CO_3 or CO_2-calcite is:

$$\Delta^{13}C_{CO_2-CC} \sim 1000 \ln \alpha_{CO_2-CC}$$
$$= -2.9880(10^6/T^2) + 7.6663(10^3/T) - 2.4612$$

Bottinga (1968)

For HCO_3^--calcite the fractionation curve can be defined by:

$$\Delta^{13}C_{HCO_3^- - CC} \sim 1000 \ln \alpha_{HCO_3^- - CC}$$
$$= -2.9880(10^6/T^2) + 17.2183(10^3/T) - 26.5612$$

Mook and others (1974).

Where T is in degrees K for both equations.

Given that the carbon species in solution is known we can calculate the oxygen and carbon isotopic compositions of calcite that would be

precipitated over a temperature range from a fluid of fixed isotopic composition. Figure 6A shows the theoretical curve describing the $\delta^{13}C$ and $\delta^{18}O$ systematics of calcite that would result if calcites were precipitated over the temperature range of 100 to 350 degrees C from an aqueous solution (>99 percent H_2O) in which H_2CO_3 or CO_2 was the carbon species present in solution. A similar curve is shown in figure 6B for the case in which HCO_3^- is the carbon species in solution. Trends of this sort are very different from the type shown for the vein host-rock data set. Other types of trends result if the isotopic composition of the fluid phase is modified by interaction with the wall rocks throughout the precipitation and exchange history. The calculated $\delta^{13}C$ versus $\delta^{18}O$ relationships hold true only for calcites precipitated directly out of a fluid that has not been exchanged with the wall rocks. For pre-existing wall rock carbonates that have undergone exchange with a fluid phase we must consider the fluid-to-rock (W/R) ratio. The same holds true for the isotopic compositions of a fluid that has exchanged with a previously existing carbonate.

Sverjensky (ms) and Shelton (ms) calculated the theoretical composition of host-rock carbonates that would be produced by exchange with a fluid at constant temperature (constant Δ values) as a function of progressively increasing fluid-to-rock ratios. The equation they derived for oxygen is a simple mass balance equation:

$$\text{Molar fluid-rock ratio (W/R)} = n_o\left[\frac{\delta^{18}O^f_{CC} - \delta^{18}O^i_{CC}}{\Delta^{18}O_{CC-H_2O} + \delta^{18}O^i_{H_2O} - \delta^{18}O^f_{CC}}\right]$$

The equivalent equation for carbon is:

$$\text{Molar fluid-rock ratio (W/R)} = \frac{n_c}{X_{\Sigma C}}\left[\frac{\delta^{13}C^f_{CC} - \delta^{13}C^i_{CC}}{\Delta^{13}C_{CC-\Sigma C} + \delta^{13}C^i_{\Sigma C} - \delta^{13}C^f_{CC}}\right]$$

where n_o is the number of moles of oxygen per mole of calcite, $\delta^{18}O^f_{CC}$ and $\delta^{18}O^i_{CC}$ are the final and initial oxygen isotopic compositions of the calcite in the rock, $\Delta^{18}O_{CC-H_2O}$ is the oxygen isotopic fractionation between H_2O and calcite, $\delta^{18}O^i_{H_2O}$ is the initial oxygen isotopic composition of the H_2O, n_c is the number of moles of carbon per mole of calcite, $X_{\Sigma C}$ is the number of moles of C in solution per mole of fluid, $\delta^{13}C^f_{CC}$ and $\delta^{13}C^i_{CC}$ are the final and initial carbon isotopic compositions of the calcite in the rock, $\Delta^{13}C_{CC-\Sigma C}$ is the carbon isotopic fractionation between aqueous carbon and calcite, and $\delta^{13}C^i_{\Sigma C}$ is the initial carbon isotopic composition of carbon in solution. Because $\Delta^{13}C_{C-\Sigma C} + \delta^{13}C^i_{\Sigma C}$ is equal to the $\delta^{13}C$ value of calcite in equilibrium with the initial fluid ($\delta^{13}C^i_{\Delta-\delta}$) before exchange, we can replace the denominator in the carbon mass balance equation with the expression ($\delta^{13}C^i_{\Delta-\delta} - \delta^{13}C^f_{CC}$). Furthermore, because $\Delta^{18}O_{CC-H_2O} + \delta^{18}O^i_{H_2O}$ can be replaced by the $\delta^{18}O$ value of calcite in equilibrium with the initial fluid ($\delta^{18}O^i_{\Delta-\delta}$) before exchange, we can replace the denominator in the oxygen isotope mass balance equation

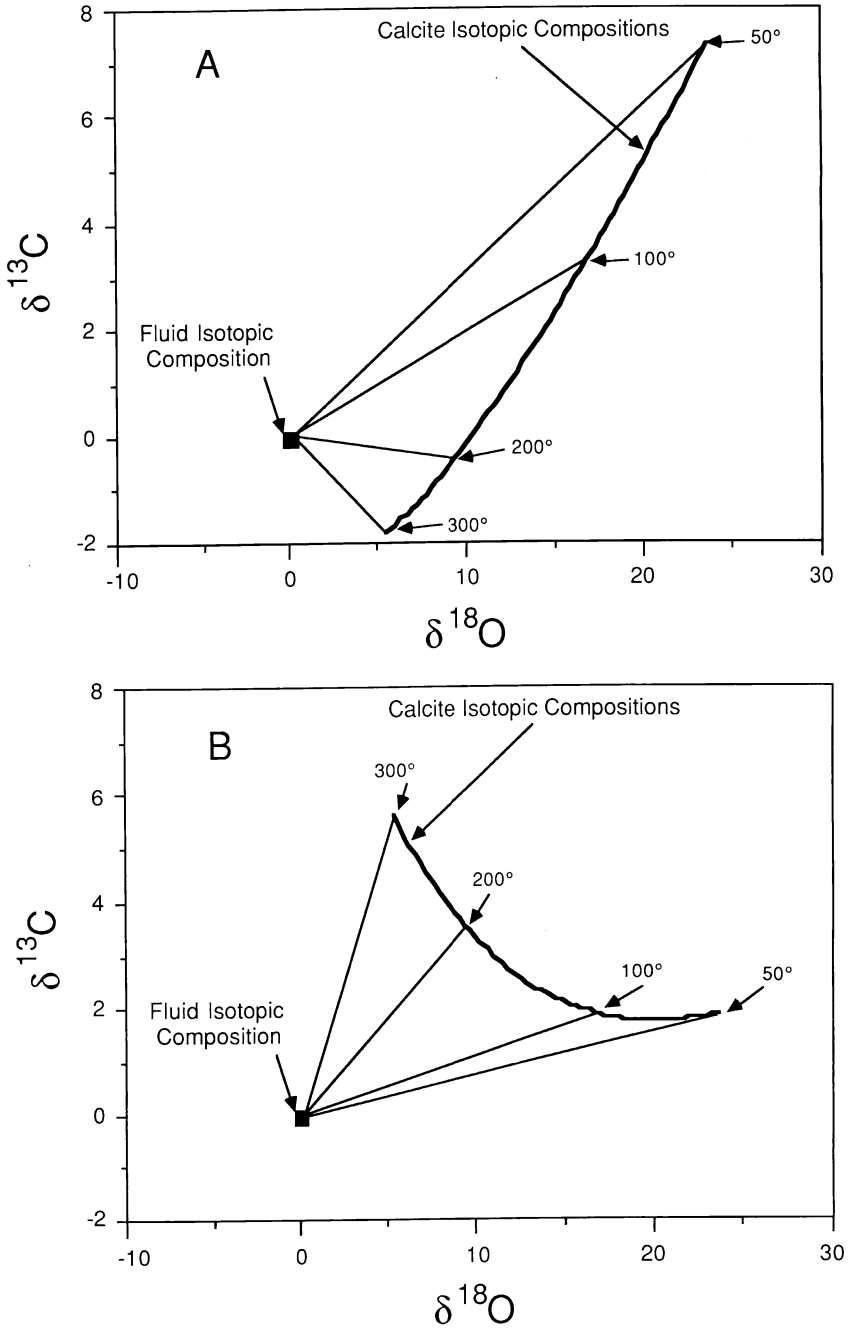


Fig. 6. This figure illustrates the expected oxygen and carbon isotopic compositions of calcite precipitated out of an aqueous fluid (>99 percent H_2O) of uniform isotopic composition over the temperature range of 50 to 300 degrees C. The curve shown in (A) is for an aqueous (>99 percent H_2O) fluid in which the dominant carbon species in solution is CO_2 or H_2CO_3. The curve shown in (B) is for an aqueous fluid in which the dominant carbon species in solution is HCO_3^-.

with the expression ($\delta^{18}O^{i}_{\Delta-\delta} - \delta^{18}O^{i}_{CC}$). If we make this substitution in the oxygen isotope mass balance equation, the equation becomes:

$$\text{Molar fluid-rock ratio (W/R)} = n_o \left[\frac{\delta^{18}O^{f}_{CC} - \delta^{18}O^{i}_{CC}}{\delta^{18}O^{i}_{\Delta-\delta} - \delta^{18}O^{f}_{CC}} \right]$$

Note that, if the $\delta^{18}O^{i}_{\Delta-\delta}$ value can be specified, the fluid-rock ratios can be calculated without knowledge of the temperature or the isotopic composition of the initial water.

Strictly, the above oxygen and carbon isotope mass balance equations allow calculation of the integrated fluid-calcite ratio at a constant temperature if no other oxygen or carbon bearing phase took place in the exchange reactions. Further, the equations assume a closed system, that is one in which fluid is confined to a certain rock volume and is continuously re-equilibrated throughout the isotopic exchange history.

By contrast, an open system is defined as one in which fluid is not recirculated through a rock volume but passes through the rock from some external source. For the extreme open system case in which fluids make a single pass through a rock unit, Taylor (1974, 1977) was able to relate the integrated fluid-to-rock ratios for open and closed systems according to the expression: $W/R_{Open} = \ln [W/R_{Closed} + 1]$.

Without being able to specify the residence times of fluids, particularly in relation to the kinetics of isotopic exchange, no system can adequately be described as either entirely open or closed. However, in the present context we will define a closed system as one in which isotopic exchange within the evolving vein-host rock system could have been achieved utilizing residual basin-derived fluids originally trapped within the local primary pore spaces and/or within grain boundary films. An open system is therefore one in which fluids have been supplied from some source external to the immediate carbonate section.

Let us now consider some aspects of the isotopic exchange paths expected to take place in carbonate rocks. From the mass balance equations discussed above an exchange path can be calculated for a carbonate that has exchanged with a fluid. The form of the exchange profile on a $\delta^{13}C$ versus $\delta^{18}O$ plot is a function of the concentration of the carbon bearing species in the fluid. Even if speciation is not certain, the carbon species in solution do not affect the shape of the exchange curve as long as there is no change in speciation during exchange. Therefore, we can use $X_{\Sigma C}$ to represent the concentration of carbon in solution. Figure 7 illustrates the salient features of the possible isotopic exchange paths for different concentrations of carbon in solution for fixed oxygen and carbon isotopic compositions for the initial calcite in the rock and the initial calcite in equilibrium with the fluid.

The path represented by curve A in figure 7 illustrates the expected exchange path for a system in which the molar $(C/O)_{fluid}$ value is much less than molar $(C/O)_{rock}$ value (system with a very low $X_{\Sigma C}$). For

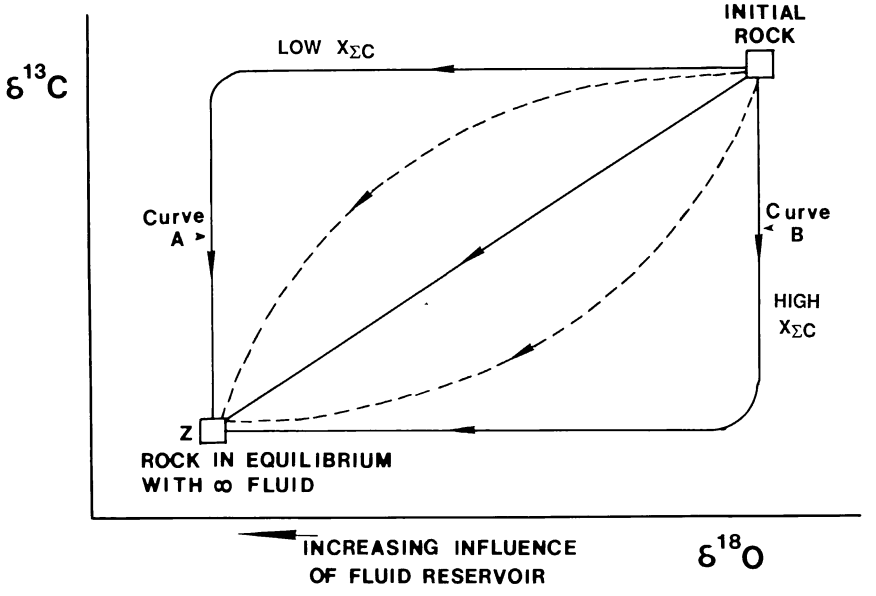


Fig. 7. Schematic isotopic exchange pathways for calcite, from an initial rock value to a value in equilibrium with an initial external fluid at constant temperature. Curve A is the path followed in a system in which the $(C/O)_{fluid}$ value is much less than the $(C/O)_{rock}$ value (system in which the $X_{\Sigma C}$ value is very small). Curve B represents the expected path for a system in which the $(C/O)_{fluid}$ value is much greater than the $(C/O)_{rock}$ value (system in which $X_{\Sigma C}$ value is very large). Exchange pathways for intermediate concentrations of carbon are shown as dashed lines. Note that for a fluid the calcite precipitated out of it will be at point Z if the fluid has not been affected by the rock, and will approach the initial rock value as the fluid interacts with the rock.

such a system the exchange path is characterized by pure oxygen isotopic shifts in the low W/R region of the curve, where the rock oxygen isotope reservoir dominates the system, and by nearly pure carbon isotopic shifts in the high W/R region where the fluid isotopic reservoir dominates the system. Importantly, under the condition of very low $X_{\Sigma C}$, further oxygen exchange is not expected once the carbon isotopic shifts are observed. In other words, the oxygen isotopic composition of the carbonate at the sharp bend along curve A in figure 7 is essentially equal to the oxygen isotopic composition of a carbonate in equilibrium with the initial fluid. Therefore, for such an exchange profile we can use the $\delta^{18}O_{CC}$ value at the sharp bend in the exchange curve to estimate the oxygen isotopic composition of the calcite in equilibrium with the initial water ($\delta^{18}O^{i}_{\Delta-\delta}$ value).

Curve B illustrates the expected exchange path for a system in which the molar $(C/O)_{fluid}$ value is much greater than the molar $(C/O)_{rock}$ value (system where $X_{\Sigma C}$ is very high). This type of system is characterized by carbon isotopic shifts at lower fluid-to-rock ratios and by oxygen isotopic shifts at higher fluid-to-rock ratios.

Between these extreme endmember cases there is an exchange curve for each possible $X_{\Sigma C}$ value. Several of these cases are illustrated in figure 7. Importantly, for any naturally occurring system that has undergone isotopic exchange between a preexisting rock and a fluid, if the isotopic data define an array that approximates one of these theoretical exchange curves, we can estimate the $X_{\Sigma C}$ value and the reactive fluid to rock ratios in the system.

The same exchange process we discussed for wall rocks will also affect the isotopic compositions of the fluid. For very high reactive fluid to rock ratios the fluid will retain its initial isotopic compositions; for very low fluid to rock ratios, in a reactive system, the fluid will reach isotopic equilibrium with the initial rock; and for intermediate reactive water to rock ratios the fluid will reach isotopic values along the exchange path. If calcite is precipitated as vein material out of the fluid, the isotopic compositions of the vein material should record the integrated reactive fluid to rock ratio experienced by the fluid during its flow through the rock prior to calcite precipitation.

Isotopic Thermometry

Theoretically, the oxygen isotopic fractionation between dolomite and calcite can be used to calculate the temperature of isotopic equilibration. Unfortunately, there is no general agreement between the experimentally derived fractionation curves involving dolomite-water or dolomite-calcite (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Mathews and Katz, 1977). This fact may be due in part to sluggish reactions and/or in part due to the fact that the composition of calcite in chemical equilibrium with dolomite is a function of temperature. Sheppard and Schwarcz (1970) derived an empirical fractionation curve from naturally occurring calcite-dolomite pairs. They measured the isotopic fractionation between calcite and dolomite and plotted the measured values against the temperatures obtained from the calcite-dolomite solvus of Goldsmith and Newton (1969). Below 400 degrees C they used a linear extrapolation of the solvus. Recently, Woodwell (ms) has recalculated the Sheppard and Schwarcz equation using the Richardson and Powell (1976) fit to the solvus data. This is a reasonable procedure, because it gives a calcite-dolomite isotopic fractionation curve based on the same fit to the solvus data that we have used to calculate solvus temperature. The equation derived by Woodwell is:

$$\Delta O^{18}{}_{Do-CC} \sim 1000 \ln \alpha = [0.95(10^6/T^2)] - 1.2; \text{ with T in degrees K}$$

This equation yields an isotopic temperature of 275 degrees C for the observed oxygen isotopic fractionation of 2.0 permil. Within the uncertainties of the technique this temperature is indistinguishable from the solvus temperature of 320 degrees C. Given all the uncertainties in both thermometry techniques employed we will use an average temperature of 300 degrees C in all our subsequent calculations that require temperature.

Timing of Wall Rock Exchange and Vein Formation

Before we can model the isotopic exchange process, we must establish the relative timing between exchange in that wall rocks and the fluid-rock exchange history recorded in the vein arrays. There are three critical aspects of the data that suggest that wall-rock exchange occurred prior to the formation of the stylolites and vein arrays. They are: (1) There is no evidence of any exchange of wall-rock calcites on either side of the stylolites. Isotopic compositions are absolutely uniform as stylolites are approached from the surrounding host rock. (2) The heaviest $\delta^{18}O$ values observed in vein fibers are similar to the lightest $\delta^{18}O$ values observed in the matrix calcites. (3) There is very little overlap in the isotopic compositions of matrix calcites and vein calcites (about 1 permil), and no veins have isotopic compositions heavier than the heaviest isotopic compositions observed in the wall-rock calcites. These facts suggest that the calcite matrix values record an exchange history that was pervasive (that is, porous flow), whereas the vein arrays represent the fluid history when flow was localized along stylolites, openings, and fractures. No exchange took place along stylolites because they were sites of dissolution without reprecipitation; whereas veins were sites of precipitation that recorded the fluid wall-rock interactions. Thus, the pervasive exchange history recorded in wall rocks was completed before the veins formed, and fluids that formed the veins interacted with rocks that had already been depleted in ^{18}O.

The questions that remain are: (1) Was the fluid history continuous or discontinuous? (2) Was the system open to external fluids?

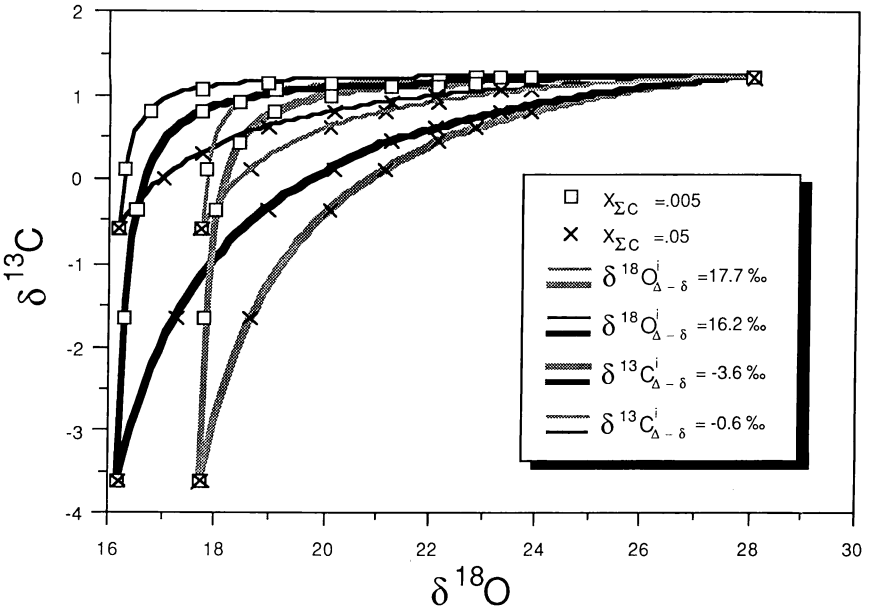
To answer these questions we now develop isotopic exchange models for the data set illustrated in figure 5. We can proceed with these isotopic models either by assuming that the exchange history was continuous with a single fluid or by assuming that the exchange process took place in two or more steps. The models developed below make use of the mass balance equations for closed and open systems presented earlier.

DISCUSSION OF ISOTOPIC RESULTS

Isotopic Model Parameters

The shape of the envelope drawn to the data set in figure 5 appears to match the expected exchange profile for a very low $X_{\Sigma C}$ system as illustrated in figure 7 and discussed above. Several exchange curves for a variety of $X_{\Sigma C}$ values and $\delta^{13}C$ values of calcite in equilibrium with the initial fluid are shown in figure 8A. To illustrate that the data set is representative of a typical very low $X_{\Sigma C}$ system, the data are compared to several of these curves (fig 8B). Note that for $X_{\Sigma C}$ values greater than about 0.05 the calculated exchange curves fall outside the data envelope.

For a system with a very low $X_{\Sigma C}$ value, we have shown that the $\delta^{18}O$ value at the sharp bend in the exchange curve should closely approxi-



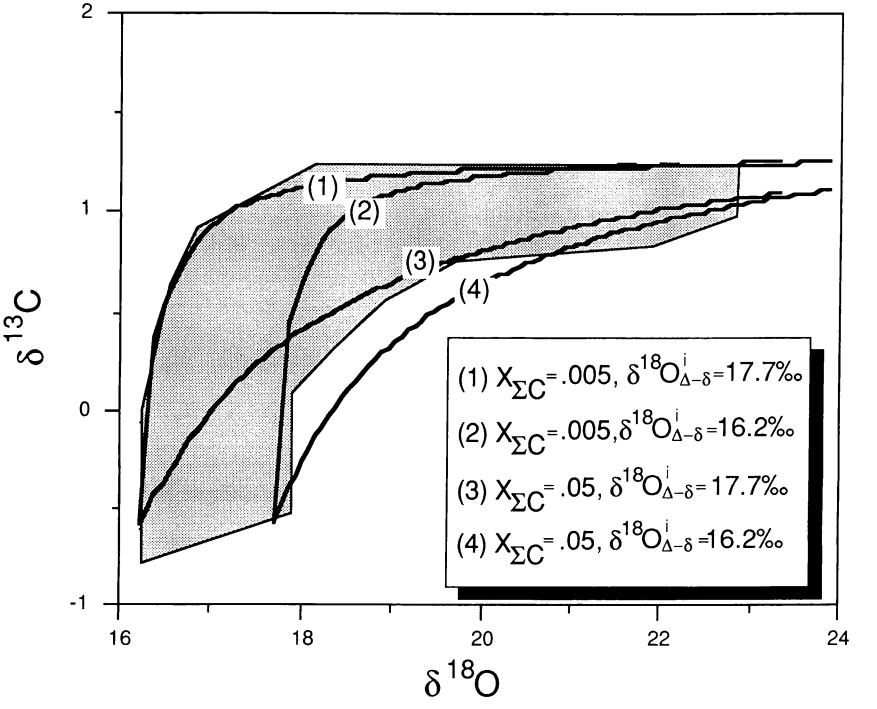


Fig. 8(A) represents several model isotopic exchange curves. Different symbols are for different $X_{\Sigma C}$ values (open square is for $X_{\Sigma C} = 0.005$, X is for $X_{\Sigma C} = 0.05$). Lines of the same width are for external fluids of the same carbon isotopic composition (thick lines are for $\delta^{13}C^{i}_{\Delta-\delta} = -3.6$ permil, thin lines are for $\delta^{13}C^{i}_{\Delta-\delta} = -0.06$ permil). Lines of the same pattern are for external fluids of the same oxygen isotopic composition (stippled pattern is for $\delta^{18}O^{i}_{\Delta-\delta} = 17.7$ permil, solid line is for $\delta^{18}O^{i}_{\Delta-\delta} = 16.2$ permil). The $\delta^{18}O$ of the initial rock is taken to be 28 permil, the $\delta^{13}C$ of the initial rock is taken to be 1.1 permil. (B) compares several exchange curves to the data envelope shown in figure 5. Note that for $X_{\Sigma C}$ values greater than 0.05 the model curves fall outside the data set envelope.

mate the $\delta^{18}O$ value of calcite in equilibrium with the initial fluid ($\delta^{18}O^{i}_{\Delta-\delta}$). For the vein array-host rock data set shown in figure 5 the sharp bend in the data array is at a $\delta^{18}O$ value of between 16.2 and 17.7 permil.

The measured $\delta^{18}O$ values of calcite, shown in figure 5, represent the final $\delta^{18}O$ values of calcite ($\delta^{18}O^{f}_{CC}$) in the exchange equation. The $\delta^{18}O$ value of the initial calcite in the rock is more problematical. Because the host rock has undergone isotopic exchange we must find a way to estimate the original oxygen isotopic composition.

Micropaleontological examination of the carbonate matrix demonstrated the presence of Discocyclinid-A Superfamily formanifera, bryozoa, and other marine benthonic fauna of probable age between Maastrichtian and Selandian. The measured oxygen isotopic composition of carbonates of the same age collected in undeformed sections of the thrust sheet have an average value of 28 permil (Hoffman, Bradbury, and Rye, 1983). This value is consistent with the expected oxygen isotopic composition of unexchanged Maastrichtian to Selandian age carbonates (Hoefs, 1973). We therefore are confident that an appropriate value for unexchanged matrix carbonate ($\delta^{18}O^{i}_{CC}$) is 28 permil.

We now can consider if the host rocks were open or closed with respect to fluid.

Closed System Models

One-step model.—From the model parameter values described above, the integrated fluid-rock ratios for different parts of the isotopic data set of figure 5 have been calculated using the mass balance equation for a closed system. The calculated fluid-to-rock ratios are indicated on figure 9.

The present carbonate matrix has $\delta^{18}O$ values ($\delta^{18}O^{f}_{CC}$) between 20.7 and 22.3 permil. Using the model parameters discussed above ($\delta^{18}O^{i}_{CC}$ = 28 permil, $\delta^{18}O^{i}_{\Delta-\delta}$ = 16.2 to 17.7 permil), the minimum integrated molar fluid-to-calcite ratio required to change the matrix calcite $\delta^{18}O$ value from 28 to 22.3 permil is between 2.8 and 3.7, and the minimum molar fluid-to-calcite ratio required to change the matrix from 28 to 20.7 permil is between 4.9 and 7.3. Thus to produce all the $\delta^{18}O$ values observed in the matrix calcite requires a fluid-to-calcite ratio in excess of 4.9.

To understand the significance of these values, it is necessary to recalculate the ratio as a volume ratio, taking into account the rock modes. Within the biomicrites, only calcite and quartz are significant phases. Taking the average mode of the biomicrite (21 percent quartz, 74 percent calcite, and 5 percent opaque minerals), the calcite density of 2.7 g/cc and molecular of weight of 100, a volumetric fraction of 0.02 moles/cc is calculated for calcite. An equivalent of approx 0.05 moles/cc can be calculated for water. A molar water-rock ratio of 1, therefore, is the same as a rock porosity of 0.29.

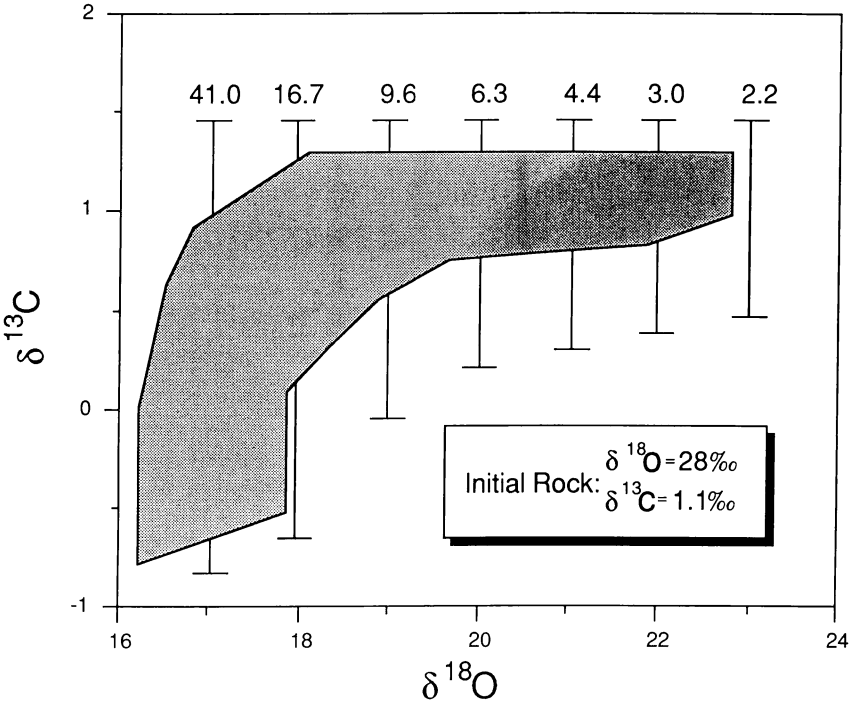


Fig. 9. Data envelope shown with calculate fluid to rock ratios necessary to produce the isotopic values observed in a one stage closed system. Note that for the matrix isotopic values, if the rocks started with a $\delta^{18}O$ value of 28 permil, the calculated fluid to rock ratio is much too high for the closed system model to be realistic.

Reframing the calculated fluid-calcite ratios for rock matrix exchange in terms of rock porosity would mean that the apparent shift in the oxygen isotopic signature from 28 to 20.7 permil by the same fluid that produced the veins would, in a closed system, require a primary porosity of between 0.66 and 0.74. It is clear that a one-step exchange history under closed system conditions is impossible.

Two step model.—Another possibility is that the rock calcite had already been exchanged before the fluids that produced the veins entered the rock. Again we can ask if the system was open or closed with respect to fluids. If the rock was closed to fluids from an external source, then by definition the initial trapped fluid was sea water. Because, the fractionation between H_2O and calcite becomes smaller at high temperatures, for a given fluid isotopic composition less fluid is required to produce the same isotopic shift in the original rock at higher temperatures than at lower temperatures. These two facts require that we choose 0 permil (sea water value) for the isotopic composition of the

water and a temperature of 320 degrees C (approx the highest temperature reached) to obtain the minimum amount of original pore fluid needed to cause the isotopic shifts produced in the rocks.

Putting these values into the oxygen isotope mass balance equations yields a minimum fluid-to-calcite ratio of 0.98 to 1.38 to shift the $\delta^{18}O$ value from 28 to the observed values of 20.7 to 22.3 permil. These values translate into a minimum porosity of 0.28 to 0.36. Again, we conclude that closed system exchange cannot account for the $\delta^{18}O$ values observed in the biomicrites.

There are two open system models that can explain the relationship between the isotopic ratios observed in the calcite matrix and the vein system. The first of these models we shall call the continuous open system. The second model we shall call the two-stage or multistage open system.

Open System Model

Continuous open system.—All the isotopic data from calcites define a continuous array on a $\delta^{18}O$ versus $\delta^{13}C$ plot. This fact suggests that the isotopic values of the matrix calcite, the isotopic values recorded in the vein arrays, and the isotopic values associated with fractures were part of a continuous fluid history.

Assuming a continuous fluid history for both the matrix calcite and the vein array, we can calculate the fluid-to-calcite matrix ratio in an open system using the model parameters derived above. A minimum molar fluid to calcite ratio of 1.3 is required to obtain a matrix calcite $\delta^{18}O$ value of 22.3 permil, and a minimum ratio of 1.8 is required to obtain the matrix calcite $\delta^{18}O$ value of 20.7 permil. This part of the exchange history was probably dominated by porous flow, which allowed calcite in the entire rock to undergo exchange.

For the continuous model we would argue that at some point in time the flow changed from porous to localized flow along the developing stylolite-vein network. The individual fibers that precipitated from fluid packets that drained the local rock probably had isotopic compositions reflecting the local fluids (producing fibers with isotopic compositions identical to the surrounding matrix calcite), whereas fibers formed from fluid packets that had longer path lengths had isotopic compositions that recorded the initial fluid composition of the introduced fluid and the amount of exchange experienced by the fluid on its trip through the rock to the vein site. As the flow became concentrated in the stylolites less exchange with the wall rocks was permitted, and the isotopic compositions began to reflect more closely the external fluid. This phase of the fluid history is recorded as fibers in the vein arrays with highly variable $\delta^{18}O$ values, because the amount of exchange in individual stylolites was highly variable.

Near the end of the fluid history recorded in the vein system the rock fractured, and external fluids had direct access to the vein array

without any significant exchange with the enclosing matrix calcite. This phase of the fluid history is represented by the late stage calcite fracture fillings.

In this scenario we can calculate formal water to rock ratios for the fluid system from the fibrous vein data. However, we point out that this has little meaning for the overall fluid-rock system, because once fluid flow was channelized into discreet zones the fluids could not exchange with the whole rock but only with the walls of the discreet pathways. For the vein infillings we argue that the W/R was essentially infinite, and the vein $\delta^{18}O$ and possibly the $\delta^{13}C$ values reflect the source of the externally derived fluid. When we refer to W/R in the vein arrays we are refering to the number of moles of oxygen that are from the original fluid divided by the number of moles of oxygen in the fluid derived from the rock it passed through. The $\delta^{18}O$ of each fiber reflects the nature of the fluid path, the length of the path, the rate of the fluid flow, the rate of exchange, and the temperature of exchange. All or some of these parameters could and apparently did vary a great deal during the evolution of the vein array system. We discuss this fact at some length in a subsequent section of the paper.

A significant problem with the above scenario is that a two stage or multistage model is indistinguishable from the continuous single fluid model.

Two stage or multistage open system.—In the scenario presented above, we suggested that an early porous fluid flow was recorded in the matrix calcite, whereas a latter flow system controlled by stylolites was recorded in the vein arrays and fracture fillings. Unfortunately, the data do not require that these two parts of the fluid history were produced by the same fluid. The porous flow exchange could have been produced by any fluid that would produce a calcite that was depleted in ^{18}O relative to the final matrix calcite value. Any subsequent discreet flow system would first sample any residual pore fluid followed by partially exchanged externally derived fluid.

Importantly, closed system models cannot account for the observed vein system or wall-rock carbonate isotopic values. It is therefore necessary to accept that the system was open to fluids both prior to and during vein formation. Before commenting on the nature and possible source terrain of the fluid responsible for the vein system it is necessary to consider the spatial and temporal variations in isotopic composition of the vein-wall rock system on a fine scale.

SOME IMPLICATIONS OF THE ISOTOPIC MODELS

Nature of the Flow System

An enlarged drawing of part of the fibrous vein and its surrounding wall rock is shown in figure 10. The plotted oxygen and carbon isotopic values further illustrate a number of facts that are important for understanding vein fiber growth mechanisms and fluid migration pathways.

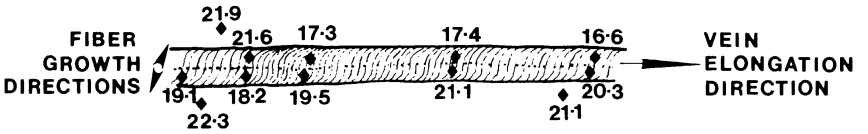


Fig. 10. Oxygen isotope data shown on a detailed drawing of vein limb and surrounding matrix. The oxygen isotopic values vary by up to 3.7 permil across the median suture, and by up to 4.3 permil in adjacent samples on the same side of the median suture.

Irrespective of position in relation to either stylolites or vein margins, the oxygen and carbon isotopic composition of the wall-rock matrix carbonate is essentially uniform. By contrast, there is a significant variation in the $\delta^{18}O$ values of fibrous calcite both along and across the length of the vein.

There are two important aspects of the isotopic data from vein fibers that can be observed in figure 10: (1) In the direction of vein propagation, there are large variations in the oxygen isotopic composition of adjacent samples (up to 4.3 permil), but there is apparently no regular pattern to these variations. (2) Although there is an apparent textural continuity in calcite fibers from one side of the median suture to the other, there is a sharply defined change in the oxygen isotopic signatures across the suture of up to 3.7 permil.

Although sampling difficulties make it impossible at present to provide a definitive statement concerning variations in the isotopic composition of an individual fiber on one side of a median suture, close spaced sampling has so far shown the individual fibers to be homogeneous. It appears therefore that vein median sutures are discreet surfaces of marked oxygen isotopic discontinuity. Boundaries between isotopic populations along the length of a vein are more difficult to define texturally and may be more diffuse isotopic transitions.

The alteration of discreet isotopic signatures along the length of a vein and across the median suture suggests that there was not any extensive vein-parallel fluid migration related to exchange during vein formation. Rather, fluids must have entered the vein system from the sides. This fact, plus the fact that the location of distinctive oxygen values within different parts of the vein appears to correlate with the position of dominant stylolitic surfaces abutting the vein wall, suggests that the variations in the fluid-to-rock history recorded in the fibers correspond to a localization of fluid migration within stylolites during fibrous vein growth.

The textural evidence cited earlier demonstrates that dissolution took place in stylolites at the same time precipitation took place in the sigmoidal veins. This process alone cannot account for the isotopic variations observed in the veins because the amount of oxygen that could have been incorporated in the fluid would have been limited by the solubility of calcite. Yet, there is no textural or isotopic evidence that

anything but dissolution took place along the stylolite surfaces next to the veins. It therefore appears that significant and variable amounts of exchange of the fluid took place before the fluid entered the local stylolite system. This conclusion is consistent with the observation that only 40 percent of the vein material could have been derived from the local stylolite network.

If a stylolite delivered fluid to the vein that was derived from trapped pore fluids within the local biomicrite, the isotopic values recorded in the vein would be identical to the values in the calcite matrix regardless of how far the fluid may have migrated through the rock. On the other hand, if a stylolite delivered fluid that migrated from outside the carbonate unit to a growing fiber, the isotopic values recorded in the fiber would depend on the fluid flow path length, flow rate, the isotopic composition of the fluid that entered the stylolite, and the exchange rate within the stylolite that supplied the fluid to the vein fiber. The fact that the isotopic composition of an individual vein fiber appears to be uniform suggests that these parameters remained nearly constant within a given stylolite during the growth of a given vein fiber.

Successful models for the propagation of stylolites (for example Fletcher and Pollard, 1981) predict they must be finite in length. In the present context, this indicates that, in spite of the extensive nature of the stylolite network as a whole, individual zones are likely to have tapped fluids from some part of the carbonate matrix, at least at their terminations. It seems reasonable therefore to speculate from the combination of the isotopic observations and the nature of stylolites that different flow regimes co-existed and fed the stylolites at their terminations throughout the period of vein growth.

Thermal Conditions

Limits can be set on the possible fluctuations in temperature that could have occurred during the exchange history by reference to the form of the envelope to the data set shown in figure 5. The range of isotopically light oxygen values within the field of $\delta^{13}C$ variation (the region where the $\delta^{18}O$ value of calcite closely represents the initial oxygen isotopic composition of H_2O plus the fractionation between calcite and H_2O) may reflect variations in $X_{\Sigma C}$ or variations in temperature during the precipitation of the non-fibrous part of the vein. If the temperature was at 300 degrees C or less, the entire observed variation in these $\delta^{18}O$ values of 1.3 permil can be accounted for if the temperature variation was 50 degrees C or less. Thus, in the late stages of the vein development the temperature variations were probably on the order of less than 50 degrees C. In fact; although the data do not require that the entire exchange history was nearly isothermal, all the data can be accounted for if the temperature only varied by 50 degrees C or less over the entire exchange history.

Origin of Fluids

Isotopic constraints.—From the oxygen isotopic fractionation curve for calcite-H_2O we can now estimate the initial oxygen isotopic composi-

tion of the fluid responsible for the exchange process recorded in the vein array. Using the estimated temperature of 300 degrees C and the $\delta^{18}O^{i}_{\Delta-\delta}$ value ($\delta^{18}O$ value of calcite in equilibrium with the initial fluid) of 16.2 to 17.7 permil, determined from the theoretical $\delta^{18}O$ versus $\delta^{13}C$ exchange curve, the calcite-H_2O oxygen isotope fractionation curve yields a $\delta^{18}O$ value of between 10.6 and 12.1 permil for the water. These values are within the range expected for fluids derived from a silicate source under a broad range of metamorphic conditions. However, a carbonate source for the fluids is also possible.

Carbonate Source Model

As the isotopic composition of carbonate in equilibrium with the initial fluid has a lighter $\delta^{18}O$ value (16.2–17.7 permil) than either the original (28 permil) or the most exchanged host rock carbonates (20.8 permil), the fluid could only have been derived from an area dominated by carbonates, if the fluids were equilibrated in the source region at a lower temperature than the temperature achieved during vein precipitation. For example, if the fluid reached a temperature of 300 degrees C during vein development and the fluid composition was set by a carbonate with a $\delta^{18}O$ value of 28 permil, the temperature in the source region would have been 97 to 112 degrees C. If the carbonate had a value of 20.8 permil (the most exchanged host rock) the temperature would have been between 188 and 216 degrees in the source region.

The above conclusion requires that if the fluid was derived from the carbonate section the fluids must have been descending. If fluids were descending they would have had to have gone through a carbonate sequence while being heated and remained at saturation with respect to calcite as they entered the carbonate unit of study and not have come to isotopic equilibrium with carbonates on the downward fluid flow path. Given that the solubility of calcite in H_2O decreases with increasing temperature for any P_{CO_2} (Ellis, 1963) and increases with P_{CO_2} at any given temperature (Ellis, 1963), this scenario is possible.

One possible model is illustrated in figures 11 and 12. As the temperature effect on solubility of calcite dominates over the pressure effect in any reasonable geothermal gradient (Holland, 1967), descending fluids, along path A–B in figures 11 and 12, that have equilibrated with carbonate reservoir I at low temperatures (~100 degrees C), will continuously precipitate calcite. This means that the fluids will remain at or near saturation with respect to calcite, however, because no dissolution will take place it is possible that little or no isotopic exchange will take place with the rocks. As these fluids enter carbonate reservoir II they are at saturation with respect to calcite and have an isotopic composition that is about 10 to 12 permil out of equilibrium with the matrix calcite. Along flow path B–C conditions are essentially isothermal, and porous flow dominates. As the fluids are at saturation, recrystalization of the carbonate takes place, and the matrix calcite undergoes isotopic exchange with the fluid. Finally, as deformation proceeds, the rocks, hence the fluids, encounter a thrust ramp. Within the ramp

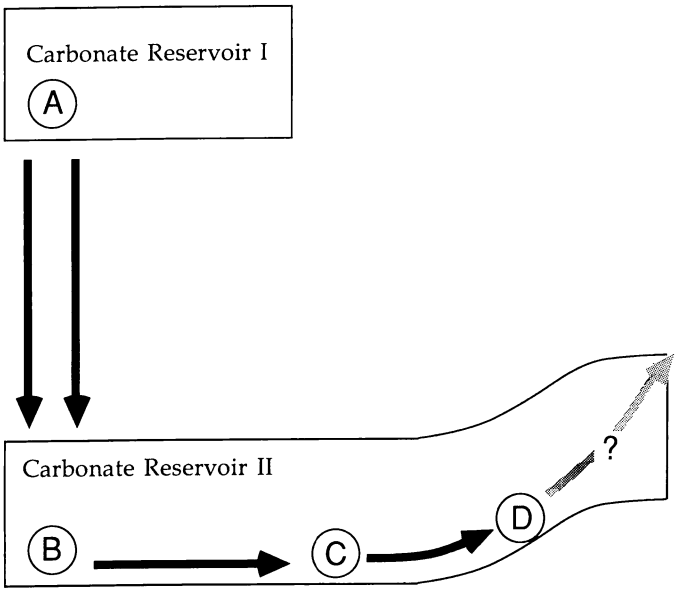


Fig. 11. Schematic flow path for fluids, assuming a carbonate reservoir for the external fluid. The conditions are illustrated in figure 12 (opposite page).

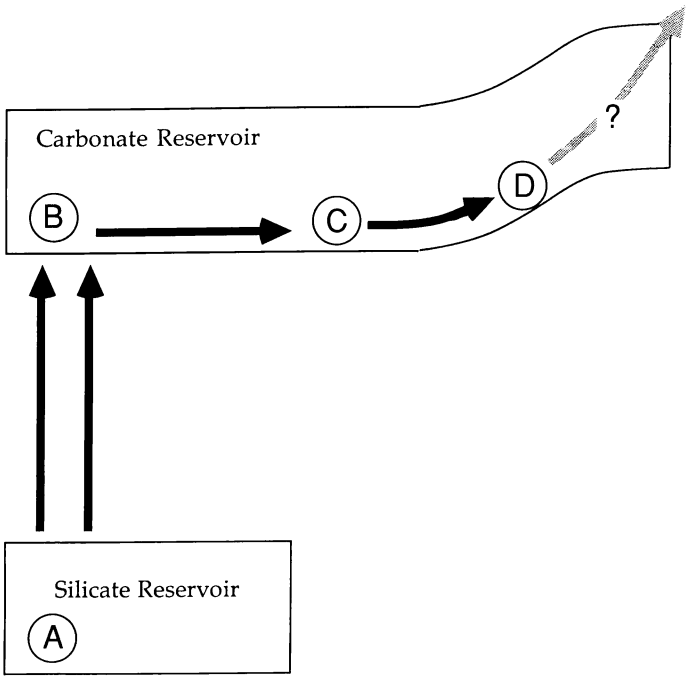


Fig. 13. Schematic flow path for fluids, assuming a silicate reservoir for the external fluid. The conditions from points B to point D are illustrated in figure 12 (opposite page).

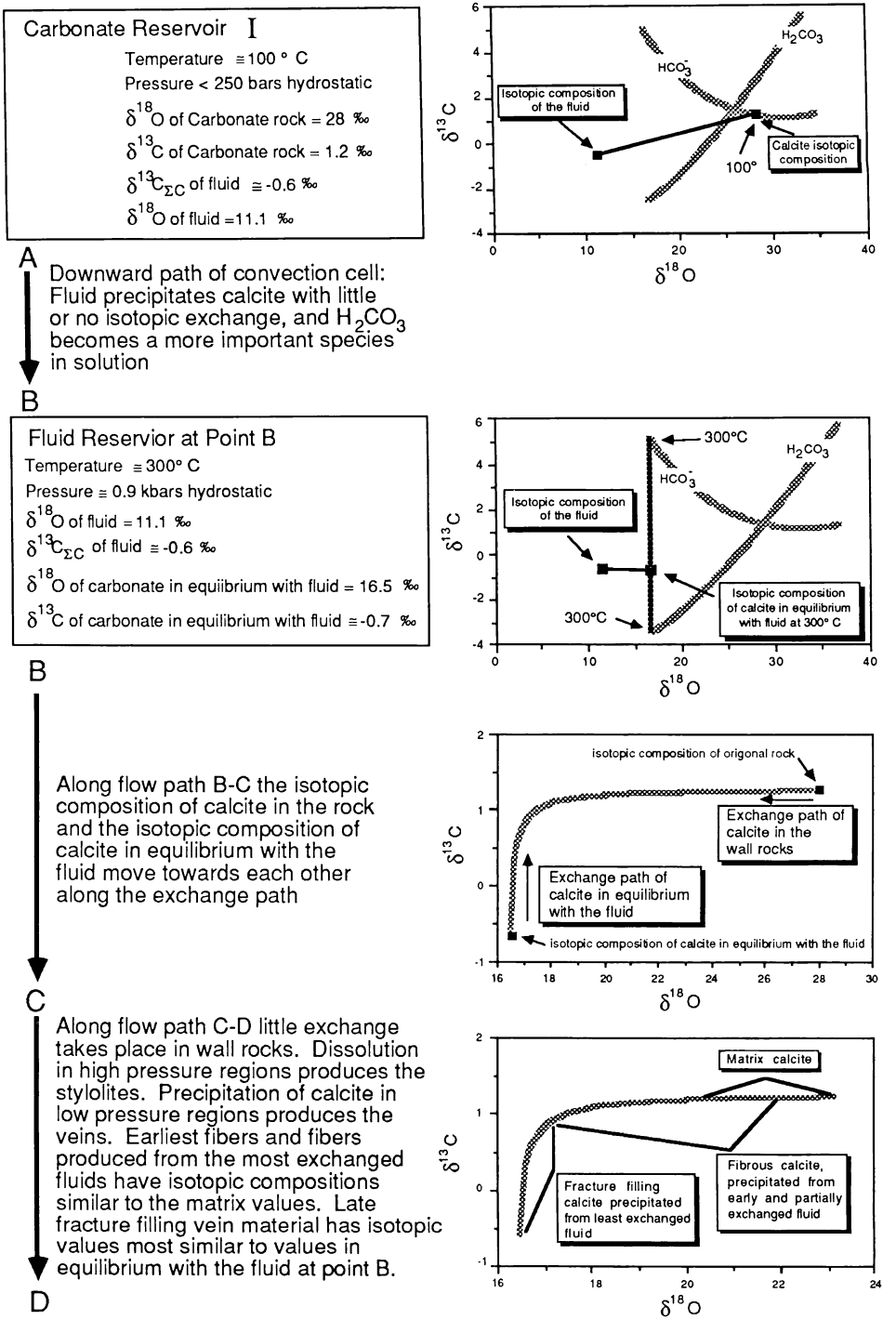


Fig. 12. Schematic representation of carbonate source model. Reservoir I is at ~100 degrees C. Reservoir II is at ~300 degrees C. Along flow path A-B fluids are heated and calcite is precipitated. Along path A-B fluids do not experience isotopic exchange with the wall rocks but do remain near saturation with respect to calcite. Along flow path B-C conditions are nearly isothermal (~300 degrees C), calcite is recrystallized during porous fluid flow, and isotopic exchange between the wall rocks and the fluid occurs. Along flow path C-D, the fluids encounter a thrust ramp. At this point dissolution takes place in high pressure regions, producing the stylolites, and precipitation occurs in the low pressure regions, producing the vein arrays. The rock matrix does not exchange to any significant degree, because fluid flow is restricted to the stylolite-vein array system. Fluids experience different amount of exchange depending on the plumbing characteristics of the individual stylolites. Finally, when brittle fracture occurs fluids flow fast enough and in a narrow enough zone that they are essentially unexchanged with the wall rocks.

dissolution takes place in the higher pressure regions, producing the stylolites, and precipitation takes place in the low pressure regions, producing the vein array (path C–D in figs. 11 and 12). At this point the flow becomes controlled by the stylolite-vein network. As the scale of fluid flow becomes more localized, ending in fracture controlled flow, there is less opportunity for exchange to place with the wall rocks, and the fluid composition approaches the composition it had at point B in the flow path. This scenario requires a minimum path length for the fluid flow system on the order of kilometers. We note that the temperature of approx 300 degrees C may have significance in this model because the addition of salt to H_2O causes the solubility of calcite to go through a minimum at about 300 degrees C (Holland, 1967).

Silicate source models.—An oxygen isotopic composition for water of 10.6 to 12.1 permil is within the range of values expected of fluids equilibrated with metamorphic pelitic rocks or of fluids generated by low grade metamorphic devolatilization reactions in pelites (for example, Rye and others, 1976). Dewatering of the Permo-Triassic during slaty cleavage development is one possibility. This scenario would imply a minimum path length for the fluid of a few tens of meters but could be appreciably greater. We have already demonstrated that the fluid flow was probably within discreet zones within the carbonate prior to entering the local stylolite network. This fact implies that if fluids came from below they did not enter the carbonates from directly below the vein array but rather some considerable distance down "dip."

Alternatively, the estimated fluid isotopic composition may correspond to a source terrain within basement igneous complexes (for example, Taylor, 1977), such as the granodioritic massifs. This scenario would imply a significantly greater path length for fluid transport which cannot be specified at present. However, it can be noted here that primary crystallization of the massifs was a Hercynian event, and that our research to date on such problems suggests that derivation of fluids from these complexes, or beneath them, would probably require fluid focussing through basement shear zones (compare Lamouroux and others, 1979) concomitant with uplift.

The salient features of the silicate rock source region for the fluids are shown in figures 12 and 13. For either possible silicate rock source region the fluid enters the carbonate rock system with a $\delta^{18}O$ value 10.6 to 12.1 permil. Initially, along path B–C, porous flow dominates, and the wall rocks undergo wholesale isotopic exchange. Eventually, during deformation the fluids encounter a ramp (path C–D in figs. 12 and 13). Within the ramp, dissolution takes place in the higher pressure regions, producing the stylolites, and precipitation takes place in the low pressure regions, producing the vein array. At this point the flow becomes controlled by the stylolite-vein network. As the scale of fluid flow becomes more localized, ending in fracture controlled flow, there is less opportunity for exchange to place with the wall rocks, and the fluid composition approaches the composition it had at point B in the flow path.

Importantly, although we do not have sufficient information more clearly to identify the specific fluid source, we can conclude that the open system defined earlier was probably large regardless of whether the fluid came from silicates below or from the carbonates above. Significantly, it should be possible to test which of these source models is correct. We might expect that if the fluids were derived from the carbonate section the Sr isotopic composition of the veins will be identical to the host rock carbonate compositions, whereas, if the fluids were derived from the underlying basement, the Sr isotopic composition in the veins may be much more radiogenic than the carbonate host rock composition.

CONCLUSIONS

Consideration of the volume of material lost in stylolites and gained in veins indicates that only about 40 percent of the material in veins could have come from the local stylolite network. This observation requires that the vein stylolite system was open to external fluids. The stable isotopic study of the vein-host rock system puts several constraints on the nature of this flow system and leads to the following conclusions:

1. *Exchange and mass transfer occurred in the presence of water rich fluids.*—Variations in temperature, fluid-rock interactions, and fluid chemistry can generate characteristic data populations in $\delta^{18}O$ versus $\delta^{13}C$ space. For the vein-host rock data examined here, the $\delta^{18}O$ and $\delta^{13}C$ data array cannot be explained by simple variations in temperature and/or fluid chemistry, rather the array is best explained as representing an exchange profile between a water rich fluid and the carbonate host rock. Mass transfer of carbonate from the host rock to the vein array took place in a fluid with a $X_{\Sigma C}$ value of less then 0.05.

2. *The system was open to external fluids.*—Solutions to isotopic mass balance equations require that the system was open to externally derived fluids both prior to and during vein-stylolite formation. Closed system models require unrealistic porosities. The single stage closed system model requires a minimum porosity of 0.66, whereas the two stage model requires a minimum porosity of 0.28 at a depth of 9 km.

3. *Early exchange and flow were controlled by porous flow behavior.*—The calcite matrix underwent wholesale isotopic exchange before the development of the stylolite-vein array system. This fact requires that the fluids had access to all the grains and almost certainly means that the early open system fluid flow was porous.

4. *Fluid flow was controlled by the stylolite network during vein development.*—Once stylolites developed, apparently no further significant exchange took place in the calcite matrix around the stylolite network. The isotopic variations across the median suture in fibrous veins and along the direction of vein growth indicate that there was little or no fluid flow and exchange along the vein length and that the fluid flow and exchange was controlled by the stylolite network during vein growth.

5. *Local fluid flow evolved from porous flow to flow within the styolite-vein network.*—The exchange history changed from wholesale carbonate matrix exchange to essentially no exchange in the local carbonate

matrix as stylolites developed. In addition, the fibrous veins record a highly variable amount of exchange of the fluid on a scale that corresponds to the spacing of stylolites. These facts are compelling evidence that the fluid flow system evolved from porous flow to flow along individual stylolites and veins.

6. *Conditions in the host rock may have been nearly isothermal during the local exchange history.*—The entire envelope to the vein array-host rock data set can be fitted to a model in which the maximum temperature range is less than 50 degrees C. It is therefore possible that conditions were nearly isothermal over the time that the matrix underwent wholesale exchange through the time that vein development ceased.

7. *The oxygen isotopic composition of the water that entered the local system was estimated to be between 10.6 and 12.1 permil.*—The temperature estimated from the calcite-dolomite solvus and from the oxygen isotopic fractionation between calcite and dolomite is approx 300 degrees C. The estimated $\delta^{18}O$ of calcite in equilibrium with the initial fluid, estimated from the theoretical isothermal isotopic exchange curve, is between 16.2 and 17.7 permil. Using these values and the H_2O-calcite oxygen isotope fractionation curve yields a $\delta^{18}O$ value for the water of between 10.6 to 12.1 permil.

8. *If the fluids were derived from a carbonate terrain they must have been descending fluids.*—Fluids with an oxygen isotopic composition of around 10.5 to 12.0 permil could be produced in exchange equilibrium with a carbonate of 28 permil at about 100 degrees C. If fluids of this type descended through the carbonate pile they would precipitate calcite and probably not exchange isotopically with the carbonate wall rocks as the temperature increased. The result would be that at 300 degrees C the fluid would be at near saturation with respect to calcite and still have an oxygen isotopic composition of between 10.5 and 12.0 permil.

9. *Fluids may have been derived from or equilibrated with metamorphic rocks of the basement.*—The calculated oxygen isotopic composition of the externally added water of 10.6 to 12.1 permil is within the range expected of fluids in equilibrium with a wide range of metamorphic silicate rocks. This fact means that fluids may have been derived from or equilibrated with basement rocks such as the Permo-Triassic slates or the Hercynian granodiorites.

10. *The scale of fluid transport may have been on the order of kilometers.*—Fluids may have been generated or equilibrated with metamorphic rocks, or they may have been introduced from the carbonate section above. Two potential source regions exist for derivation of metamorphic fluids during basin development. The first is the immediately subjacent Permo-Triassic section in which slaty cleavage development occurred at the same time as stylolite formation in the overlying carbonates. Basement shear zones are a second alternative metamorphic rock source region. A fluid source within the Permo-Triassic implies a

minimum path length for fluids on the order of tens to hundreds of meters. Fluid focussing within basement shear zones implies a minimum path length on the order of a few hundreds of meters to kilometers. If fluids were derived from the carbonate section the fluid path length was on the order of kilometers. All these source regions require that fluid flow occurred on a large scale.

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