

Carbon and oxygen isotope geochemistry of chlorite-zone rocks of the Waterville limestone, Maine, U.S.A.

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ABSTRACT

Analyses of 266 samples of calcite and dolomite from veins and wall rocks of the Waterville limestone from the chlorite zone have been made for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. The least altered samples of limestone have $\delta^{18}\text{O}$ values of +19.5 to +20.5‰ (SMOW) and $\delta^{13}\text{C}$ is -1 to +1‰ (PDB). The isotope values have been shifted by 3 to 7‰ in $\delta^{18}\text{O}$ and 0 to 4‰ in $\delta^{13}\text{C}$ relative to unaltered marine limestones of equivalent stratigraphic age. The shifts are similar to isotopic changes observed in unmetamorphosed but diagenetically altered limestones. The shifts are also consistent with the infiltration of H_2O -rich fluids during metamorphism. We cannot make a definite choice, at the present time, between the two explanations of changes in isotopic compositions, diagenetic or metamorphic.

The limestone in the chlorite zone is crosscut by four generations of veins and two sets of solution cleavages. Two older generations of veins and one of solution cleavage preceded metamorphism. The growth of metamorphic minerals was accompanied by solution of calcite along solution cleavage and its precipitation in synmetamorphic veins. During a postmetamorphic episode of vein formation, isotope alteration halos with depletions of 1–2‰ in $\delta^{18}\text{O}$ and of 4‰ in $\delta^{13}\text{C}$ were imposed on wall rocks. The Waterville limestone therefore has had a protracted history of fluid infiltration, involving both pervasive and fracture flow, that was not limited just to the peak of regional metamorphism.

INTRODUCTION

Infiltration of rock by chemically reactive fluids may be an essential driving force of prograde metamorphic mineral reactions (Rice and Ferry, 1982; Ferry, 1983). Instances of such infiltration-driven metamorphism can be identified by studies of reaction progress (Ferry, 1986a), and one of the first documented examples was the regionally metamorphosed Waterville Formation, Maine (Ferry, 1980a, 1984). A subsequent more detailed petrologic study of the limestone member of the Waterville Formation (Ferry, 1987) indicated that metamorphic fluid flow was highly channelized along lithologic layering at low metamorphic grades (chlorite, biotite, and garnet zones) and more pervasive at high grades (staurolite-andalusite and sillimanite zones). Calculated fluid/rock ratios increase from 0–0.4 in the chlorite zone to 0.8–1.2 in the sillimanite zone.

More recently the petrology of the Waterville limestone has been reinterpreted in terms of a model for coupled fluid flow and devolatilization reactions (Baumgartner and Ferry, 1991; Ferry, 1989). Results confirm that fluid flow

was highly channelized along lithologic layering at low grades, but more importantly they allow one to deduce the direction of flow (from low- to high-temperature portions of the terrane) and estimate the time-integrated fluid fluxes involved (1 to $40 \times 10^4 \text{ cm}^3/\text{cm}^2$ depending on lithologic layer). The reinterpretation implies that enormous quantities of fluid flowed through all parts of the limestone unit studied by Ferry (1987) from the chlorite zone in the northeast to the sillimanite zone in the southwest.

The magnitude of pervasive metamorphic fluid flow in the Waterville Formation, deduced from petrologic data, however, proved controversial and has prompted much discussion (e.g., Wood and Graham, 1986; Ferry, 1986b; Stewart, 1989). We are conducting an isotopic study of the limestone member of the Waterville Formation to seek evidence for or against metamorphic fluid flow that is independent of petrologic arguments. A similar approach was used in an earlier collaboration in which stable isotope data confirmed petrologic evidence that pre- to synmetamorphic granitic stocks, intruded into the Waterville Formation in the sillimanite zone, were infiltrated

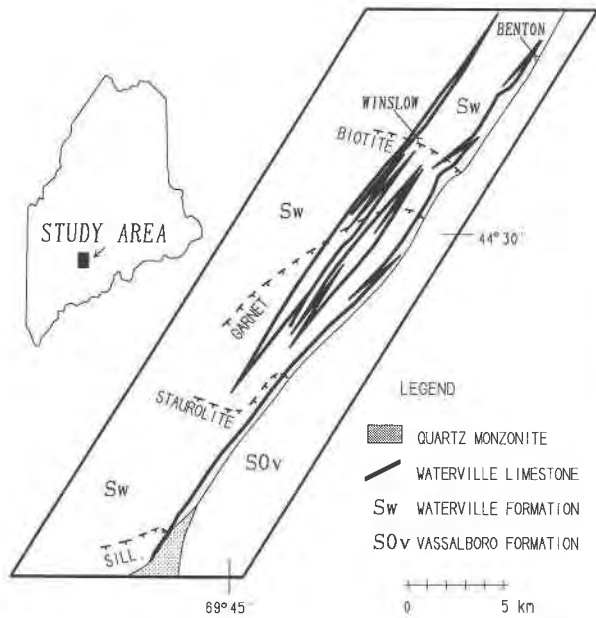


Fig. 1. Geologic sketch map with mineral isograds and sample localities (e.g., Benton, Winslow) in the study area. Isograds based on distribution of minerals in pelites of the Waterville Formation (after Ferry 1987; Osberg, 1968).

by metamorphic fluids (Rumble et al., 1986). In addition to testing the hypothesis of infiltration-driven metamorphism, the goals of the investigation are to (1) evaluate the effects of fluid flow along fractures in the Waterville Formation, as recorded by veins and their alteration halos, (2) assess the extent to which diagenesis and intrusion of dikes affected the stable isotopic composition of the formation, and (3) establish a chronology of deformation, metamorphic recrystallization, and vein formation in the area.

METHODS OF INVESTIGATION

The study focused on two outcrops of the limestone member of the Waterville Formation at Winslow and Benton, Maine (Fig. 1; location 7 of Ferry, 1987, Fig. 1; "bf" of Ferry 1976, Fig. 2). Both exposures lie in the chlorite zone with respect to mineral assemblages in pelitic schists; Benton lies ~7 km from Winslow in rocks of lower metamorphic grade, perpendicular to the strike of isograds. Detailed examination of these low-grade outcrops provides a base line against which may be measured isotopic changes at higher metamorphic grade. The orientation of bedding, two generations of folds, four generations of veins, and a set of felsic dikes were measured. Crosscutting and superposition relationships in outcrop were used to develop an internally consistent chronology of folding, vein formation, and igneous intrusion.

Large specimens 5–10 kg in size were collected from minor folds, veins, and diagenetic features. Specimens were slabbed with a rock saw, polished, and stained with

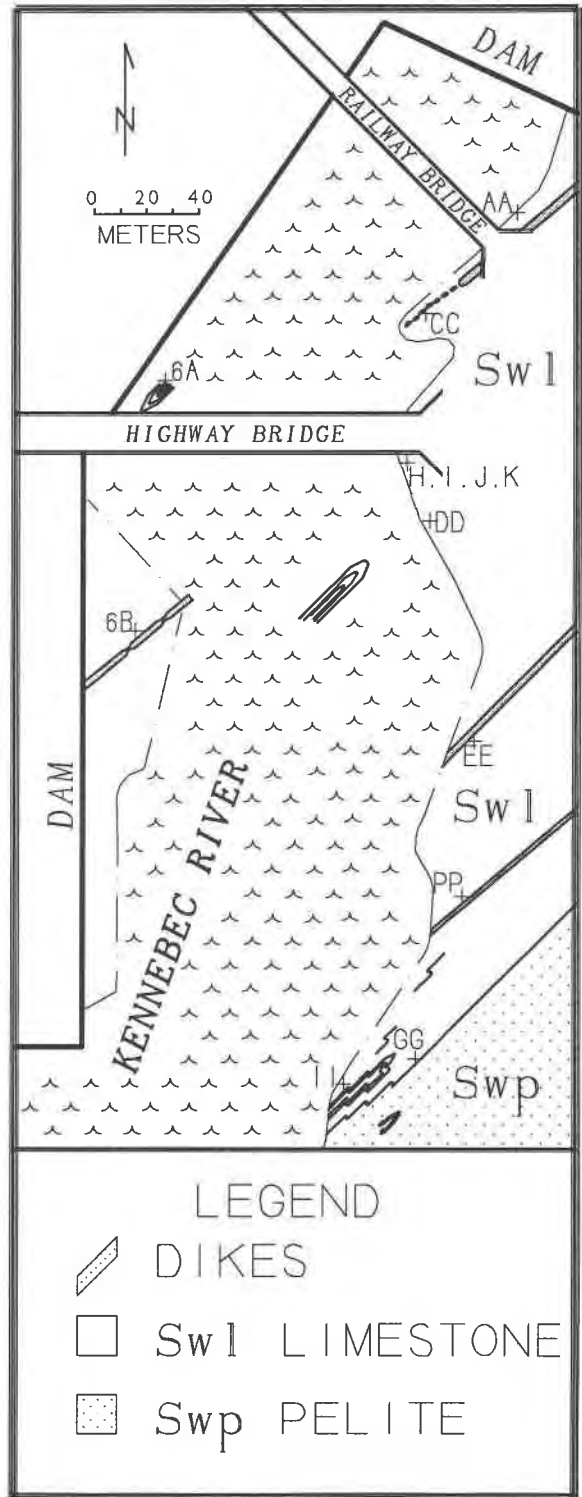


Fig. 2. Geologic sketch map with sample localities at the Winslow locality. Note extreme boudinage of dike at CC. Refolding of F2 folds by F3 is visible between GG and II. Stippled pattern in southeast corner denotes graded bedded pelites of Waterville Formation. Outcrop width of limestone extends from contact with pelite to northwest at least as far as dam.

TABLE 1. Chronology of Waterville limestone

	Diagenesis	F1	F2	F3	Post-F3
Folds		Recumbent, very large	Upright, isoclinal, 10 m to 1 km amplitudes, NE trend, common	Upright, monoclinical to tight, cm to m amplitudes, N to NNE trend, common	F4, upright monoclinical and conjugate kinks, cm to m amplitudes, E to SE trends, rare
Foliations/ solution cleavages	Dark solution seams, 0.2 to 1 mm spacing, poorly developed		S2: differentiated cleavage, 0.1 to 5 mm spacing, axial planar to F2	S3: solution cleavage in limestone, 5 to 30 mm spacing, broad crenulation cleavage in pelite, axial planar to F3	No cleavage
Veins	V1: deformed fibrous black calcite, 2 to 4 cm, also calcite + quartz + pyrrhotite veins, rare		V2: Irregular, 2 to 12 cm, calcite + quartz ± galena, common	V3: 1 to 10 mm, calcite + quartz ± white mica ± pyrite ± chlorite, axial planar to F3, but some boudinaged in S3, common	V4: 1 to 10 mm, quartz ± calcite, shallow-dipping, crosscutting, localized
Metamorphism/ mass transfer	Pervasive dolomitization	Dissolution of quartz and carbonates in S1	Dissolution of quartz and carbonates in S2	Metamorphic peak, extensive dissolution and precipitation of calcite + quartz in cleavage (S3) and veins (V3)	C isotope halos around V4 veins
Igneous intrusion			Granitic stocks, 381–394 m.y., felsic dikes		

alizarin red and potassium ferricyanide. Staining the polished slabs helps to locate and identify carbonate minerals and to recognize the age relations of stylolites, veins, minor folds, cleavage, and schistosity. Samples of carbonate minerals were drilled out with a diamond-tipped drill having a diameter of either 1 or 2 mm. Sample sizes ranged from 5 to 60 mg, as dictated by the size of the feature to be analyzed and the abundance of carbonate. Immediately after drilling, sample powders were loaded into two-legged reaction vessels for reaction with 100% phosphoric acid at 25 °C (McCrea, 1950).

Problems of cross contamination of evolved CO₂ by simultaneous reaction of calcite and dolomite (Epstein et al., 1964) were avoided by carefully drilling out either calcite-rich or dolomite-rich samples. Such a mineral separation was easily achieved on the polished, stained slabs. Aliquots of CO₂ taken at 5 min to 3 h after the initiation of phosphoric acid reaction give reproducible results for calcite-rich samples. Aliquots at 24 and 48 h yield δ¹³C and δ¹⁸O values for dolomite with a precision of ±0.1‰. The δ¹⁸O data are reported relative to standard mean ocean water (SMOW) and δ¹³C, relative to Pee Dee belemnite (PDB). Results in our laboratory were calibrated with NBS-18 [δ¹⁸O = 7.2‰ (SMOW) and δ¹³C = -5.0‰ (PDB)] and NBS-19 [δ¹⁸O = 28.65‰ (SMOW) and δ¹³C = 1.92‰ (PDB)] (Copen et al., 1983).

GEOLOGIC HISTORY

Understanding the geologic history of the Waterville limestone is essential for interpreting the stable isotope data because the unit has been subjected to at least four episodes of fluid infiltration, as well as intrusion by felsic dikes, metamorphism, and repeated folding. Our chronology (summarized in Table 1) is consistent with regional relationships mapped by Osberg (1968, 1979) and

Osberg et al. (1985), from whose work the following synopsis of regional relationships has been taken.

The Waterville limestone was deposited in Early Silurian time in a basin that contained in excess of 5000 m of turbidites. Primary sedimentary features such as current bedding are visible in both chlorite-zone outcrops. Diagenetic features are well preserved, including stylolites and secondary dolomitization. Stylolites are the locus of thin dolomite seams and of 2 mm pyrite cubes. Very fine-grained secondary dolomite pervasively replaces coarser-grained current-bedded limestone in rocks with no apparent stylolites.

The earliest folds (F1) were recumbent and of alpine proportions. The existence of the oldest folds was deduced from regional structural and stratigraphic relationships; they are not readily seen at outcrop scale. The recumbent folds were refolded by upright folds (F2) that are responsible for the repetition of the Waterville limestone displayed in Figure 1. Intrusion of felsic dikes and granitic stocks followed F2. The stocks give Rb-Sr whole rock isochrons of 381 to 394 m.y. (Dallmeyer and Van Breeman, 1981).

Regional metamorphism, accompanied by pervasive infiltration (Ferry, 1987), was superimposed on rocks that had already experienced diagenesis, two folding events (F1 and F2), and igneous intrusion. Folds of F3 developed concomitantly with metamorphism. The F3 folds are ubiquitous, frequently refolding F2 (Fig. 2), but cannot be seen in the regional outcrop pattern (Osberg, 1968). Pressure at the peak of regional metamorphism in the area was 3.5 ± 0.5 kbars (Ferry, 1980b); temperature was 390 ± 25 °C at Winslow and 375 ± 25 °C at Benton (Ferry, 1986b). Carbonate rocks at the two outcrops were recrystallized during metamorphism to the assemblage calcite + dolomite-ankerite solid solution + muscovite

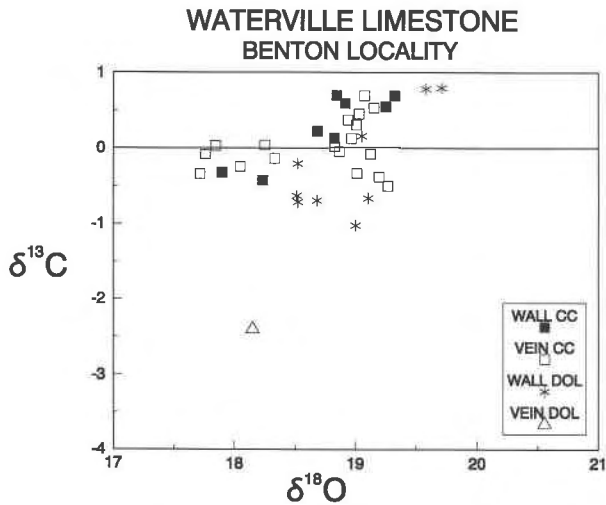


Fig. 3. Plot of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ of calcite (CC) and dolomite (DOL) from veins and their wall rocks, Benton locality. The outlying dolomite vein datum is from a vein for which field data are inadequate to assign a relative geologic age.

+ quartz + albite + rutile + graphite + pyrrhotite \pm chlorite \pm pyrite. Approximately one-third of the limestone at Winslow contains traces of biotite. Interbedded pelitic rocks are composed of muscovite + chlorite + ankerite + quartz + albite + rutile + graphite + pyrrhotite \pm siderite \pm pyrite.

VEINS

Four generations of veins indicate significant fracture permeability in the Waterville limestone throughout its geologic history. The earliest veins (V1) are composed of sigmoid fibers of intensely twinned black calcite and have been folded by F2 (locality DD, Fig. 2). The V1 veins are 2–4 cm thick, laterally extensive, and were probably planar and parallel to bedding prior to folding. The V1 veins are clearly premetamorphic in age; they may well be of diagenetic origin. Other very early veins, possibly related to the black calcite veins, contain calcite, quartz, and pyrrhotite.

The next generation of veins (V2) contain calcite, quartz, and rare galena and are irregular in shape and thickness (up to 12 cm). The veins characteristically contain angular fragments of locally derived wall rock. They are folded by F3 and crosscut by V3 veins. Emplacement of V2 veins was prior to metamorphism.

The V3 veins are up to 1 cm thick, planar, and laterally extensive, and strike north to northeast. These veins are the most commonly observed type and are typically intimately associated with a well-developed solution cleavage (S3). They lie parallel to the axial surfaces of F3 folds and crosscut older veins. The veins are composed of calcite quartz, white mica, and pyrite. There is microscopic and macroscopic evidence that some of the planar, north-striking veins classified as V3 are older than F3, i.e., some V3 veins are boudinaged by S3. A specimen of Waterville

pelite at Winslow shows biotite porphyroblasts overgrowing S2 but crosscut by S3 and V3. At higher grades, fibrolite mats lie within and parallel to axial surfaces of F3 (Osberg, 1968). The age of V3 veins extends from before to during the F3 folding event and overlaps the time of peak metamorphism.

The youngest veins (V4) are composed almost entirely of quartz with minor calcite. They are restricted to the vicinity of localities AA and CC (Fig. 2). The veins are thin (up to 1 cm), laterally extensive, irregularly planar, dip at 20–40°NW, and crosscut all older structures. The veins postdate F3 but it is not known either how much younger the veins may be than metamorphism or whether they are related to the weak F4 deformation. As discussed below in detail, the pattern of isotopic alteration of wall rocks by V4 fluids demonstrates that V4 veins are younger than the episode of metamorphic infiltration documented by Ferry (1987).

Dolomite-bearing veins were not recognized consistently in the field; thus, there are insufficient data to constrain the timing of their emplacement. The outlying data points in Figure 3 are analyses of such dolomite veins. The veins may represent an additional, but as yet unrecognized, episode of fracture permeability. Taken together, the (at least) four generations of veins demonstrate that there was fracture flow through the Waterville limestone over an extended period of time, both prior to and after the peak of regional metamorphism.

CONTROLS ON STABLE ISOTOPE COMPOSITION

The measured range of isotope values of the Waterville limestone is from -4 to $+1\%$ in $\delta^{13}\text{C}$ and from 17.5–20.5‰ in $\delta^{18}\text{O}$ in chlorite-zone outcrops. Such a range is comparable to the isotope shifts observed from the biotite to the sillimanite zone in marbles from many sites of regional metamorphism (cf. Valley, 1986, Fig. 6). The ultimate goal of our study, i.e., to establish the effects of metamorphism upon isotope systematics, cannot be achieved without first understanding the controls on isotope composition at the lowest levels of metamorphic intensity. Accordingly, we give an analysis of pre-, syn-, and postmetamorphic controls on isotopic compositions at Benton and Winslow.

Premetamorphic controls

The premetamorphic controls on isotopic composition considered are sedimentation, diagenesis, dolomitization, and intrusion of felsic dikes. The effects of premetamorphic processes are likely to be obscured by the cumulative overprinting of subsequent events. We sought samples such as those at primary stratigraphic contacts in which premetamorphic controls might be strongest and best preserved.

Sedimentation. Sedimentation may exert a control on isotopic composition because fluctuations in the proportions of the biogenic, authigenic, and detrital material can affect the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of a rock. There are no felsic dikes observed within 0.6 km of the Benton locality, and the

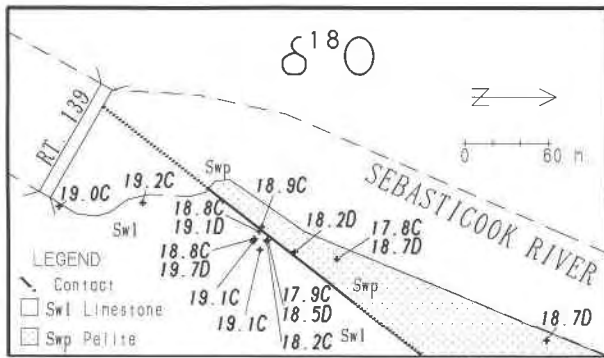


Fig. 4. Distribution of $\delta^{18}\text{O}$ values of analyzed samples of Waterville limestone in relation to pelites, Benton locality. Suffix C denotes calcite, D is dolomite.

rocks, although recrystallized to chlorite-zone assemblages, show no evidence of prograde metamorphic mineral reaction. The locality, therefore, is more likely to preserve the effects of sedimentation and diagenesis. The limestone is not pristine, however, as it contains S2 and S3 solution cleavages as well as V2 and V3 veins. The slightly lower values of $\delta^{18}\text{O}$ of calcite in pelite than in limestone at the locality and variations within the limestone unit (Figs. 3 and 4) demonstrate sedimentary variations in the O isotope composition of the Waterville limestone of 1‰. Results for the Winslow locality show a similar pattern of sedimentological control on isotopic composition. Measured $\delta^{18}\text{O}$ values of calcite adjacent to the limestone-pelite contact (box C, Fig. 5) are 1–2‰ lower than $\delta^{18}\text{O}$ values of calcite far removed from the contact (box A, Fig. 5). Analyses of individual hand specimens also show small but significant differences of up to 1‰ in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ between adjacent rock layers (Fig. 6). Results from both localities suggest that sedimentological heterogeneities in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were no more than 1–2‰ in the Waterville limestone.

Diagenesis. Diagenesis is known to lead to changes in texture and chemical and isotopic composition of limestones. Unaltered Silurian marine limestones are believed to have $\delta^{18}\text{O}$ values of 23 to 27‰ and $\delta^{13}\text{C}$ of 0 to +4‰ (Veizer and Hoefs, 1976). The marine limestone samples of low magnesium calcite were chosen as least altered by evaluating the diagenetic trends of trace amounts of Mn and Sr in the calcites (Brand and Veizer, 1981). Values at the highest end of the range of Waterville limestone (box A, Fig. 5) are lower by 3–7‰ in $\delta^{18}\text{O}$ and 0–4‰ in $\delta^{13}\text{C}$ relative to unaltered stratigraphic equivalents. Diagenesis is known to decrease $\delta^{18}\text{O}$ in limestones in proportion to the amount of meteoric H_2O involved. Values of $\delta^{13}\text{C}$ in limestones may be reduced by isotopic exchange between calcite and bicarbonate ions derived from organic matter. The apparent depletion in ^{18}O and ^{13}C of Waterville limestone shows the same trend that accompanies diagenesis (Brand and Veizer, 1981; O'Neil, 1987). Because we have not found outcrops lacking dia-

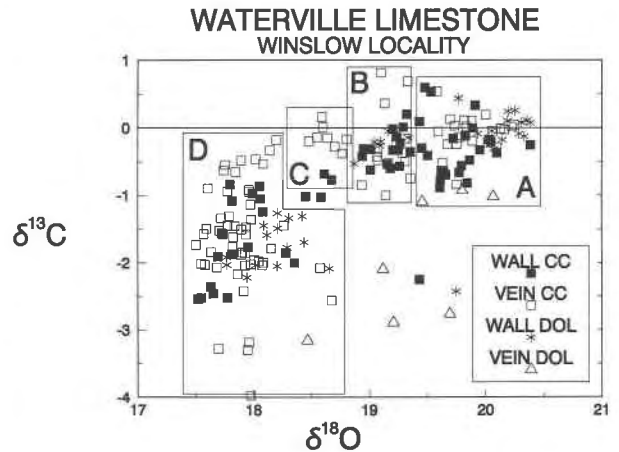


Fig. 5. Plot of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ of calcite (CC) and dolomite (DOL) from veins and their wall rocks, Winslow locality. Box A denotes samples 50–100 m distant from felsic dikes and 150 m across strike from the contact with a pelitic unit that has graded bedding (localities H, I, J, K, Fig. 2 and samples of Ferry, 1987). Box B outlines samples within 1 m of felsic dikes (localities EE and PP, Fig. 2). Box C refers to samples 1–7 m from contact with pelite (localities GG and II, Fig. 2). Samples affected by infiltration from V4 veins at localities AA and CC (Fig. 2) are in box D. Outlying dolomite vein data are from veins for which field data are inadequate to assign a relative geologic age.

genetic features, however, it is not possible to verify that the apparent depletion was caused by diagenesis.

Dolomitization. Dolomitization may change the isotopic composition of limestones if isotopic exchange accompanies the process of chemical exchange. The stable isotopic consequences of dolomitization on limestone are difficult to predict because, in addition to the influences of meteoric H_2O and organic-derived bicarbonate, there is the possible effect of brines enriched in ^{18}O by evaporation (Coniglio et al., 1988). Analysis of adjacent layers of calcite-rich, current-bedded limestone and replacement dolomite from the same hand specimen shows dolomite to be the same or enriched in both ^{18}O and ^{13}C by 0.5–1.0‰ relative to calcite (Fig. 6). Because all of the rocks in the chlorite-zone are pervasively dolomitized, however, it is impossible to measure the isotopic effects of dolomitization by direct comparison with unaltered limestone.

Intrusion of felsic dikes. The intrusion of dikes may alter the isotopic composition of wall rocks either by isotopic exchange between dike and walls or because of devolatilization reactions in wall rocks induced by heating. Comparison of data bounded by boxes A and B, Figure 5, demonstrates that intrusion of the felsic dikes at the Winslow locality caused no shifts in $\delta^{13}\text{C}$ of the Waterville limestone and shifts in $\delta^{18}\text{O}$ of 1–2‰.

Metamorphic controls

The isotopic composition of minerals can be affected by a number of metamorphic processes (Rumble, 1982;

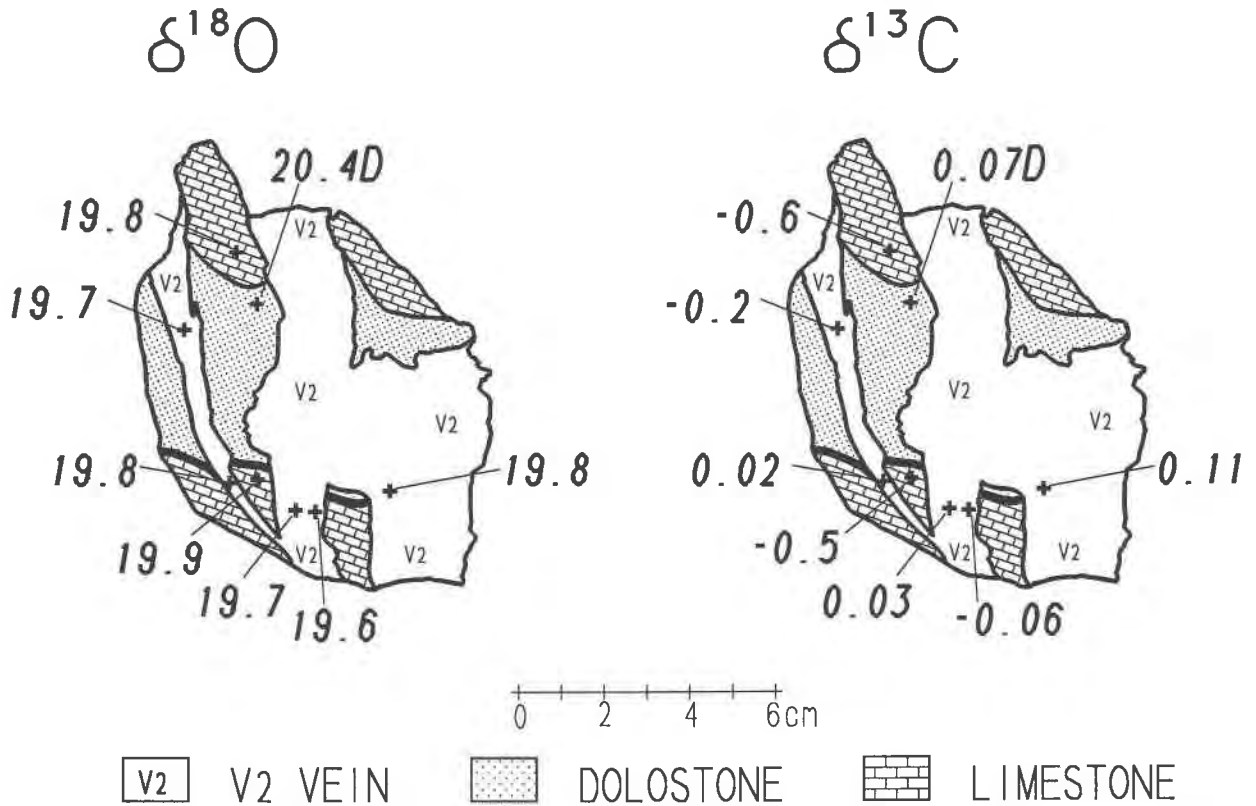


Fig. 6. Sketch of polished slab with isotopic data for calcite and dolomite (suffix D). Brickwork pattern is current-bedded limestone. Stippled pattern is fine-grained dolomite replacing limestone. Note characteristic vein breccia of V2. Sample from locality K, Figure 2.

Valley, 1986): (1) Isotopic species may be redistributed among minerals as their proportions change as a result of mineral reactions ("lever rule" effects) or as temperature increases (caused by the temperature dependence of isotopic fractionation). (2) Isotopic species may be lost to volatiles produced by devolatilization reactions (Rayleigh distillation). (3) Isotopic species may be exchanged with an external fluid reservoir if infiltration accompanies metamorphism.

Rayleigh distillation and lever rule effects. Solid products of decarbonation reactions in rocks may differ greatly in isotopic composition from solid reactants if CO_2 escapes from reaction sites because product CO_2 is strongly enriched in both ^{18}O and ^{13}C . Further shifts in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of minerals will occur because of changes in proportions of minerals caused by the reaction. We calculated the magnitude of expected shifts from measured progress of the prograde devolatilization reactions at the Winslow locality (Ferry, 1987) by the method of Rumble (1982). The calculations are based on isotopic analyses of the same samples whose mineral abundances were measured by Ferry (1987, sample numbers 7 + suffix). The fractionation factors used were those of Clayton et al. (1989), Kieffer (1982), Garlick and Epstein (1967), Sheppard and Schwarz (1970), Matsuhisa et al. (1979), and Bottinga

(1968). Calculated changes in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for both calcite and dolomite caused by reaction are less than 0.3‰. Because no decarbonation reactions are observed in samples from Benton, no isotopic effects caused by mineral reaction can be attributed to these rocks. Although decarbonation reactions can, in principle, change $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of rocks, reaction progress was so small at the two exposures of the Waterville limestone that no significant shifts of this kind occurred during metamorphism.

Synmetamorphic infiltration and temperature-induced isotope exchange. Except for rocks in the immediate vicinity of V4 veins, the Waterville limestone at the Winslow and Benton localities has $\delta^{13}\text{C}$ similar to unmetamorphosed Silurian marine limestone but is depleted in ^{18}O by 3–7‰. There are three possible explanations for the difference in $\delta^{18}\text{O}$. First, the Waterville limestone simply may have developed its low $\delta^{18}\text{O}$ during sedimentation or diagenesis. Unfortunately, completely unmetamorphosed equivalents of the Waterville limestone are not exposed in the vicinity of Figure 1, and we were not able to confirm or refute the possibility directly. If the Waterville limestone were depleted in ^{18}O prior to metamorphism, there would be no need to appeal to synmetamorphic infiltration or significant temperature-induced isotopic exchange. There is indirect evidence, however,

that the low $\delta^{18}\text{O}$ of the Waterville limestone is not a primary prediagenetic sedimentary feature (discussed below).

Second, the low $\delta^{18}\text{O}$ of carbonates from the Waterville limestone could be caused by isotope exchange between sedimentary carbonate of normal composition ($\delta^{18}\text{O} = 25\text{‰}$) and detrital silicates with low $\delta^{18}\text{O}$ at the elevated temperatures of regional metamorphism. This second possibility is unlikely because of the relationship between measured $\delta^{18}\text{O}$ of calcite and carbonate content illustrated in Figure 7. Unaltered Silurian marine calcite has $\delta^{18}\text{O} = +23$ to $+27\text{‰}$ (vertical thick shaded line on the right in Fig. 7). Calcite in isotopic exchange equilibrium at 390 °C with clastic silicates from unmetamorphosed Paleozoic sandstones and shales from the Appalachians (Burt and Taylor, 1989) have $\delta^{18}\text{O} = +12.6$ to $+16.7\text{‰}$ (vertical thick shaded line on the left in Fig. 7, assuming $\Delta_{\text{silicates-calcite}} = +1\text{‰}$, Clayton et al., 1989). If the low $\delta^{18}\text{O}$ of the Waterville limestone were caused by ^{18}O - ^{16}O exchange between normal marine carbonates and normal clastic silicates at the temperature of metamorphism, data for the Waterville limestone on Figure 7 should (1) lie within the inclined solid lines and (2) define a linear array that is parallel (or nearly so) to those lines. Measured $\delta^{18}\text{O}$ (this study) and modes (Ferry, 1987) for nine samples of the Waterville limestone from the Winslow locality fail to meet either prediction. Most samples lie outside the area bounded by the solid lines and the samples define a near-horizontal linear array rather than an inclined array.

Another related argument that the low $\delta^{18}\text{O}$ of the Waterville limestone cannot have been the result of carbonate-silicate isotope exchange at elevated temperature is that $\delta^{18}\text{O}$ of detrital silicate would have been unreasonably low. For example, one representative limestone from the Winslow locality contains calcite (15.83 mol/L), ankerite (2.14), quartz (6.50), plagioclase (1.02), muscovite (0.22), ilmenite (0.05), and biotite (0.03). Given a pre- and postmetamorphic $\delta^{18}\text{O}$ of carbonate of 25.0 and 19.0‰, respectively, and a silicate-carbonate ^{18}O - ^{16}O fractionation of 1‰ at 390 °C, premetamorphic silicate must have had $\delta^{18}\text{O} = 5.1\text{‰}$. Given that $\delta^{18}\text{O}$ of silicates in typical unmetamorphosed Paleozoic clastic sediments is $\geq 14\text{‰}$ (Burt and Taylor, 1989), it is unlikely that an ^{18}O depletion of carbonates in the Waterville Formation was caused by high-temperature isotope exchange between carbonate and silicate.

The data array in Figure 7 further argues that the low $\delta^{18}\text{O}$ of the Waterville limestone is not a primary depositional feature. If the low $\delta^{18}\text{O}$ were primary, not only would the $\delta^{18}\text{O}$ of the carbonate be abnormally low, but the admixed silicates must have had an unusually heavy $\delta^{18}\text{O}$ ($\sim 20\text{‰}$) and one that would correspond to O isotope exchange equilibrium with the abnormal calcite at the elevated temperature of a later regional metamorphic event. This would be too coincidental to be plausible. A more likely explanation for the low $\delta^{18}\text{O}$ of the limestone is that it resulted from postsedimentary processes.

Third, the low $\delta^{18}\text{O}$ of the limestone could have been

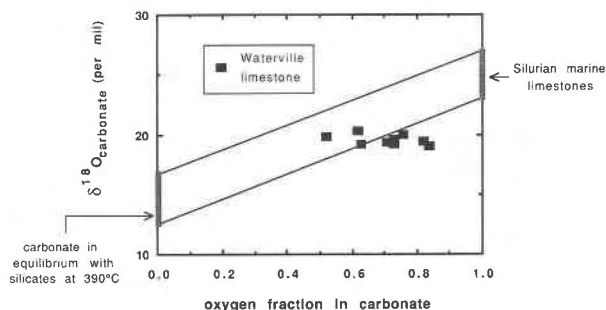


Fig. 7. Measured $\delta^{18}\text{O}$ of carbonate from Waterville limestone at the Winslow locality plotted vs. O fraction of rock in carbonate (squares). Inclined lines outline area of expected values if $\delta^{18}\text{O}$ of carbonate resulted from ^{18}O - ^{16}O exchange between normal Silurian carbonate and normal Paleozoic clastic silicates at the elevated temperature of regional metamorphism (390 °C). Because the data points mostly lie outside the area and define a horizontal array, the low $\delta^{18}\text{O}$ of the Waterville limestone is unlikely to be the result of high-temperature O isotope exchange between carbonate and silicate.

caused by infiltration of the rock by large quantities of H_2O -rich, and CO_2 -poor low- $\delta^{18}\text{O}$ fluid. In fact the linear, horizontal array of data in Figure 7 is most simply explained by thorough equilibration of detrital silicates and carbonates in the Waterville limestone with a very large quantity of a third O-bearing phase (i.e., fluid). This interpretation of the inferred isotopic shift of the Waterville limestone is consistent with the substantial amount of fluid flow through the unit recorded by the progress of peak prograde mineral reactions (Ferry, 1987; Baumgartner and Ferry, 1991). The isotopic data, however, unfortunately do not provide definitive, independent confirmation of the petrologic evidence for synmetamorphic infiltration because diagenetic effects cannot be ruled out.

Postmetamorphic infiltration

Calcite from V4 veins and both calcite and dolomite from the wall rocks adjacent to the veins are depleted in ^{18}O and ^{13}C relative to samples free from the premetamorphic effects of sedimentation and igneous intrusion (compare boxes A and D, Fig. 5). The pattern of alteration is somewhat obscured in Figure 5 by premetamorphic differences between calcite and dolomite in the wall rock. Examination of vein compositions alone (Fig. 8), however, shows an L-shaped pattern (rotated 90° clockwise) that is characteristic of isotopic alteration by infiltrating H_2O -rich, CO_2 -poor fluids (cf. Baumgartner and Rumble, 1988, Figs. 5 and 6; Rye and Bradbury, 1988, Fig. 7; Valley, 1986, Fig. 6). The L-shaped pattern arises when pristine rocks with compositions like those in box A (Fig. 5) are infiltrated by H_2O -rich fluids that are in isotopic equilibrium with samples at the bottom of box D (Fig. 5). The O values change first, at low fluid/rock ratios, following a near-constant $\delta^{13}\text{C}$ pathway toward lower $\delta^{18}\text{O}$ values. Because of the low concentration of C in infiltrating fluid, changes in $\delta^{13}\text{C}$ are not realized

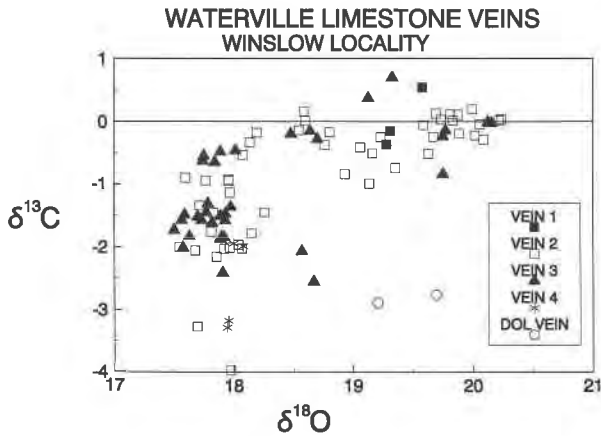


Fig. 8. Values of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ for veins from Waterville limestone.

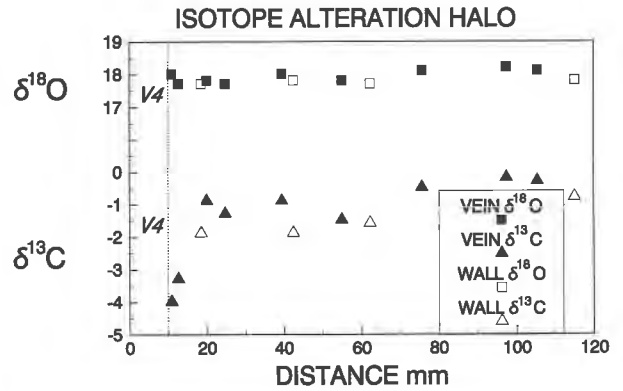


Fig. 10. Profile of isotopic composition vs. distance perpendicular to the contact between V4 and the wall rock in Figure 9. Vertical dotted line shows contact.

until high fluid/rock ratios have been reached. Changes in $\delta^{13}\text{C}$ occur only at high fluid/rock ratios, after ^{18}O equilibrium has been achieved, thus leading to a vertical, near-constant $\delta^{18}\text{O}$ pathway toward lower $\delta^{13}\text{C}$ values.

The cm-scale distribution of isotope values in the alteration halo of a V4 vein is shown in Figures 9 and 10. O isotope ratios are almost uniform (17.8–18.2‰) and are 1–2‰ lower than premetamorphic values (box A, Fig. 5). C isotope values, however, show a much larger variation from -4.0‰ adjacent to the vein to -0.2‰ at a distance of 8 cm. Note that the entire range of variation has been measured in one rock type, a V2 vein. There are no mineralogical changes associated with the isotopic gradient. The unusual nature of the $\delta^{13}\text{C}$ variation may

be appreciated by comparison with Figure 6 where the typical isotopic homogeneity of V2 veins is illustrated.

There is a striking contrast between the homogeneity of $\delta^{18}\text{O}$ and the gradient in $\delta^{13}\text{C}$ displayed in Figures 9 and 10. Such relationships have been predicted based on infiltration theory (Baumgartner and Rumble, 1988, Eq. 39, as corrected). The velocity of alteration fronts in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ propagating downstream during infiltration is proportional to the concentration ratio ($C^{\text{fluid}}/O^{\text{fluid}}/C^{\text{solid}}/O^{\text{solid}}$). For H_2O -rich fluids the ratio is low and the ^{18}O homogeneity front travels faster downstream than that for ^{13}C . We interpret the disparity between ^{18}O homogeneity and ^{13}C heterogeneity, illustrated in Figures 9 and 10, as evidence that the ^{18}O alteration front swept through

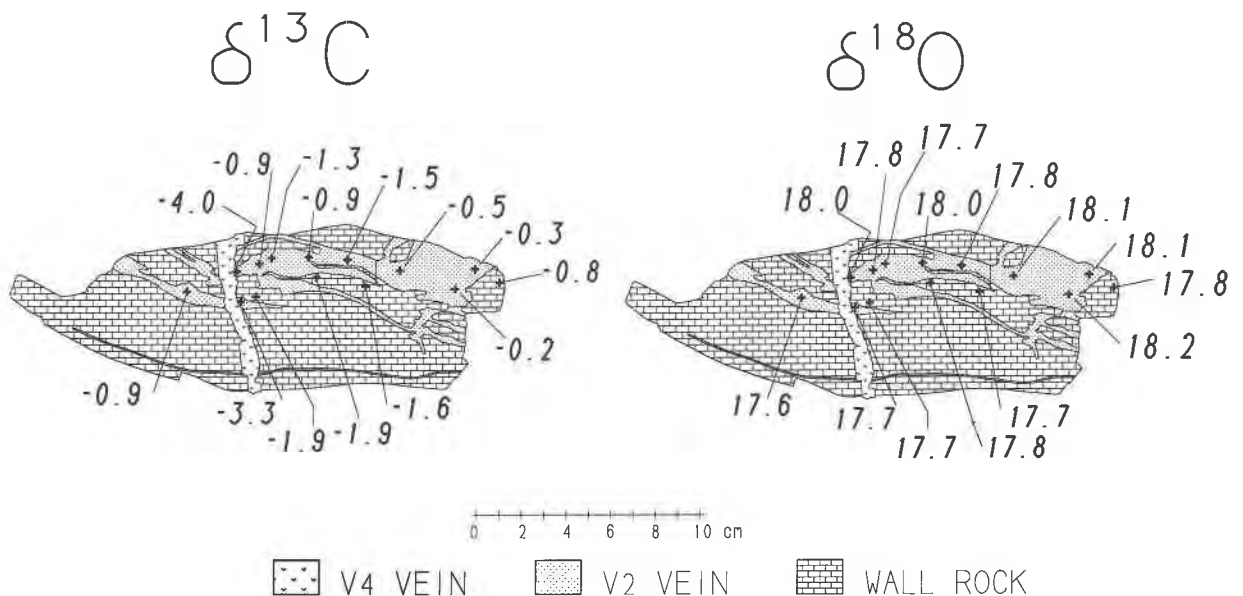


Fig. 9. Sketch of polished slab showing crosscutting V4 vein with isotopic data for calcite. Brickwork pattern is current-bedded limestone, in part dolomitized. Stippled pattern is V2 vein. The "V" pattern decorates V4 vein. Sample from locality AA, Figure 2.

the rock and is now located at a distance greater than 10 cm from the V4 vein. The ^{13}C alteration front, however, traveled more slowly and remained near the vein.

Estimation of fluid/rock ratios for a single pass of fluid needed to convert premetamorphic wall rock and vein values to those observed in the alteration halos of V4 gives atomic ratios of 2.4–2.9 (equations of Rye and Bradbury, 1988, p. 214). The calculations were made assuming a 100% calcite rock with initial $\delta^{18}\text{O} = 19.5\text{‰}$ and $\delta^{13}\text{C} = -0.5\text{‰}$. The infiltrating fluid was taken as a $\text{H}_2\text{O}-\text{CO}_2$ mixture with $X_{\text{CO}_2} = 0.07$ (Ferry, 1987, Table 6). The isotopic composition of infiltrating fluid is $\delta^{18}\text{O} = 14.0\text{‰}$ and $\delta^{13}\text{C} = -0.6\text{‰}$, in equilibrium with average V4 calcite at 390 °C. The calcite undergoing infiltration reaches $\delta^{18}\text{O} = 18.0\text{‰}$ and $\delta^{13}\text{C} = -1.6\text{‰}$ at a water/rock ratio (W/R) of 2.4 (atomic) for a single pass of fluid and, with increased infiltration, $\delta^{18}\text{O} = 17.8\text{‰}$ and $\delta^{13}\text{C} = -2.0\text{‰}$ at W/R = 2.9. These final calcite values embrace the range seen in box D of Figure 5. Fractures associated with V4 were evidently pathways for significant fluid flow following the peak of metamorphism. It should be remembered, however, that postmetamorphic infiltration was restricted to fractures found only at the north end of the Winslow outcrop (Fig. 2, localities AA and CC).

HISTORY OF FLUID INFILTRATION

Our results show that the Waterville limestone was infiltrated at least four times. The oldest event is recorded by V1 veins and dolomitization and occurred prior to F2 folding, possibly during diagenesis. The second episode, indicated by V2 veins, occurred after F2 folding but prior to the peak of regional metamorphism. The third infiltration event embodied both grain boundary and fracture flow. It left behind a variety of records including the presence of veins (V3) and solution cleavages (S3) as well as mineral assemblages and textures indicating infiltration-driven metamorphism. The isotopic evidence for the third episode is equivocal. Measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ depletions could be diagenetic or metamorphic in origin. The youngest event is recorded by isotopic alteration halos around the postmetamorphic V4 veins. The integration of structural observations in the field, stable isotope analyses of rocks and minerals, and petrologic data has thus revealed a history of fluid flow through the Waterville limestone that is far more complete than could be obtained by consideration of each type of data by itself.

The evolution of the isotopic composition of vein fluids may be seen in Figure 8. Samples of V1, V2, and V3 calcite, unaffected by V4, cluster in the range 19–20‰ $\delta^{18}\text{O}$ and -1 to +1‰ $\delta^{13}\text{C}$. These vein values overlap the range of least altered wall rocks (cf. box A, Fig. 5). Note, however, that despite the general overlap in isotopic values of V1, V2, and V3 veins with their wall rocks, isotopic disequilibrium does exist. In Figure 6 it may be seen that V2 calcite has the same $\delta^{18}\text{O}$ as calcite in its wall rocks but differs in $\delta^{13}\text{C}$ by 0.5‰. The V1 calcite at locality DD (Fig. 2) shows identical $\delta^{18}\text{O}$ to the calcite in its wall rock but is 2‰ greater in $\delta^{13}\text{C}$. Analyses of V1,

V2, and V3 infiltrated by V4 follow a constant $\delta^{18}\text{O}$ trend ($\delta^{18}\text{O} \sim 18.0\text{‰}$) but $\delta^{13}\text{C}$ decreases with increasing infiltration of V4 fluids. The V4 calcites are depleted in ^{18}O by 1–2‰ and in ^{13}C by 4‰ relative to older vein generations. We conclude that fluids of V1, V2, and V3 approached isotopic equilibrium with their wall rocks during vein formation but were limited in the attainment of $^{13}\text{C}-^{12}\text{C}$ exchange equilibrium by the low C contents of the fluids. The H_2O -rich fluids of V4, however, were neither in O nor C isotope exchange equilibrium with the wall rocks.

DISCUSSION

We set out to use stable isotope geochemistry to test the hypothesis of infiltration-driven metamorphism. It became apparent, however, that metamorphic effects could not be identified unambiguously without a detailed analysis of other pre-, syn-, and postmetamorphic controls on isotopic composition. Our primary goal has been achieved, at least partially. The evidence of an episode of the formation of veins (V3) and solution cleavage (S3) overlapping the period of metamorphism verifies the availability of fluids for pervasive synmetamorphic infiltration. Indeed, the mapping of four generations of veins demonstrates the significance of fracture flow throughout the geologic history of the limestone. Flow along grain boundaries was not the primary form of fluid movement.

The isotopic evidence for synmetamorphic infiltration is ambiguous. A shift of 3–7‰ in $\delta^{18}\text{O}$ during diagenesis cannot be ruled out. If diagenesis is responsible for the apparent depletion in $\delta^{18}\text{O}$, then the early stable isotopic history of the Waterville limestone was fluid dominated. In this case, veins V1, V2, and V3 were controlled by their wall rocks and only V4 veins were able to influence their environment.

Considering the alternative, if the depletion in $\delta^{18}\text{O}$ took place during synmetamorphic infiltration, the metamorphism was fluid dominated and evidences of earlier processes have been overprinted. As in the case of diagenesis, V4 veins record the most recent event in which vein fluids altered their wall rocks.

An additional test of the infiltration hypothesis is in progress. We are analyzing garnet, staurolite, and sillimanite zone outcrops of Waterville limestone in the same detail as the chlorite-zone localities. Preliminary results show ^{18}O and ^{13}C depletions equal to or greater than shifts observed in V4 halos, but no V4 veins have been found. Completion of the analytical program may lead to stronger support for the hypothesis of infiltration-driven metamorphism.

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REFERENCES CITED

- Baumgartner, L.P., and Ferry, J.M. (1991) A model for coupled fluid flow and mixed volatile mineral reactions with applications to regional metamorphism. *Contributions to Mineralogy and Petrology*, in press.
- Baumgartner, L.P., and Rumble D. (1988) Transport of stable isotopes: I: Development of a kinetic continuum theory for stable isotope transport. *Contributions to Mineralogy and Petrology*, 98, 417–430.
- Bottinga, Y. (1968) Calculation of fractionation factors for carbon and oxygen isotopic exchange in the system calcite-carbon dioxide-water. *Journal of Physical Chemistry*, 72, 800–807.
- Brand, U. and Veizer, J. (1981) Chemical diagenesis of a multicomponent carbonate system—2: Stable isotopes. *Journal of Sedimentary Petrology*, 51, 987–997.
- Burt, E.A., and Taylor, H.P., Jr. (1989) A comparison of whole-rock oxygen isotope variations in regionally metamorphosed and unmetamorphosed sedimentary rocks. *Geological Society of America Abstracts with Programs*, 21, A274.
- Clayton, R.N., Goldsmith, J.R., and Mayeda, T.K. (1989) Oxygen isotope fractionation in quartz, albite, anorthite, and calcite. *Geochimica et Cosmochimica Acta*, 53, 725–733.
- Coniglio, M., James, N.P., and Aissaouis, D.M. (1988) Dolomitization of Miocene carbonates, Gulf of Suez, Egypt. *Journal Sedimentary Petrology*, 58, 100–119.
- Coplen, T. B., Kendall, C., and Hoppie, J. (1983) Comparison of stable isotope reference samples. *Nature*, 302, 236–238.
- Dallmeyer, R.D., and Van Breeman, O. (1981) Rb-Sr whole rock and $^{40}\text{Ar}/^{39}\text{Ar}$ mineral ages of the Togus and Hallowell quartz monzonite and Three Mile Pond granodiorite plutons, south central Maine. *Contributions to Mineralogy and Petrology*, 78, 61–73.
- Epstein, S., Graf, D.L., and Degens, E.T. (1964) Oxygen isotope studies on the origin of dolomite. In H. Craig, S.L. Miller, and G.T. Wasserburg, Eds., *Isotopic and cosmic chemistry*, p. 169–180. North Holland, Amsterdam.
- Ferry, J.M. (1976) P,T, f_{CO_2} , and $f_{\text{H}_2\text{O}}$ during metamorphism of calcareous sediments in the Waterville-Vassalboro Area, south-central Maine. *Contributions to Mineralogy and Petrology*, 57, 119–143.
- (1980a) A case study of the amount and distribution of heat and fluid during metamorphism. *Contributions to Mineralogy and Petrology*, 71, 373–385.
- (1980b) A comparative study of geothermometers and geobarometers in pelitic schists from south-central Maine. *American Mineralogist*, 65, 720–732.
- (1983) On the control of temperature, fluid composition, and reaction progress during metamorphism. *American Journal of Science*, 283-A, 201–232.
- (1984) A biotite isograd in south-central Maine, USA: Mineral reactions, fluid transfer, and heat transfer. *Journal of Petrology*, 25, 871–893.
- (1986a) Reaction progress: A monitor of fluid-rock interactions during metamorphic and hydrothermal events. In J.V. Walther and B.J. Woods, Eds., *Fluid-rock interactions during metamorphism*. *Advances in Physical Geochemistry*, vol. 5, p. 60–88. Springer-Verlag, New York.
- (1986b) Infiltration of aqueous fluid and high fluid: Rock ratios during greenschist facies metamorphism: A reply. *Journal of Petrology*, 27, 695–714.
- (1987) Metamorphic hydrology at 13-km depth and 400–550 °C. *American Mineralogist*, 72, 39–58.
- (1989) Contact metamorphism of roof pendants at Hope Valley, Alpine County, California, USA. *Contributions to Mineralogy and Petrology*, 101, 402–417.
- Garlick, G.D., and Epstein, S. (1967) Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks. *Geochimica et Cosmochimica Acta*, 31, 181–214.
- Kieffer, S.W. (1982) Thermodynamics and lattice vibrations of minerals: 5. Applications to phase equilibria, isotopic fractionation, and high-pressure thermodynamic properties. *Reviews of Geophysics and Space Physics*, 20, 827–849.
- Matsuhisa, Y., Goldsmith, J.R., and Clayton, R.N. (1979) Oxygen isotope fractionation in the system quartz-albite-anorthite-water. *Geochimica et Cosmochimica Acta*, 43, 1131–1140.
- McCrea, J.M. (1950) On the isotopic chemistry of carbonates and a paleo temperature scale. *Journal of Chemical Physics*, 18, 849–857.
- O'Neil, J.R. (1987) Preservation of H, C, and O isotopic ratios in the low temperature environment. In T.K. Kyser, Ed., *Stable isotope geochemistry of low temperature processes*, Short course Handbook vol. 13, p. 85–128. Mineralogical Association of Canada, Toronto.
- Osberg, P.H. (1968) Stratigraphy, structural geology, and metamorphism of the Waterville-Vassalboro Area, Maine. *Maine Geological Survey, Bulletin* 20, 64 pp.
- (1979) Geologic relationships in south-central Maine. In J.W. Skehan and P.H. Osberg, Eds., *The Caledonides in the USA. Geological excursions in the Northeast Appalachians*, p. 37–62. Weston Observatory, Boston College, Weston, Massachusetts.
- Osberg, P.H., Hussey, A.M., II, and Boone, G.M. (1985) Bedrock geologic map of Maine. *Maine Geological Survey, Department of Conservation*, Augusta, Maine.
- Rice, J.M., and Ferry, J.M. (1982) Buffering, infiltration and the control of intensive variables during metamorphism. In *Mineralogical Society of America Reviews in Mineralogy*, 10, 263–326.
- Rumble, D., (1982) Stable isotope fractionation during metamorphic devolatilization reactions. In *Mineralogical Society of America Reviews of Mineralogy*, 10, 327–353.
- Rumble, D., Ferry, J.M., and Hoering, T.C. (1986) Oxygen isotope geochemistry of hydrothermally-altered synmetamorphic granitic rocks from south-central Maine, USA. *Contributions to Mineralogy and Petrology*, 93, 420–428.
- Rye, D.M., and Bradbury, H.J. (1988) Fluid flow in the crust: An example from a Pyrenean thrust ramp. *American Journal of Science*, 288, 197–235.
- Sheppard, S.M., and Schwarcz, H.P. (1970) Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite. *Contributions to Mineralogy and Petrology*, 26, 161–198.
- Stewart, D.B. (1989) Crustal processes in Maine. *American Mineralogist*, 74, 698–714.
- Valley, J.W. (1986) Stable isotope geochemistry of metamorphic rocks. In *Mineralogical Society of America Reviews in Mineralogy*, 16, 445–489.
- Veizer, J., and Hoefs, J. (1976) The nature of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ secular trends in sedimentary carbonate rocks. *Geochimica et Cosmochimica Acta*, 40, 1387–1395.
- Wood, B.J., and Graham, C.M. (1986) Infiltration of aqueous fluid and high fluid:rock ratios during greenschist facies metamorphism: A discussion. *Journal of Petrology*, 27, 751–761.

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