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Microlithon alteration associated with development of solution cleavage in argillaceous limestone: textural, trace-elemental and stable-isotopic observations

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Abstract—Comparison of microlithons (the rock between adjacent cleavage domains) in strongly cleaved argillaceous limestone with samples of uncleaved limestone from the same stratigraphic horizon (Lower Devonian Kalkberg Formation, Hudson Valley of eastern New York) indicates that the process of cleavage formation results in significant changes in microlithon fabric and in the chemistry of microlithon calcite. Petrographic observation indicates that at least 50% of the calcite in microlithons is recrystallized as calcite fibers whose long axes are subparallel to cleavage domains. The fibrous calcite occurs as overgrowths on larger grains, in thin bed-parallel veins, and in 'diffuse extension zones' (areas of the microlithons in which inequant crystals of microcrystalline calcite are aligned parallel to cleavage domains). Chemical analyses show that calcite in microlithons of strongly cleaved limestone is enriched in Mn and Sr relative to calcite in uncleaved limestone. $\delta^{18}O$ and possibly $\delta^{13}C$ values for calcite in strongly cleaved rock are significantly smaller than values for calcite in uncleaved rock. These results indicate that microlithon calcite is completely recrystallized (i.e. much more calcite is recrystallized than is visible in thin section) and that it underwent exchange with a fluid external to the local rock system. Calculation of the water/rock ratio suggests that 0.1–2.6 volumes of water may have exchanged with the calcite during cleavage formation. Comparison of the minimum integrated and the inferred instantaneous water/rock ratios suggests that bulk fluid flow occurred during microlithon recrystallization. Comparison of the amount of shortening across cleavage domains with the amount of extension in microlithons, and of the volume of calcite dissolved in domains with the amount of fibrous (presumably added) calcite in microlithons, suggests that microlithons are a major sink for the calcite dissolved in domains during cleavage formation, and that at this locality, development of disjunctive solution cleavage in the Kalkberg Formation resulted in volume-constant plane strain.

INTRODUCTION

THE development of disjunctive tectonic cleavage in sedimentary rocks is largely a manifestation of water–rock interaction ('pressure solution' and free-face dissolution; e.g. Engelder & Marshak 1985). Typically, such cleavage is spaced, and is manifested by an array of domains (composed of selvages relatively rich in insoluble grains, particularly aligned phyllosilicates) that are separated by intervening microlithons. Key issues remain concerning the cleavage-formation process, including: (1) how does texture of microlithons change, if at all, as cleavage develops; (2) where does the dissolved material from cleavage domains go; and (3) how much fluid interacts with the rock during cleavage formation? To date, most of the work that has addressed these issues has focused on documenting major-element mobility during cleavage formation either by describing compositional contrasts between cleavage domains and intervening microlithons (e.g. Stephens *et al.* 1979, Gray 1981, Erslev & Mann 1984, Waldron & Sandiford 1988) or by describing bulk-rock chemical changes accompanying progressive development of cleavage (e.g. Marshak & Engelder 1985). Such work shows that, in argillaceous limestone, calcite is preferentially removed from cleavage domains. Major-element analysis alone cannot completely characterize the changes that microlithons undergo during cleavage formation.

In this paper, we describe changes in rock fabric, trace-element content in calcite and stable-isotope composition of calcite that take place in microlithons during progressive cleavage development in argillaceous limestone. We found that calcite in microlithons of strongly cleaved specimens has distinct trace-element and stable-isotope signatures from calcite in uncleaved specimens of nearby outcrop. This result, coupled with petrographic evidence, demonstrates that microlithons undergo substantial recrystallization and can undergo significant extensional strain during cleavage formation.

GEOLOGICAL CHARACTERISTICS OF SAMPLE LOCALITIES

To characterize the changes in microlithons that accompany progressive development of cleavage, it is necessary to compare cleaved and uncleaved versions of the same original lithology. Excellent material for such a comparison can be found in the roadcuts along New York State Route 23 near the town of Catskill in the Hudson River Valley (Fig. 1). In the roadcuts, a distinct stratigraphic horizon of the Kalkberg Formation can be traced from localities where there is no cleavage to a locality nearby where there is very strong cleavage. We were able, therefore, to compare uncleaved, weakly

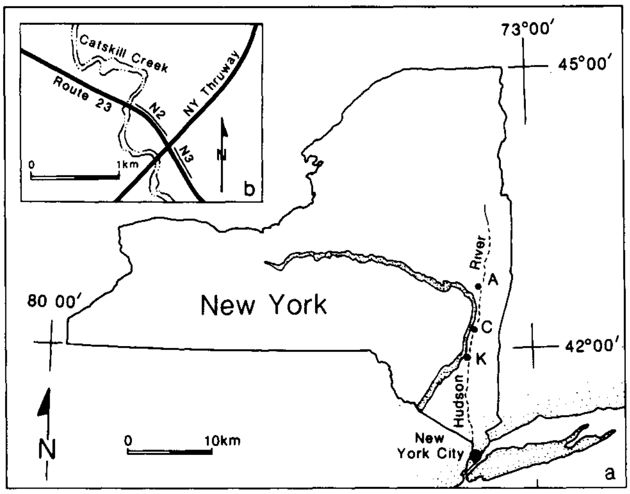

Fig. 1. (a) Location map showing the outcrop belt of Silurian–Devonian strata in eastern and central New York. Study area is in the Silurian–Devonian belt northwest of Catskill. C = Catskill, A = Albany, K = Kingston. (b) Detailed map of study area showing location of sample outcrops N2 and N3 near Catskill.

cleaved, and strongly cleaved specimens of the same original lithology.

New York Route 23 cuts obliquely across the strike of a 3 km-wide W-verging 'miniature' fold-thrust belt (Marshak 1986) involving Lower Devonian shallow-marine carbonate units that are composed of biosparite, micrite and argillaceous biomicrite. First-order folds in the belt have wavelengths of up to 300 m. The development of folds and faults in this belt was accompanied by the creation of disjunctive spaced solution cleavage and of veins. Cleavage is not uniformly distributed in the belt; it occurs exclusively in lithologies that contain greater than about 10% argillaceous material, and within a given argillaceous unit, its intensity varies with structural position (Marshak & Engelder 1985). Limestone and vein samples examined in the present study were obtained from the lower three units (Manlius, Coeymans and Kalkberg) of the Helderberg Group exposed in Route 23 roadcuts N2 and N3 (outcrop designation follows Marshak 1986) near the New York State Thruway (Fig. 1b). Roadcut N3 exposes the east limb of an open first-order syncline, and roadcut N2 exposes two anticlines and an intervening syncline. The western anticline of N2 (the Central anticline) involves several folded thrust faults (Fig. 2).

Microlithon samples of argillaceous biomicrite (~30% non-carbonate component) were collected from a distinctive stratigraphic interval of the lower Kalkberg Formation in three localities (N3 in roadcut N3, N2E and N2W on the southeast and northwest limbs, respectively, of the Central anticline in roadcut N2); the top of the sample interval is defined by a distinctive shale bed and the bottom by a black chert layer. The Kalkberg Formation at N3 does not contain an obvious cleavage, though close examination reveals the presence of a very weak or incipient cleavage in the rock. For purposes of comparison, we refer to samples from this locality (N3) as 'uncleaved'. At locality N2E (Fig. 2) Kalkberg contains a weak cleavage. Using the method of Sansone (1982), we calculate that bulk shortening measured in the direction perpendicular to the cleavage domains at N2E is about 7%. Locality N2W contains the leading tip of a horse at which two faults merge. In this fault-bounded wedge (Fig. 2) Kalkberg contains strong to very strong cleavage, and Sansone's (1982) method indicates cross-cleavage shortening of about 34%.

Vein calcite was collected from roadcut N2 for comparison with microlithon calcite (positions of specific vein samples are indicated on Fig. 2). The Manlius and Coeymans Formations, which are relatively pure carbonate lithologies (micrite and biosparite with >90% calcite), experienced brittle deformation and fractured in the core of the Central anticline. The calcite in these fractures provided specimens of blocky calcite spar. Vein calcite was also obtained from fibrous veins which occur on fault surfaces in all three units and from blocky spar that occurs in pods at fault bends (Fig. 2).

OBSERVATIONS OF ROCK FABRIC

Rock fabric of uncleaved and weakly cleaved samples

The Kalkberg Formation at locality N3 is composed of mottled gray, medium-bedded, argillaceous biomicrite

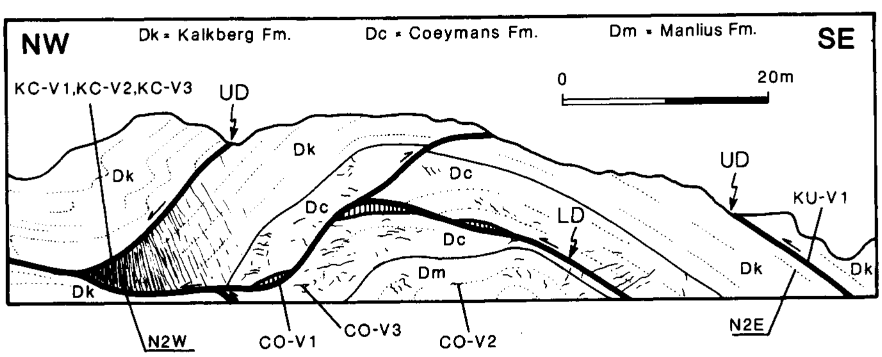

Fig. 2. Simplified structural cross-section of the Central anticline (locality N2) showing sample locations for limestone (N2E and N2W) and for calcite veins. Thick lines are major faults, thin lines are formational contacts, wispy lines in the fault-bounded wedge (on the northwest limb) represent cleavage traces, vertical ruled areas are pods of calcite, and short squiggly lines are calcite filled fractures. UD = Upper Detachment; LD = Lower Detachment.

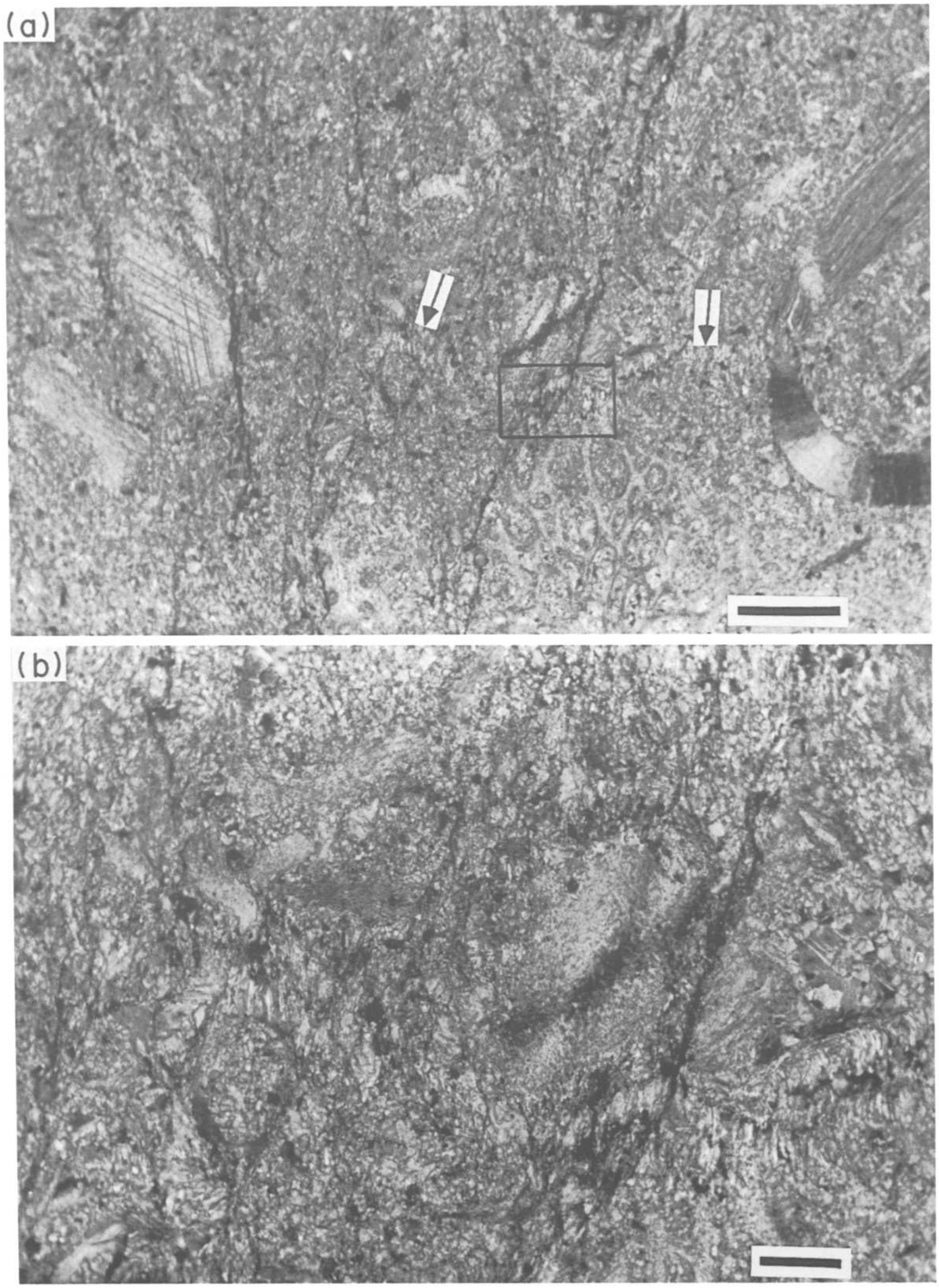

Fig. 3. (a) Photomicrograph (crossed nicols; scale bar = 300 μm) of strongly cleaved Kalkberg showing fibrous calcite in reactivated bed-parallel stylolite (arrows). Fibers are subparallel with cleavage domains in the sample. Note the near-vertical microstylolite that cuts the reactivated stylolite (indicated by the rectangle). (b) Enlargement of area in vicinity of rectangle shown in (a). Scale bar = 100 μm.

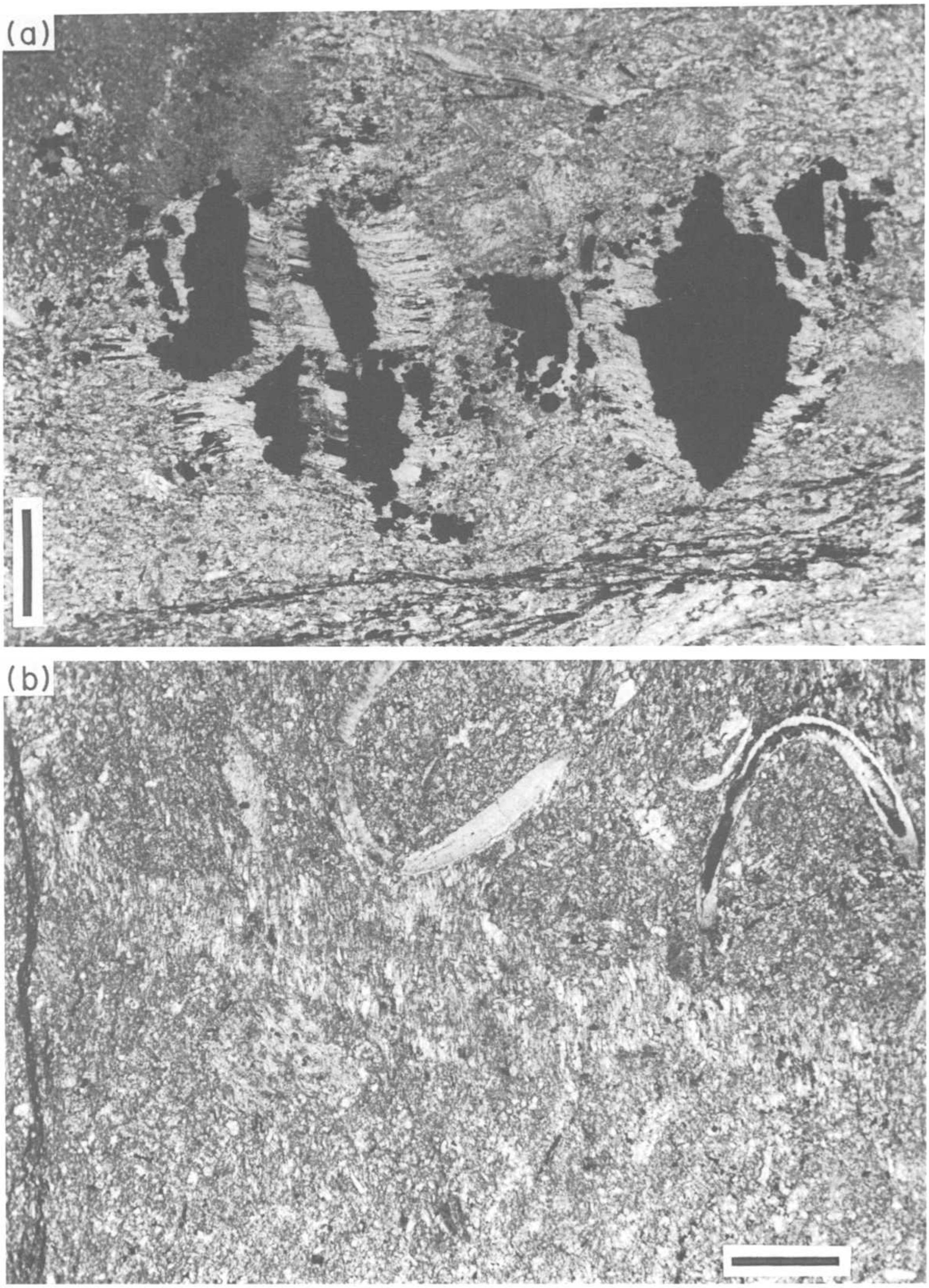

Fig. 4. (a) Photomicrograph (crossed nicols; scale bar = 300 μm) showing fibrous calcite growing on a pyrite grain in the microlithon of strongly cleaved Kalkberg from locality N2W. Fibers are subparallel to cleavage. (b) Photomicrograph (crossed nicols; scale bar = 300 μm) showing diffuse extension zone in a microlithon of strongly cleaved Kalkberg. Note how this zone merges with the 'pressure shadow' region of the concave-up skeletal fragment. Fibers are subparallel to cleavage domains.

Table 1. Summary of rock-fabric changes accompanying cleavage development in the Kalkberg Formation. See Powell (1979) for discussion of microlithon–fabric terminology

Uncleaved (locality N3)	Strongly cleaved (locality N2W)
Thin, discontinuous domains (<0.5 mm)	Thicker, more continuous domains (0.5 cm)
Poorly defined domains	Well defined domains
Large average domain spacing (~10 cm)	Smaller average domain spacing (~2 cm)
Variable domain spacing	Uniform domain spacing
Non-planar domains	More planar domains
Pronounced color mottling	Less pronounced color mottling
Few microstylolites in microlithons	More microstylolites in microlithons
Random to weak microlithon fabric	Strong microlithon fabric
Poorly defined microlithons	Well defined microlithons
Few pressure fringes (straight only)	Abundant pressure fringes (straight and curved)
No pulled-apart grains	Common pulled-apart grains
No extension veins	Common veins (microscopic) w/fibrous minerals

that occurs in poorly defined beds (see Table 1 for a concise summary of cleavage fabric). Color mottling of limestone at locality N3 is defined on a polished hand-specimen surface by irregularly-shaped patches of light and dark gray, and is probably a consequence of prelithification bioturbation by burrowing organisms (Laporte 1969). Transmitted light microscopy indicates that this rock is composed of fossil fragments scattered in a microcrystalline matrix (5–25 μm particle size) of equant calcite, clay minerals and quartz. Matrix minerals lack any dimensional preferred orientation and 'pressure fringes' or 'beards' on larger calcite or pyrite grains are rare. Limestone at locality N3 is cut by an incipient cleavage oriented at between 65 and 85° to bedding. Cleavage domains are thin (less than 0.5 mm), are traceable for up to a few centimeters on the outcrop face and are spaced about 10 cm apart. Macroscopically, the domains are discrete, non-sutured and wavy (terminology of Borradaile *et al.* 1982 and Wanless 1979), and microscopically, they can be seen to be composed of accumulations of aligned phyllosilicates, quartz, opaque minerals and residual corroded grains of calcite.

Rock fabric of weakly cleaved Kalkberg Formation from the southeast limb of the Central anticline differs from the fabric of uncleaved Kalkberg in that the spacing of cleavage domains is less (interdomain distance is 2–5 cm) and the domains themselves are thicker (~1 mm). Microlithons of samples from roadcut N2E have the same mottled appearance in hand specimens as those from N3, but under a microscope, the microlithons contain local very thin microstylolites.

Rock fabric of strongly cleaved samples

Cleavage at locality N2W is very strong and is readily apparent in outcrop. It is the dominant surface of parting, and is so strong that it obscures bedding (see photographs in Marshak & Engelder 1985). Domains are sinuous to subparallel and can be traced for 15–25 cm. Domain thickness is generally 0.5 cm and domain spacing is relatively uniform, rarely exceeding 2 cm (Table 1). In thin section, clay minerals in the thicker domains typically exhibit simultaneous extinction when viewed with crossed nicols (Fig. 3).

Microlithon fabric at locality N2W is quite distinct both macroscopically and microscopically from the fabric found in microlithons of N2E and N3. In hand specimen, it is apparent that color mottling is much less pronounced at N2W than at N2E and N3. Microlithons of N3W contain numerous thin incipient cleavage domains, and of particular interest contain features indicative of cleavage-parallel extension. Similar insoluble residue contents for the three sample suites (Table 2) indicate that growth of fibrous calcite is paralleled by the development of more microstylolites in the microlithons (Table 1). Thus, the relative amount of calcite and insoluble residue in the microlithons of N2W is similar to that of N2E and N3.

Cleavage-parallel extension fabrics

Cleavage-parallel extension in the microlithons of strongly cleaved samples from locality N2W is visible in

Table 2. Summary of trace-element data from microlithon calcite in the Kalkberg Formation at localities N3 (uncleaved), N2E (weakly cleaved) and N2W (strongly cleaved), plus vein calcite from N2. Insoluble-residue values are for microlithons only. Numbers represent mean values, with 1 SD and the coefficient of variation, expressed as a percentage, given in parentheses

Locality	No. of samples	Mn (ppm)	Sr (ppm)	Insoluble residue (wt%)
N3	17	231 (21; 9%)	665 (89; 13%)	34.2 (4.7; 14%)
N2E	19	240 (22; 9%)	676 (55; 8%)	33.2 (4.3; 13%)
N2W	19	266 (29; 11%)	754 (83; 11%)	32.1 (8.3; 26%)
N2 vein calcite	6	207 (72; 35%)	1714 (803; 47%)	

thin section and is defined by regions of fibrous calcite that occur in three basic settings. The first setting is in pressure fringes adjacent to rigid grains and between segments of pulled-apart grains (Fig. 4a). Pressure fringes are up to 300 μm long, and some are sigmoidal. The second setting is in bed-parallel reactivated stylolites (Fig. 3) (see also Mullenax & Gray 1984) or in thin bed-parallel fibrous veins. The third setting is in irregularly-shaped areas that we term 'diffuse extension zones' (Fig. 4b). In diffuse extension zones, microcrystalline calcite is elongate parallel to cleavage and the zone boundaries are typically diffuse and gradational with the surrounding microlithon. Clay content within these zones is less than that of adjacent areas. Borders of these zones are gradational. The diffuse extension zones occur adjacent to larger grains as well as within the fine-grained matrix of the microlithon away from any larger grains.

The development of cleavage-parallel extension in the microlithons is compatible with an outcrop observation mentioned by Marshak and Engelder (1985) that beds appear to thicken by about 35% at locality N2W. The amount of cleavage-parallel extension observed at outcrop appears to be comparable to the amount of shortening across cleavage domains. Examination of mutually orthogonal thin sections indicates that extension occurs only in the X-direction (if it is assumed that cleavage parallels the XY-plane of the finite strain ellipsoid). Thus, cleavage formation at locality N2W is the result of plane strain deformation.

Extent of syntectonic calcite recrystallization in microlithons

Optical petrographic observations indicate that calcite is the only component in the Kalkberg Formation to have undergone significant dissolution and precipitation (recrystallization) during cleavage formation. Detailed TEM observations of the illite and chlorite fraction of the Kalkberg by Kreutzberger & Peacor (1988) confirm the largely passive behavior of clay minerals at localities N2E and N2W. A minimum estimate of calcite recrystallization in microlithons can be made by optical determination of the percent area of a thin section that is composed of fibrous calcite. Weakly cleaved samples generally have less than 7% fibrous calcite. In strongly cleaved samples, the area of a thin section occupied by fibrous calcite ranges from 20 to 50%, which, considering that Kalkberg samples are composed of about 70% calcite (Table 2), indicates that 50% of the calcite fraction has recrystallized. It is likely that calcite in the microcrystalline matrix also recrystallized during cleavage development, because the small size of crystals in this matrix makes them susceptible to reaction with water (Bathurst 1975, Rutter 1983), but this recrystallization is difficult to distinguish due to its non-fibrous morphology. The observation of a decrease in color mottling accompanying cleavage formation may indicate widespread recrystallization of the matrix grains (i.e. recrystallization might homogenize the mottled matrix).

GEOCHEMICAL CHANGES ACCOMPANYING PROGRESSIVE CLEAVAGE DEVELOPMENT

Trace-element analyses (Mn *and* Sr)

In order to determine whether the process of cleavage formation affects the trace-element makeup of calcite in microlithons, we compared Mn and Sr concentrations in the calcite fraction of microlithon samples from site N2W to samples from sites N2E and N3. Our working hypothesis was that the chemical composition of samples from N3 represent the pre-cleavage composition of samples at N2W. We also measured these concentrations in samples of vein calcite in order to provide an estimate of the trace-element content of fluids circulating through the rock at the time of deformation.

Calcite was digested by reacting powdered samples with 0.5 N HCl at room temperature, followed by centrifuging to remove the insoluble residue. Leaching of Mn and Sr from the insoluble residue during sample preparation is unlikely, for our calcite dissolution method is similar to that of Robinson (1980), who demonstrated that 1 N HCl does not produce measurable leaching of clay minerals in impure limestones. Reproducibility of the trace-element analyses, which were done using atomic absorption spectrophotometry, is ±16 ppm Mn and ±26 ppm Sr (2 SDs) based on replicate analyses of National Bureau of Standards (NBS) argillaceous limestone NBS-1c. Accuracy of the measurements is within the uncertainty specified by NBS.

Mn and Sr concentrations measured in microlithons exhibit moderate scatter for each locality, although the overall trend indicates that calcite from strongly cleaved rocks at N2W is enriched in Mn and Sr relative to calcite from other localities (Fig. 5 and Table 2). There is a rough inverse relationship between Mn and Sr at N2W. Comparison of mean values at the three localities indicates that calcite at roadcut N2W contains 11–15% more Mn and 12–13% more Sr than does calcite from outcrops N2E or N3. Samples used in this work were obtained

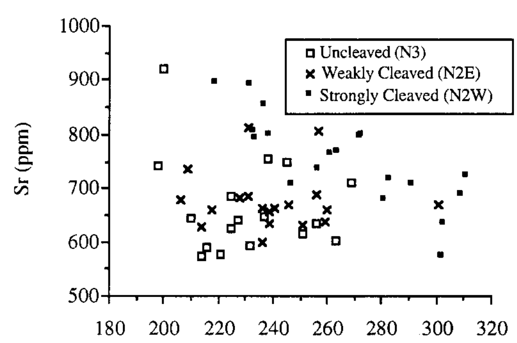

Fig. 5. Mn and Sr data for microlithon calcite in the Kalkberg Formation from localities N3, N2E and N2W.

Table 3. Summary of the one-way ANOVA comparing paired outcrops for mean Mn and Sr concentrations. α is the probability of incorrectly concluding that the mean trace-element concentration is different. The level of confidence represents the certainty with which it can be concluded that the means are significantly different

Localities	Element	α	Level of confidence (%)
N3 vs N2E	Mn	0.351	64.9
	Sr	0.105	89.5
N2E vs N2W	Mn	0.054	94.6
	Sr	0.025	97.5
N3 vs N2W	Mn	0.002	99.8
	Sr	0.011	98.9

from an interval spanning about 2 m of stratigraphic section, but there are no clear variations in Mn, Sr, or Mn/Sr ratio as a function of stratigraphic level.

We used analysis of variance (ANOVA; e.g. Dixon & Massey 1969) to determine whether the differences in Mn and Sr between different sites as shown in Fig. 5 are statistically significant (Bhagat 1988). Results of the one-way ANOVA (Table 3) show that the mean concentrations of Mn and Sr in the uncleaved (N3) and strongly cleaved (N2W) sample suites are statistically different at the specified level of $\alpha = 0.05$. Mn and Sr concentration in uncleaved and weakly cleaved suites are not statistically different at the specified level of $\alpha = 0.05$.

Figure 6 shows the concentrations of Mn and Sr in vein calcite from the Central anticline in roadcut N2 (Fig. 2) compared with concentrations in the Kalkberg microlithons. Concentration of Mn and Sr in veins show much more scatter than do the measurements in the microlithons (microlithon measurements lie in the circled area of Fig. 6). In the veins, the mean Mn concentration is lower and the mean Sr concentration is higher compared with the means for microlithons (Table 2). Note that the KC veins (KC-V1, -V2 and -V3), which contain fibrous calcite and were collected from the upper detachment fault surface immediately above the strongly cleaved suite (Fig. 2), display a marked Mn depletion and Sr enrichment relative to all other samples. There is no clear temporal relationship among the veins (cf. Dietrich *et al.* 1983).

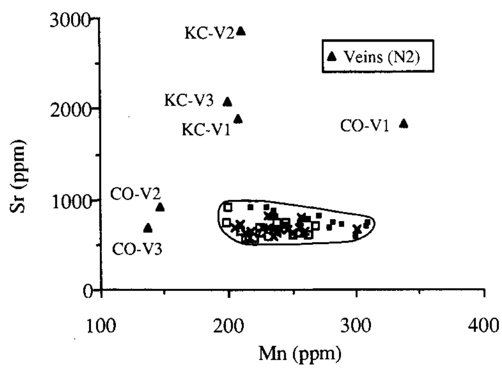

Fig. 6. Mn and Sr data for vein calcite from outcrop N2 (triangles), compared with Mn and Sr data from microlithon calcite also shown in Fig. 6 (plotted in the enclosed region). See Fig. 2 for location of vein samples.

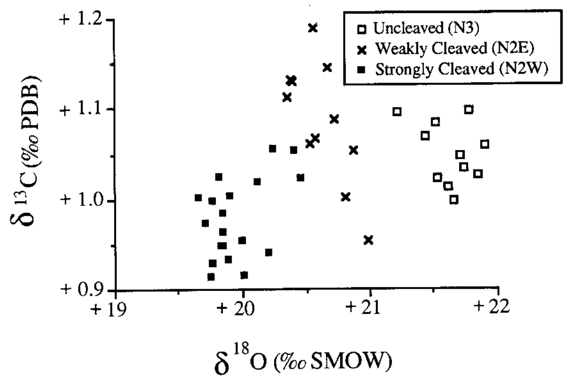

Fig. 7. $\delta^{18}O$ and $\delta^{13}C$ data for microlithon calcite from the Kalkberg Formation from localities N3, N2E and N2W.

Stable-isotope analyses

Samples for isotopic analyses were taken from the same sample suites that were used for the trace-element analyses. Our goal was to determine whether or not the isotopic composition of calcite in microlithons of cleaved rocks changed during cleavage formation. We assumed that the pre-cleavage composition of microlithons at N2W was the same as the present composition of samples from N3. Determination of carbon- and oxygen-isotope content was done using established sample preparation methods (McCrea 1950) and mass-spectrometric correction procedures (Craig 1957). Isotopic compositions are given in the standard δ-notation. Reproducibility for both the carbon- and oxygen-isotope analyses is $\pm 0.1‰$ (2 SDs), based on replicate analyses of National Bureau of Standards limestones (NBS-18, NBS-19 and NBS-20).

The data in Fig. 7 and Table 4 indicate distinct oxygen-isotope signatures for outcrops N3, N2E and N2W. $\delta^{18}O$ values become increasingly lighter in the succession from N3 to N2E to N2W. Analysis of variance of the isotope data (Table 5) indicates that the $\delta^{18}O$ values of samples from N2W are statistically different from those of either N2E or N3. There is a trend toward lighter $\delta^{13}C$ values over the same succession, although the magnitude of the overall shift in $\delta^{13}C$ values is equal to the analytical uncertainty of 0.1‰. Statistical analysis of the $\delta^{13}C$ reveals that $\delta^{13}C$ values for samples from N2W differ significantly from those of both N2E and N3, but the $\delta^{13}C$ values of N2E do not differ from those of N3 (Table 3). Due to the analytical uncertainty, however, the $\delta^{13}C$ statistical tests are not necessarily meaningful.

Table 5. Results of the one-way ANOVA for $\delta^{18}O$ and $\delta^{13}C$ data shown in Fig. 7. See Table 3 for explanation of column headings

Localities	Element	α	Level of confidence (%)
N3 vs N2E	C	0.14	86
	O	10^{-4}	99+
N2E vs N2W	C	10^{-4}	99+
	O	10^{-4}	99+
N3 vs N2W	C	10^{-4}	99+
	O	10^{-4}	99+

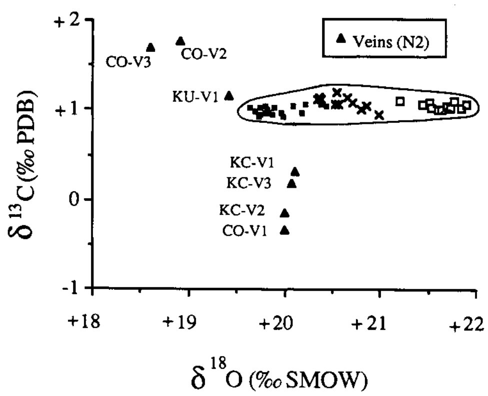

Fig. 8. $\delta^{18}O$ and $\delta^{13}C$ data for vein calcite (outcrop N2) and for microlithon calcite in the Kalkberg (plotted in the enclosed region). Note that the mean $\delta^{18}O$ of 20.07‰ for veins KC-V1, -V2 and -V3 is analytically identical with the mean of 19.95‰ for calcite in strongly cleaved Kalkberg (Table 4).

The $\delta^{13}C$ and $\delta^{18}O$ data do not show any clear variation as a function of stratigraphic position.

The $\delta^{13}C$ and $\delta^{18}O$ data for calcite in macroscopic veins are plotted in Fig. 8 along with the same data for calcite in Kalkberg microlithons for comparison. The vein $\delta^{13}C$ values exhibit slightly more scatter than vein $\delta^{18}O$ and significantly more scatter than Kalkberg microlithon $\delta^{13}C$ values. Note that the $\delta^{18}O$ values of the KC veins (mean = +20.07‰) are similar to that of calcite from strongly cleaved samples (mean = +19.95‰). Overall, vein calcite is depleted in $\delta^{13}C$ and $\delta^{18}O$ relative to all other samples (Table 4).

Interpretation of geochemical results

Both the incorporation of Mn and Sr into the calcite structure (occurring primarily by substitution for Ca; Veizer 1983) and calcite–water isotopic exchange requires dissolution–precipitation if accomplished at low temperatures. Lower Devonian strata in the Catskill area were probably subjected to temperatures in the range 100–200°C (based on stratigraphic constraints and paleotemperature indicators; Fisher 1977, Harris *et al.* 1978, Friedman & Sanders 1982, Lakatos & Miller 1983, Friedman 1987). If we assume that the samples taken at locality N3 are representative of the Kalkberg Formation before cleavage had developed, then the chemical contrasts between calcite in N3 and calcite in N2W can be considered to be indicative of dissolution and precipitation of calcite in microlithons during cleavage formation. We interpret the differences of Mn, Sr and $\delta^{18}O$ (and possibly $\delta^{13}C$) in calcite of locality N2W relative to that of calcite from locality N3 to indicate that an increase in cleavage intensity corresponds to an increase in the amount of recrystallized calcite in microlithons, and thus that microlithons were not inert during cleavage formation. Comparison of $\delta^{18}O$ from KC-veins and calcite at N2W (Figs. 2 and 8) indicates that in the strongly cleaved samples, calcite completely recrystallized. This result suggests that the 50% recrystallization that we proposed based on petrographic observation of the amount of fibrous calcite in microlithons from strongly cleaved samples is an underestimate of the total amount of recrystallization in these microlithons.

To affect the changes in Mn, Sr, $\delta^{18}O$ and $\delta^{13}C$ that we observed, the fluid that interacted with the rock during cleavage formation must have had a different composition than the fluid that had been in equilibrium with the rock during the crystallization of pre-cleavage calcite. We cannot exclude the possibility that Mn-enrichment in N2W calcite resulted from local dissolution of chlorite during cleavage development, as chorite can contain significant amounts of MnO (Newman & Brown 1987). It is unlikely, however, that chlorite and illite were significant sources for Sr, and furthermore, it can be shown that dewatering of smectite interlayers would have released only a negligible amount of water. Thus, it appears the fluid present during deformation must have originated from a reservoir external to the Kalkberg Formation, indicating that the Kalkberg must have been an open system during cleavage development.

If the vein composition is representative of the fluid composition at the time of cleavage formation, and microlithon calcite is completely recrystallized, then the veins should have the same composition as the recrystallized calcite of microlithons. We did not observe this similarity for every geochemical species. The contrast between the vein composition and the microlithon calcite composition may indicate that the vein calcite represents precipitation from a fluid that had evolved by prior reaction with the microlithons—Mn had been preferentially removed from the fluid and incorporated into microlithon calcite, as might be expected considering that the Mn distribution coefficient is much greater than 1 (Veizer 1983). The excess Sr in the vein calcite may indicate that the fluid passing through the cleaved Kalkberg was initially so rich in Sr, that it contained a large Sr concentration even after exchanging with micro-

Table 4. $\delta^{18}O$ and $\delta^{13}C$ data for microlithon calcite in the Kalkberg and for vein calcite. Explanation of numbers is same as for Table 2. For the water/rock ratio (W/R) calculations (equation 2), δ_c^i is the mean $\delta^{18}O$ for locality N3 and δ_c^f is the mean $\delta^{18}O$ for N2W

Locality	No. of samples	$\delta^{18}O$ (‰ SMOW)	$\delta^{13}C$ (‰ PDB)
N3	11	+21.63 (0.20; 0.9%)	+1.05 (0.03; 3.2%)
N2E	11	+20.63 (0.21; 1.0%)	+1.08 (0.07; 6.2%)
N2W	19	+19.95 (0.23; 1.2%)	+0.98 (0.04; 4.5%)
N2 vein calcite	7	+19.60 (0.62; 3.2%)	+0.66 (0.87; 131%)

lithon calcite. Furthermore, the apparent linearity of the Mn/Sr ratios in N2W calcite (Fig. 5) may reflect precipitation from a fluid whose trace-element composition was evolving during the interval of cleavage formation. The values for $\delta^{18}O$ in the KC vein calcite (see Fig. 2 for location) and in the microlithon calcite in N2W are the same within analytical uncertainty, suggesting that essentially all N2W microlithon calcite recrystallized. We cannot explain the contrast between $\delta^{13}C$ observed in the KC vein calcite and $\delta^{13}C$ observed in the microlithon calcite.

The oxygen isotope data can be used to estimate the water/rock ratio (W/R) during recrystallization of calcite in Kalkberg microlithons. The calculated W/R represents the relative proportions of *isotopically-exchanged* water and calcite integrated over the lifetime of the water–rock system (see Taylor 1977). We used a slightly modified version of the conventional equation for a closed system to calculate W/R:

$$(W/R)_{Closed} = (\Delta b)[F\{\Delta_{c-w} - (\delta_c^i - \delta_w^i)\} - \Delta b]^{-1}. \quad (1)$$

Δ_{c-w} is the equilibrium isotope fractionation factor between calcite and water calculated from the equation given in Friedman & O'Neil (1977), and $\Delta b = \delta_c^f - \delta_c^i$. The superscripts i and f stand for initial and final, and the subscripts c and w for calcite and water, respectively. The $\delta^{18}O$ value for calcite or water is symbolized by δ, and F is the fraction of recrystallized calcite. For an open system, W/R is given by:

$$(W/R)_{Open} = \ln[(W/R)_{Closed} + 1], \quad (2)$$

where $(W/R)_{Closed}$ is the water/rock ratio for a closed system (Taylor 1977). Note again that only the amount of exchanged water and calcite, not the total amount of water that flowed through the system, is accounted for by W/R in equations (1) and (2); the estimated W/R ratios from equations (1) and (2) actually represent 'water/recrystallized calcite' ratios (see Ohmoto 1986 for further discussion of water/rock ratios). It is assumed that calcite–water isotopic exchange occurs isothermally at equilibrium, and that no water is consumed or released during exchange (e.g. by chemical reactions or by dewatering of clays). In this paper we report W/R ratios in volumetric units for water at standard pressure and temperature.

To estimate W/R during cleavage formation in the Kalkberg, we substituted measured values into equations (1) and (2). For δ_c^i and δ_c^f, we used the mean $\delta^{18}O$ values of uncleaved and strongly cleaved Kalkberg (Table 4), respectively. The value for F depends on whether we use petrographic observations of fibrous calcite or isotopic results as the basis for specifying F. Petrographic evidence indicates that $F \geq 0.5$, however the similarity of the $\delta^{18}O$ values for the KC veins and N2W calcite suggests that $F = 1$, and in our W/R calculations we use $F = 1$ (for $F < 1$, calculated values for W/R tend to increase). The fractionation factor (Δ_{c-w}) is calculated from Friedman & O'Neil (1977) for exchange in the temperature range 100–200°C.

The influence of δ_w^i on W/R ratio is very significant,

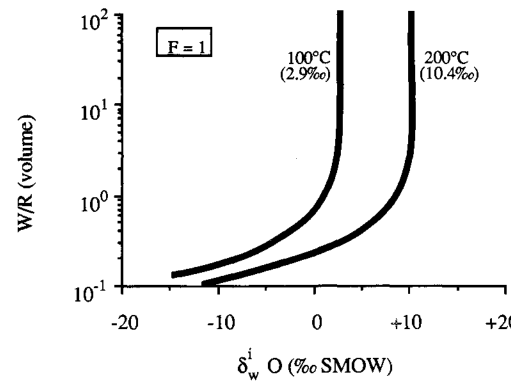

Fig. 9. W/R ratio for an open system as a function of initial $\delta^{18}O$ of water (δ_w^i) for $F = 1$ at 100 and 200°C (equation 2). Numbers in parentheses are the critical δ_w^i values for which the curves become vertically asymptotic. For δ_w^i greater than the critical value, the curves approach zero asymptotically from negative infinity (not shown).

but it is the least well constrained parameter in equation (1). Using values for δ_c^i, δ_c^f, Δ_{c-w} and F from above, it is apparent that at a critical δ_w^i value (~3–10‰ SMOW) the calculated W/R ratio approaches infinity (Fig. 9). Using an initial $\delta^{18}O$ of −10‰ SMOW, which is a reasonable low-end value for subsurface water in sedimentary basins (Sheppard 1986), we obtain values of 0.1–0.2 as a minimum estimate of the volumetric W/R ratio (Fig. 9). To determine a maximum value for W/R ratio, we assumed that δ_w^i was in equilibrium with vein calcite of 19.60‰ SMOW. Substituting values for δ_c^i, δ_c^f and F as before, yields volumetric W/R ratios of 7.0 for a closed system and 2.6 for an open system. Note that this calculation is insensitive to temperature. The trends in the geochemical data suggest open system behavior during cleavage development, therefore we suggest that the open system calculation is more appropriate.

EVIDENCE FOR BULK FLUID FLOW

A topic of interest concerning the low-grade metamorphism and deformation of sedimentary rocks is the mechanism of mass transfer (e.g. Etheridge *et al.* 1984, Waldron & Sandiford 1988). The issue centers around the relative importance of bulk fluid flow versus diffusion through a stationary fluid in rocks dominated by dissolution–precipitation processes (i.e. 'pressure solution' and free-face dissolution). Significant fluid flow during deformation of fold-thrust belts (Engelder 1984), and large-scale fluid convection during regional metamorphism (Etheridge *et al.* 1983, 1984) have been suggested to account for major volume losses. Furthermore, large volume loss associated with cleavage development has been demonstrated in low-grade rocks (Wright & Platt 1982, Beutner & Charles 1985). Grain-scale diffusion through a static pore fluid can explain the features observed in rocks deformed under low-grade conditions (e.g. Rutter 1983). Since diffusion occurs at the scale of a few mm or less, and since significant volume loss requires mass transport over much larger distances, it seems that large-scale volume loss is irreconcilable with a purely diffusive mass-transfer mechanism and that bulk fluid flow must occur. It is possible to determine whether fluid flow occurred through the use of water/rock ratios.

The porosity of a rock determines the instantaneous W/R ratio (Wood & Walther 1986), whereas conventionally calculated water/rock ratios give ratios that are integrated over the duration of water–rock interaction. An integrated W/R ratio that is significantly larger than the instantaneous ratio implies that bulk fluid flow occurred. The porosity of ancient fine-grained limestones is on the order of 1% (Bathurst 1975), indicating an instantaneous W/R ratio of 0.01 (volume) for microlithons in the Kalkberg Formation. A volumetric W/R ratio of the order of 0.01 for our study requires that the initial water had a $\delta^{18}O$ composition more negative than −60‰ SMOW, which is highly unlikely given that the $\delta^{18}O$ of modern subsurface water in sedimentary basins is generally greater than −10‰ (Sheppard 1986). Our estimate of 0.1–0.2 for the minimum integrated W/R ratio (compared with an instantaneous W/R ratio of the order of 0.01) implies that bulk fluid flow occurred in the microlithons during cleavage development. Fluid flow may have been focused through the limestone at N2W because of increased access to major fluid conduits (the horse-bounding faults), dilatancy caused by elevated stress, or increase in mass-transfer pathways provided by cleavage domains and microstylolites.

DISCUSSION AND CONCLUSIONS

In order to determine how microlithons changed in association with the development of spaced solution cleavage in argillaceous limestone, we compared the fabric and chemistry of microlithon samples from strongly cleaved limestone to samples from weakly cleaved or uncleaved limestones of the same stratigraphic horizon in nearby outcrops. Petrographic analysis indicates that the fabric of microlithons in strongly cleaved samples is distinct from that of uncleaved samples. In the microlithons from strongly cleaved samples, there are abundant microstylolites, and, most notably abundant fibrous calcite. The fibers in the microlithons are oriented parallel to cleavage domains and occur as beards on larger grains, as vein fill (locally in bed-parallel stylolites) and in 'diffuse extension zones'. Diffuse extension zones, which can only be seen in thin section, are regions of the microlithon in which microcrystalline calcite grains of the rock matrix have a dimensional preferred orientation subparallel with cleavage domains. Petrographic evidence suggests that, on average, at least 50% of the calcite fraction in the microlithons of strongly cleaved samples was recrystallized as fibrous calcite during cleavage development (an amount that is approximately equal to the amount of calcite that dissolved at cleavage domains). Thus, microlithons could provide a major sink for the calcite that dissolved in cleavage domains.

The petrographic evidence for major recrystallization of microlithons during cleavage formation is supported by chemical analysis. We found that the trace-element and stable-isotope compositions of calcite in microlithons of strongly cleaved rock is significantly different from that of nearby uncleaved rock from the same stratigraphic horizon. Relative to uncleaved samples, calcite in strongly cleaved samples is enriched in Mn and Sr and reduced in $\delta^{13}C$ and $\delta^{18}O$ signatures (though the overall $\delta^{13}C$ shift is equal to analytical uncertainty). These geochemical shifts suggest that calcite in microlithons underwent recrystallization in a fluid that was different from the fluid in which pre-cleavage calcite had equilibrated. Therefore, the fluid could not have been derived from the uncleaved rock, and the development of cleavage occurred in an open system. $\delta^{18}O$ values for microlithon calcite are the same as $\delta^{18}O$ in vein calcite immediately adjacent to strongly cleaved rock. If the $\delta^{18}O$ composition of this vein calcite is taken to be indicative of the composition of the fluid during deformation, there was complete recrystallization of calcite in microlithons from strongly cleaved rock during cleavage formation (i.e. even more than the 50% recrystallization indicated by petrographic analysis). Calculation of water/rock ratio indicates that for an open system complete exchange between Kalkberg calcite and 0.1–2.6 volumes of water could have affected the observed $\delta^{18}O$ changes. The minimum *integrated* water/rock ratio is approximately an order of magnitude larger than the inferred *instantaneous* water/rock ratio, suggesting that bulk fluid flow occurred in the microlithons during cleavage development.

The combination of outcrop, petrographic, and geochemical data reported in this paper indicates, therefore, that microlithons were not inert during the formation of adjacent cleavage domains. Water passing through the rock during cleavage formation promoted recrystallization of microlithon calcite. The new calcite that grew in the microlithons may, in part, represent calcite that had dissolved in the cleavage domains that underwent chemical and isotopic exchange with fluids that originated outside the local rock body. This calcite occurs as fibers either in distinct overgrowths on larger grains or in diffuse zones in the microcrystalline matrix. The net effect of the growth pattern is to accommodate extensional strain in a direction parallel to cleavage domains concomitant with shortening strain across domains. Thus, it is possible for cleavage formation to be a volume-constant plane-strain process.

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