A natural example of the simultaneous operation of free-face dissolution and pressure solution

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Abstract—The dissolution of crinoid columnals during tectonic deformation of the Appalachian Plateau was enhanced by stress-induced changes of chemical potential of calcite in solution at the surface of the crinoid columnal. Pressure solution on the outside surface occurred within areas of highest normal stress developed at grain to grain contacts whereas free-face dissolution on the inside bore (the axial canal) of the columnal occurred where parts of the crystal lattice next to the surface were subject to the highest strain, as indicated by the presence of mechanical twins. For free-face dissolution, the chemical potential of the solute is affected more by the larger strain energy associated with mechanical twinning than strain energy from elastic strain prior to mechanical twinning of the crystal lattice. These observations suggest that free-face dissolution as well as pressure solution may contribute significantly to dissolution during rock deformation by diffusive mass transfer.

INTRODUCTION

CHEMICAL potential is commonly used in predicting the influence of stress on the tendency of a solid to dissolve or grow in the presence of a solution (Kamb, 1959). For equilibrium of a solid under all possible states of strain (Gibbs, 1906)

$$\mu_L = F_s + P_w V_s \tag{1}$$

where μ_L is the chemical potential of the solute in solution, F_s is the molar Helmholtz free energy of the stressed solid, P_w is the pressure of the solution in contact with the solid, and V_s is the molar volume of the solid in the stressed state. Differentiating at a constant temperature, a change in μ_L is represented by three terms:

$$d\mu_L = dF_s + P_w dV_s + V_s dP_w . \tag{2}$$

In this equation, $V_s dP_w$ represents a change in normal pressure on the surface of a solid suspended in the fluid undergoing a pressure change. dF_s is the change in elastic strain energy and $P_w dV_s$ is the change in specific volume. For rocks where grains are in contact, stresses within the grains arise from a combination of pore water pressure and grain to grain contacts. To treat this situation, several including Paterson (1973) and Robin (1978) deal with a variation in pressure (P) along the surface of the grains arising from grain to grain contacts with $P \geq P_w$. Unlike the hydrostatic case, chemical potential varies along the surface of the grain because of the pressure variation from grain to grain contacts. Here the strain energy term

$$dF_s \leq V_s \sigma_{ij} de_{ij} . \tag{3}$$

In Paterson's (1973) derivation, the deformation is assumed entirely elastic and therefore dF_s is equal to the difference between the elastic strain energy

of the solid at normal stress P and at hydrostatic pressure P_w.

$$dV_s = V_s \delta_{ij} de_{ij} \tag{4}$$

so that

$$d\mu_L \leq V_s(\sigma_{ij} - P\delta_{ij})de_{ij} + V_s dP \tag{5}$$

where σ_{ij} are components of the stress tensor and e_{ij} are components of the strain tensor within the solid. $V_s(\sigma_{ij} - P\delta_{ij})de_{ij}$ represents the Riecke principle for dissolution at a free face whereas $V_s dP$ represents the Poynting principle for grain to grain contact pressure solution (Durney, 1978). Free-face dissolution may be considered a strain energy driven dissolution whereas pressure solution may be considered a surface pressure driven dissolution. The term associated with variation in pressure at grain to grain contacts is typically large compared with the elastic strain energy terms unless $P \approx P_w$ (Paterson, 1973).

The application of nonhydrostatic thermodynamics to pressure solution and free-face dissolution may include the assumption that all solid body deformations are elastic and reversible (Paterson, 1973; DeBoer, 1977). In this case, $V_s dP$ and, hence, pressure solution largely controls $d\mu_L$ with the free-face dissolution terms unimportant. This is supported by the observation that stylolitic solution cleavage develops in limestones in the absence of mechanical twinning (Alvarez *et al.*, 1976). However, if the strain in a solid becomes so large that it must be accommodated by irreversible introduction of lattice defects, the strain energy of the stressed solid may also become sufficiently large to have an effect on $d\mu_L$ comparable to the $V_s dP$ term. With this paper, I present evidence suggesting that free-face dissolution does add significantly to the tendency of calcite to dissolve and that increased strain energy associated with mechanical twinning is responsible for the enhanced free-face dissolution. An enhancement of dissolution would increase the effectiveness of dif-

fusive mass transfer as a deformation mechanism in rocks.

The rate limiting step in diffusive mass transfer in rocks is generally assumed to be diffusion of the solute in solution. In a closed system with no pore water circulation, the steeper the chemical potential gradient, the faster the diffusive mass transfer processes. In an open system with a constant pore water circulation, the larger the difference in chemical potential between the hydrostatic and nonhydrostatic situation, the greater the tendency of a solid to dissolve and be carried away by ground water circulation. Hence, any process that increases the change in chemical potential from a standard state value, will in effect make the diffusive transfer in rocks a more efficient deformation mechanism.

FREE-FACE DISSOLUTION

Examples clearly illustrate the role that the irreversible introduction of lattice defects plays in affecting the solubility of geologic materials. Experiments by Paterson (1959) indicate that the solubility product of calcite may rise by 50% after 15% strain. Gross's (1965) measurements of heats of solution as a function of plastic deformation confirm Paterson's (1959) estimates of increase in solubility. Bosworth's (1982) experiments showed that plastic deformation enhanced the free-face solubility of halite. In nature the role of free-face dissolution is illustrated by the response of crinoid columnals to tectonic stresses exerted by a quartzose matrix surrounding the columnals (Engelder, 1979).

Columnals A through E were sampled from different outcrops in western New York State (Figure 1). In all cases the axial canal is normal to bedding. It is common to see two adjacent columnals showing different amounts of strain, which illustrates that strain was inhomogeneous from point to point within outcrops. The mechanism causing inhomogeneous strain is not clear. Despite this observation, average strain correlated reasonably well from outcrop to outcrop (Engelder and Engelder, 1977).

A single crinoid columnal is a short thick-walled cylinder, consisting of a single crystal of calcite (Figure 1). The hollow interior of a columnal is the axial canal with five lobes in the case of some Upper Devonian crinoids from western New York. The radial markings in columnal A (Figure 1) are crenularia which aid in the connection of one columnal to the next and appear in thin section as variations in thickness of the single crystal of calcite. The initial round shape of an Upper Devonian crinoid columnal is preserved in both the axial canal and crenularia of columnal A (Figure 1).

The axial canal in crinoid columnals presents a loading condition for which enhancement of dissolution by mechanical twinning may be observed. The presence of a cylindrical hole distorts the pre-existing stress field in the rock. As shown in Figure 2, uniaxial stress of σ_1 at a distance from an elastic rock containing a borehole is magnified to $3\sigma_1$ at the edge of the borehole (Inglis, 1913). Even if the elastic rock is subject to two principal stresses of equal magnitude normal to the axis of the borehole, the stress at the edge of the borehole is twice the far field stress.

The following discussion of crinoid columnals assumes that the matrix exerts a load on the outside diameter of the crinoid columnal such that the normal stress on the outside boundary is magnified at the axial canal of the columnal. This loading condition is similar to that used by Sprunt and Nur (1977) for experiments on the effects of stress on solution rate. That this assumption is valid even for five-lobed axial canals is illustrated by columnal C where mechanical twins within the columnal first appear next to the axial canal (Figure 1). Here the twins first form at the location on the axial canal normal to the direction of maximum compression. Stress within this columnal is high enough so that the critical resolved shear stress for calcite twinning is exceeded only where the far field stress is magnified by the distortion of the stress field around the axial canal.

Mechanisms responsible for the shape change of crinoid columnals in Figure 1 include mechanical twinning, pressure solution, free-face dissolution and elastic strain. The latter is negligible compared with visible shape changes. The shape change accompanying mechanical twinning is most dramatic in columnal B by virtue of its having the greatest number of twins. However, most columnals from the Upper Devonian section of western New York show far larger shape changes from grain to grain contact pressure solution than mechanical twinning (Engelder, 1979). Very little of the ellipticity seen in columnals A to E is from the strain associated with mechanical twinnings.

The shape of columnal A is affected by just grain to grain contact pressure solution at the outside boundary. Here calcite appears more soluble than quartz so that quartz grains are seen penetrating the calcite, thus forming a stylolitic contact between the quartzose matrix and the calcite. The apparent solubility of calcite relative to quartz is more easily seen for the coarser matrix around columnal B. The amount of calcite loss from the outer edge of columnal A can be measured by the change in distance between the circular trace of the crenularia and the elliptical edge of the columnal. The calcite removed by pressure solution is not redeposited on surfaces of the columnal subject to lower normal stresses but rather diffuses some unknown distance from the immediate vicinity of the columnal. The lack of mechanical twins in columnal A suggests that the stress responsible for pressure solution at the edge of the columnal was not magnified enough by the axial canal to exceed the critical resolved shear stress for calcite twinning ($\sim$5 MPa; Turner $et\ al.$, 1954). The elliptical shape of the outer boundary of columnal
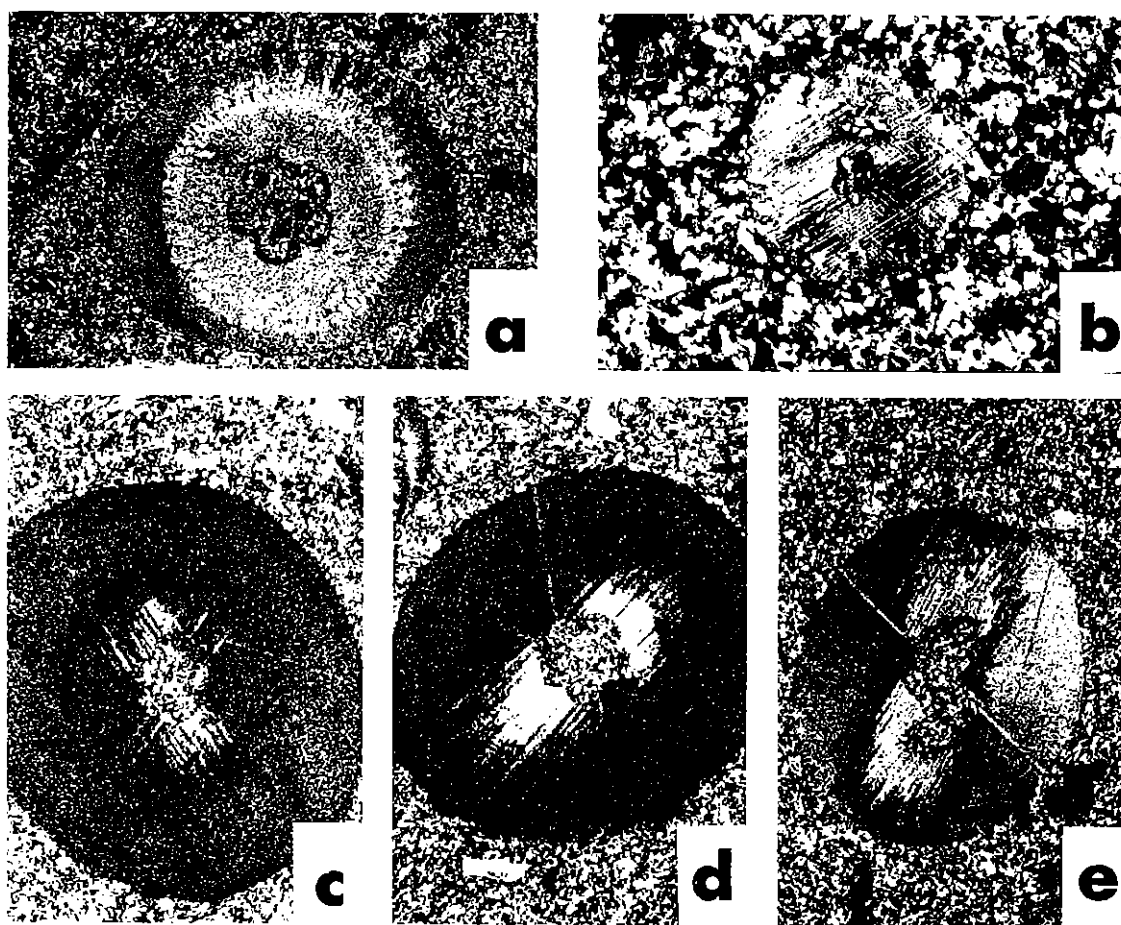
FIG. 1. Examples of shape changes of crinoid columnals as viewed parallel to the axial canal: a) Plane light. No mechanical twins are visible with crossed nicols. b–e) Crossed nicols with one or more sets of mechanical twins visible. Long direction of all photos is 7.8 mm.

A indicates maximum compression parallel to the short axis of the ellipse.

Columnals C, D, and E show the effect of increased mechanical twinning which initiated at the axial canal. Presumably C, D, and E also represent a sequence of columnals for which the resolved shear stress was higher on twin planes in D than C and highest on twin planes in E in which the area of twinned crystal extends across most of the crystal. With the increase in mechanical twinning, the axial canal has an increased tendency to dissolve, as shown in columnal E. Dissolution from the axial canal is often characterized by a much rougher boundary relative to the outer boundary associated with the grain to grain contact pressure solution, as is illustrated by columnal E. The growth of mechanical twins next to the axial canal indicates a compression direction similar to that of the apparent flattening at the outer boundary. Because dissolution at the axial canal appears to progress without surface pressure from the matrix within the axial canal, this is called *free-face dissolution*.

Calcite removal by free-face dissolution may occur if the axial canal acts as a free face where $P \approx P_w$.

If matrix fills the axial canal, grains will touch at certain points along the canal wall but will not appreciably load the canal wall at point contacts. That the matrix does not load the canal wall is seen in many columnals that have no mechanical twins (e.g., Figure 1a). The axial canal does not show the stylolitic surface that is common to grain to grain contact pressure solution on the outside of the columnal and indicative of matrix loading. Likewise, if the matrix deforms largely through pressure solution, it is viscous. The matrix sheltered by the axial canal has a smaller strain rate than matrix surrounding the columnal. A consequence of the lower strain rate is that the stresses exerted by this viscous matrix are also much smaller.

If the matrix within the axial canal acts to prevent free-face dissolution, the initiation of mechanical twins should have no effect on dissolution of the axial canal. However, dissolution within the axial canal is triggered by the presence of mechanical twins. The outer edges of untwinned columnals have obviously been loaded by the matrix during the generation of their elliptical shape by pressure solution. During this initial loading, the stress was magnified at the axial
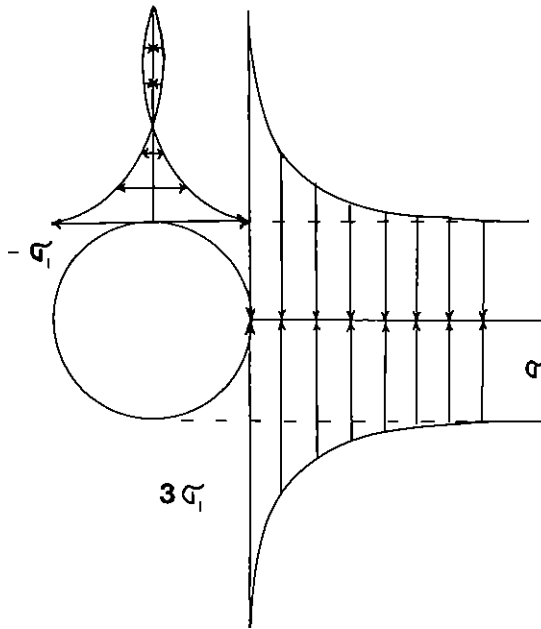
STRESS DISTORTIONS CAUSED BY A HOLE

FIG. 2. Stress distortion caused by a borehole where σ_1 is a uniaxial stress at infinity. After Hubbert and Willis, 1957.

canal but the associated elastic strain energy was not high enough to enhance dissolution at the axial canal. With additional loading, twins are produced and the strain energy associated with twinning in calcite was sufficiently higher than the elastic strain energy in untwinned columnals that free-face dissolution became effective.

Another possibility for free-face dissolution within the axial canal is that the pressure solution effect on the outside of the columnal leads to an intimate contact with the matrix and a choking of fluid flow. In contrast, continued fluid circulation may tend to be located within the sheltered axial canals of the columnals. Here it may be argued that the concentration of dissolution would have nothing to do with strain energy of calcite but merely to the availability and circulation of fluids concentrated within the axial canals. But the fact remains that free-face dissolution does not occur within the axial canal until twinning develops, even in cases with extensive pressure solution on the outside of the columnal. Hence, the favored interpretation is that free-face dissolution is driven by increased strain energy associated with twinning.

In some instances the matrix within the axial canal appears to support the columnal so that stress is not magnified at the axial canal. In this case, the entire columnal is subject to a uniform shear stress and twins uniformly as is the case for columnal B (Figure 1). Other uniformly twinned columnals have their axial canals filled and supported by overgrowths of dolomite and fine-grained silica. This suggests that

when the filling is 'strong' or impermeable, it does not allow the free-face dissolution along the axial canal.

To assess the effectiveness of calcite removal by free-face dissolution compared with grain to grain contact pressure solution, shape change measurements are used. As shown in the Appendix and Figure 4, the amount of calcite dissolved from the inside of the canals (see Figure 3) is a generally increasing function of the amount of twinning, other parameters being kept equal. However, pressure solution still accounts for a larger amount of calcite removal in more than 80% of the columnals.

DISCUSSION

The enhanced free-face dissolution associated with twinning in calcite confirms that twinning affects the chemical potential of the solid component in the pore fluid. The change in chemical potential is through the increase in Helmholtz free energy which may be associated with: 1) the addition of crystal defects into the calcite by slip or twinning; 2) bends or wedges where twin lamellae have not extended completely through the crystal (e.g., Figure 1c); and 3) twin boundaries that are not cyrstallographically coincident throughout. Free-face dissolution of the crinoid columnals from western New York suggest that the homogeneous elastic strain energy within the calcite crystal prior to twinning is small compared with the local elastic strain energy associated with twinning.

The increase in strain energy associated with mechanical twinning relative to elastic strain energy prior to twinning is significant. Goetze and Kohlstedt's Figure 1 (1977) shows that mechanical twins in Yule marble have defects at the twin boundaries. In the case of the Yule marble, the mechanical twin shown in Goetze and Kohlstedt (1977) is 0.5 μm wide, about the same width as the mechanical twins in the crinoid columnals of the Appalachian Plateau. The narrow twin has about 10 defects per μm of boundary or about 20 defects per μm of twin. For a columnal with 50 twins per mm, the defect density (ρ) is about 10^8/cm^2. Assuming a shear modulus (μ) of 0.25×10^{12} dynes/cm^2 and a Burgers vector (b) of 6.3 Å, the strain energy per unit volume for this example is $\mu b^2 \rho = 9.92 \times 10^4$ dyne-cm/cm^3. The elastic strain energy prior to mechanical twinning is $\sigma_c^2/2E$ where σ_c is the maximum stress difference that calcite can support without twinning and E is the Young's modulus for calcite. If $E = 0.5 \times 10^{12}$ dynes/cm^2 and $\sigma_c = 10^8$ dynes/cm^2 (Turner et al., 1954), then $\sigma_c^2/2E = 10^4$ dyne-cm/cm^3. If the twin in Yule marble is comparable to twins in crinoid columnals, the elastic strain energy is an order of magnitude smaller than the strain energy associated with mechanical twinning.

Of further note is that a dislocation density of 10^8/cm^2 suggests that the axial canal was subject to a differential stress ($\sigma_1-\sigma_3$) of 12.5 MPa according to

the relationship $\sigma_1-\sigma_3 = \alpha\mu b\rho^{1/2}$ (Kohlstedt and Goetze, 1974). Accounting for the magnification of stress at the axial canal, the average stress difference to which the Appalachian Plateau was subject was 6.2 MPa or less.

Geologists have appreciated that plastic deformation affects solubility (Paterson, 1959, 1973; Gross, 1965; DeBoer, 1977) but evidence that it con-
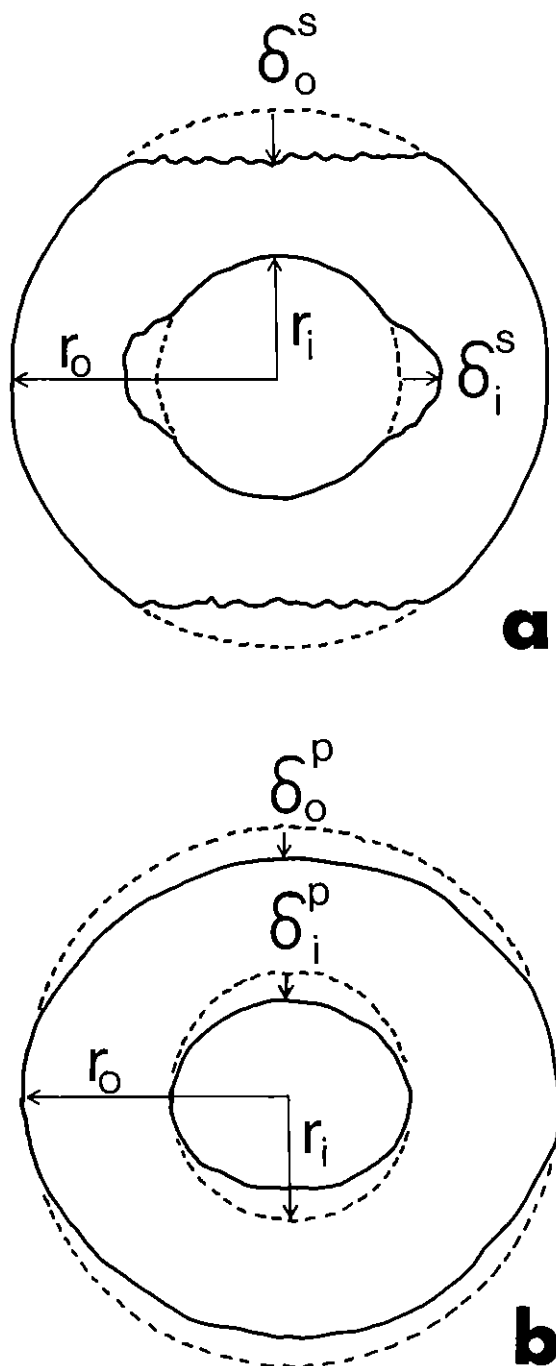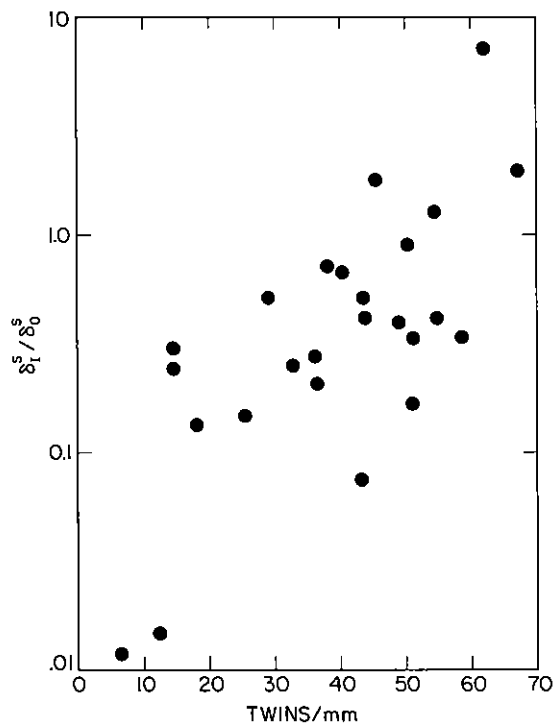

FIG. 4. Ratio of calcite removal in the inside to calcite removal on the outside of crinoid columnals versus density of microtwins.

FIG. 3. Shape changes of crinoid columnals by: a) pressure solution (δ^s_o) and free-face dissolution (δ^s_i) and b) mechanical twinning (δ^p_o and δ^p_i).

tributes significantly to diffusive mass transfer has never before been reported. To date pressure solution has been regarded as the primary mechanism leading to diffusive mass transfer. Using the shape changes of crinoid columnals from western New York, I have shown that free-face dissolution driven by the energy associated with mechanical twins contributes significantly to the total calcite removed in solution. The suggestion here is that in terrains where intragranular deformation was regarded as an important mechanism for strain, if water is present, free-face dissolution with accompanying diffusive mass transfer may also contribute significantly to the total strain.

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APPENDIX
THE CORRELATION OF FREE-FACE DISSOLUTION AND MECHANICAL TWINNING

To assess the effectiveness of calcite removal by free-face dissolution compared with grain to grain contact pressure solution, shape change measurements are used. Possible shape changes include removal of calcite from the axial canal and the outer edge as well as the apparent bending that accompanies strain by twinning (Figure 3). The removal of calcite and bending are characterized by the ratio (R) of the long over short diameters for both the axial canal (R_i) and the outside edge (R_o). These ratios are used in conjunction with a best estimate for the original inside (r_i) and outside (r_o) radii to calculate the displacement (δ) of the inside (δ_i) and outside (δ_o) boundaries (Figure 3).

The δ_i^p and δ_o^p for mechanical twinning without dissolution may be estimated from the number and width of twins within the columnal. The mechanical twins in the columnals are generally microtwins for which Groshong (1972) calculates a width of 0.5 μm. The microtwins in Figure 1 look wider because they cut the plane of the photograph at a low angle ($\sim$26°). The columnals rarely contain more than 100 microtwins per mm, which is equivalent to 5% of the calcite twinned and a $\delta_o^p = 0.014r_o$ (Engelder, 1979). If $r_i/r_o = 0.25$, then $\delta_i^p = 0.014r_i$ and $\delta_i^p = 0.25\delta_o^p$.

δ_i^s and δ_o^s for removal of calcite in solution may be estimated by assuming that r_i and r_o, as indicated in Figure 3a, are the original radii unaffected by dissolution. Then

$$\delta_i^s = r_i(R_i - 1) \quad \text{and} \quad \delta_o^s = r_o(R_o - 1) \qquad (6)$$

If mechanical twinning accompanied dissolution, δ_i^s/δ_o^s can be calculated by first calculating δ_i^p to determine $r_i = \delta_i^p + r'$ where r' is the present inside radius measured in the direction of r_i in Figure 3b. Likewise, R_i and R_o are adjusted to remove the effect of δ_o^p and δ_i^p. The relative amount of calcite removed by free-face dissolution versus grain to grain contact pressure solution can be estimated by

$$\frac{\delta_i^s}{\delta_o^s} = \frac{r_i(R_i - 1)R_o}{r_o(R_o - 1)} \qquad (7)$$

Here the assumption that r_i and r_o as measured in Figure 3a represent original radii is rarely correct. However, the preservation of parts of the five-lobed axial canal give a good indication of the reliability of r_i. r_o is most likely to be in error and δ_i^s/δ_o^s may be overestimated.

To obtain an estimate of δ_i^s/δ_o^s for crinoid columnals from the Appalachian Plateau of western New York, many thin sections were cut from samples with large numbers of columnals deposited with their axes normal to bedding. The thin section cuts were parallel to bedding so that only those best representing tectonic deformation during layer parallel shortening were analyzed. A single thin section rarely cut more than three to four columnals with axes within 2° of normal to the plane of the cut, as indicated by the C-axis of calcite. Using a flat stage microscope, the short and long inside and outside diameters of the columnals subnormal to their cylindrical axes were measured. The number of microtwins per unit length was measured along tracks normal to the microtwin plane with use of a U-stage microscope.

The δ_i^s/δ_o^s versus microtwins/mm are shown in Figure 4 for a sample of crinoid columnals taken from a road cut 4 miles north of Andover, New York on Route 21. This data set of 23 columnals comes from a 250 cm^3 sample. δ_i^s/δ_o^s becomes larger with increased plastic deformation, as indicated by the density of mechanical twins. Here δ_i^s represents free-face dissolution which becomes more effective at removing calcite when permanent strain in the calcite is larger. Figure 4 is an assessment of δ_i^s/δ_o^s parallel to bedding with no information concerning bedding normal compaction.