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## GROWTH OF DOLOMITE CRYSTALS

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**ABSTRACT.** Surfaces of growing crystals of dolomite from Deep Springs Lake, California, are Ca-rich. Variations in composition from surface inward have been studied by means of successive leachings, chemical analyses, and electron photomicrographs. The surfaces of the crystals have a calcium to magnesium ratio in excess of 4; the surface layer is about 100 Å thick and approaches the composition of dolomite at its inner side. Successive fractions have also been dated by  $C^{14}$  and thus place a time parameter on the introduction of magnesium into the rhombohedral carbonate lattice. The crystals grow by the production of a transient surface layer which can be envisaged as a moving boundary through which the magnesium must move by solid-state diffusion with concomitant migration of calcium in the opposite direction. The formation of dolomite having a rudimentary  $R\bar{3}$  space group takes place at the inner side of the surface layer. Crystal growth models are considered, along with implications concerning rates of growth and diffusion, solubility, and isotopic fractionation.

The mineral dolomite is a geological enigma. The “dolomite problem” (Ingerson, 1962) revolves mainly about the abundance of dolomite in ancient sedimentary rocks as opposed to the apparent lack of instances of recent sedimentary formation of this mineral and the lack of success in synthesizing this mineral at low temperatures in the laboratory. Geologic evidence leaves little doubt that dolomite in many ancient rocks formed either during or very shortly after the deposition of the sediments that now comprise these rocks.

Dolomite ( $CaMg(CO_3)_2$ ) is an ordered phase of the  $R\bar{3}$  space group. Its Ca and Mg are segregated into alternating cation planes, which are separated by planes of triangular carbonate groups. Recent sedimentary dolomites are not perfectly ordered; however, some have been shown to possess at least a rudimentary  $R\bar{3}$  space group (Peterson, Bien, and Berner, 1963; von der Borch, Rubin, and Skinner, 1964). Most low-temperature ancient dolomites are not ideally stoichiometric but rather contain from 3 to 6 percent excess calcium (Goldsmith and Graft, 1958).

Recent dolomite is forming in Deep Springs Lake, California; detailed radiocarbon studies have shown that the crystals of dolomite have grown exceedingly slowly, with a rate of the order of hundreds of Ångströms per thousand years (Peterson, Bien, and Berner, 1963). It now becomes of interest, both crystallochemically and geologically, to inquire by what mechanisms so slow a process may take place.

Not only is it difficult or impossible to synthesize dolomite at low temperatures (Graf and Goldsmith, 1956), but it is also difficult to deter-

mine its solubility. Reported equilibrium constants for dolomite range from  $3 \times 10^{-17}$  to  $4.7 \times 10^{-20}$  (Barnes and Back, 1964).

Dolomite-calcite pairs, taken from low-temperature situations (Degens and Epstein, 1964), do not show the fractionation of oxygen isotopes that might be expected, based on data from high-temperature situations (Clayton and Epstein, 1958; Engel, Clayton, and Epstein, 1958; Epstein, Graf, and Degens, 1964). From this information Degens and Epstein (1964) have concluded that the formation of dolomite must take place by way of metasomatism of calcite and that the dolomite must grow out of crystalline calcium carbonate under solid-state conditions. Crystals of dolomite, however, are not found in low-temperature sedimentary rocks disposed in such a manner as to suggest that they have formed by the large-scale adaptation of a preexisting rhombohedral carbonate lattice. They are predominantly very well shaped rhombohedra, which are commonly zoned and which bear no consistent crystallographic relation to the host crystals of calcite. Peterson, Bien, and Berner (1963) have suggested that *completely new crystallization* in the formation of dolomite is necessitated by the lack of long-range, solid-state diffusion of Mg and Ca, at low temperatures, in rhombohedral carbonates. Thus, again, there is a dilemma.

#### CRYSTAL GROWTH RATES

The basic strategy employed (Peterson, Bien, and Berner, 1963) in the determination of crystal growth rates of dolomite from Deep Springs Lake, California, was to determine by  $C^{14}$  the ages of various size frac-

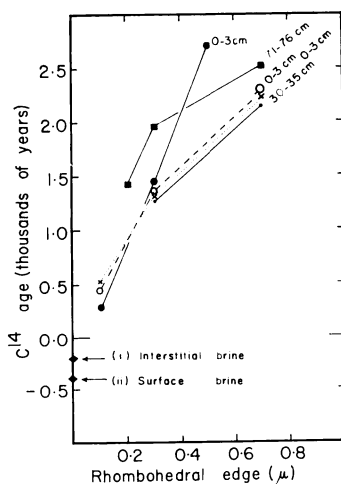


Fig. 1.  $C^{14}$  ages of size fractions of dolomite from the bed of Deep Springs Lake, California, plotted against average size of the dolomite rhombohedra. Fractions from the same sample are connected by lines; sample depths are also shown. The graphs are all of generally recent dolomite and are interpreted as growth curves of the dolomite crystals (after Peterson, Bien, and Berner, 1963). Ages of interstitial and surficial brines are also shown.

tions of dolomite crystals from a single sample (fig. 1). The larger size fractions of dolomite crystals had, in every instance, a greater average  $C^{14}$  age than the smaller size fractions from the same sample, suggesting that the relationships in figure 1 were growth curves and that the larger crystals had nucleated longer ago and had been growing for a longer time. The apparent age of the carbonate in the solutions from which the crystals grew is another point on these growth curves. Two such points have been plotted: (i) 4000 milliliters of interstitial solution squeezed from the dolomite-sediment from depth of 0 to 3 centimeters (age  $-184 \pm 50$  years), and (ii) 4000 milliliters of brine from the drying lake surface (age  $-384 \pm 50$  years). Thus the dolomite crystals in surficial sediments of Deep Springs Lake are forming in an environment of virtually zero age; slightly negative ages can be accounted for by isotopic fractionation during evaporation and possibly by some bomb fallout. The data of figure 1 suggested more or less continuous crystal growth from the time of nucleation to the present and yielded rates of growth ranging from  $0.05$  to  $0.09 \mu/10^3$  years for the edges of dolomite rhombohedra of the surficial sediments.

Using the relationship of unit cell size to composition (Goldsmith, Graf, and Heard, 1961), it was possible to demonstrate that variations in composition of dolomitic material from Deep Springs Lake existed within single samples and within their individual size fractions. This was demonstrated by differentially dissolving away the more Ca-rich material and examining by X-ray diffraction the remaining material (fig. 2). The actual variations in composition represented by these X-ray diffraction profiles will now be considered.

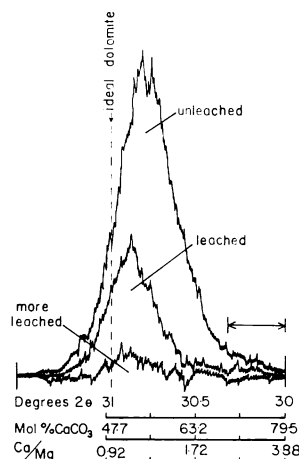


Fig. 2. Profiles of (211) composition-sensitive X-ray diffraction maximum of dolomite from Deep Springs Lake for untreated sample and for the same material after leaching 20 seconds ("leached") and 3 minutes ("more leached") with acetic acid buffered at pH 5.0, with ammonium acetate, at  $25^\circ C$ . There is a range of  $d$  (211), hence composition, within a single sample.

## THE CRYSTAL SURFACE

It has already been argued that completely new crystallization in forming dolomite is necessary because of the lack of long-range solid-state diffusion in the rhombohedral carbonates. It was postulated, however (Peterson, Bien, and Berner, 1963), that this does not preclude the possibility of short-range mobility, especially near the surface of a forming crystal. Even at the surface of these growing dolomite crystals, there must be a disordered layer, perhaps only a unit cell or two thick. Unsatisfied crystal bonds would yield a generally warped crystal structure. Only after the fundamental rhombohedral structure is present would the energetics for ordering become effective. Ordering may take place very near the surface but not *at* the surface where the structure sites are not yet well enough characterized in three dimensions to permit differentiation between Ca and Mg ions. It was also argued that if the ordering cannot take place at the surface of the crystal because of an incomplete crystal lattice and cannot take place deep in the crystal because of a lack of thermal energy, then it must take place at some intermediate depth, just below the disordered surface, but where the ionic configuration is still sufficiently defect, so that short-range migration of Ca and Mg can take place. The actual composition of the surface layer need not be that of pure stoichiometric dolomite. This, then, is the effective point of departure for the present work.

It was our hope by some way to examine more closely the nature of the surface layer on the growing crystals. The principal problem was to determine, in detail, compositional variations in crystals that were a fraction of a micron across. To do this, a technique of chemical leaching or "peeling" was used. The dolomite was purified by washing with distilled water to remove soluble salts and organic matter and then oxidized in hydrogen peroxide to remove remaining organic matter. Continuous sweeping with  $O_2$  prevented build-up of  $CO_2$  in solution. All grains larger than about  $2\mu$  were removed; the dolomite crystals ranged in size from about 1.0 to  $0.1\mu$  on the rhombohedral edge. The remaining almost pure dolomitic material was studied either as (1) a "total" sample, or as separate size fractions, each having a narrow size distribution with average sizes about (2)  $0.3\mu$ , and (3)  $0.6\mu$ . Size separation was by continuous-flow centrifuge. Each sample, about one-half gram, was suspended in 50 milliliters of distilled water to which a small amount of acetic acid buffered at pH 4.5 with lithium acetate was then added. The suspension was agitated ultrasonically for 1 minute, allowed to digest for 10 minutes while being stirred continuously, centrifuged until clear, and then the supernatant liquid was removed and analyzed for Ca and Mg by EDTA titration. This process was repeated uniformly until all of the carbonate was dissolved, each sample thereby being subjected to from 20 to 38 progressive leachings or "peelings."

The entire leaching process was followed by electron microphotography. The basic rhombohedral shape of the dolomite crystals was pre-

served well past halfway in each series, despite small-scale fraying of crystal edges and rounding of corners. No deep embayments were formed in the crystals nor was there any evidence of selective leaching of individual crystals. To a first good approximation, the crystals were dissolved progressively from outside to center.

The total amount of Ca and Mg dissolved in each progressive leaching was quite uniform during most of the leaching series and dropped off abruptly only in the last several progressive leachings (fig. 3). If grains of a more soluble phase were dissolving more readily and early in the leaching series, one would expect that the early progressive leachings in the series would show much more total Ca and Mg released by dissolving. This is not observed, so it is thus concluded that the leaching process did not remove more soluble grains or crystals preferentially but rather that it affected all the crystals more or less uniformly.

The results of six of the progressive leaching experiments are shown in figure 4, the relative distance from the surface of the crystal (cube) being based in cumulative EDTA used in titration. These data are from two samples taken from Deep Springs Lake at depths of 0 to 3 and 11 to 14 centimeters. The first several progressive leachings from each series have a Ca/Mg atomic ratio much in excess of that for dolomite. Also, in every instance, the progressive leaching curves approach asymptotically a Ca/Mg ratio slightly in excess of 1, representing the composition of the main bodies of the crystals. In several instances, the first leaching did not yield the highest Ca/Mg ratio; this effect is thought to have resulted from exchange on minor amounts of clay minerals. It was not possible to separate completely all of the clay minerals from the carbonate, especially for the "total" size fractions, but it was noted that the cleanest fractions did not show this effect. In any event, it does not obscure the fundamental relation, which is that there is a range of compositions of the Ca-Mg carbonates studied and that the Ca-rich material is removed first in the leaching sequence. The main bodies of the crystals have composi-

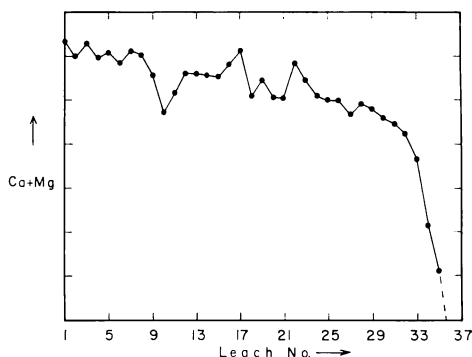


Fig. 3. Ca + Mg, in arbitrary units, in each progressive leaching in a single leaching series, showing slow and uniform decline throughout most of the series, with abrupt drop-off near the end.

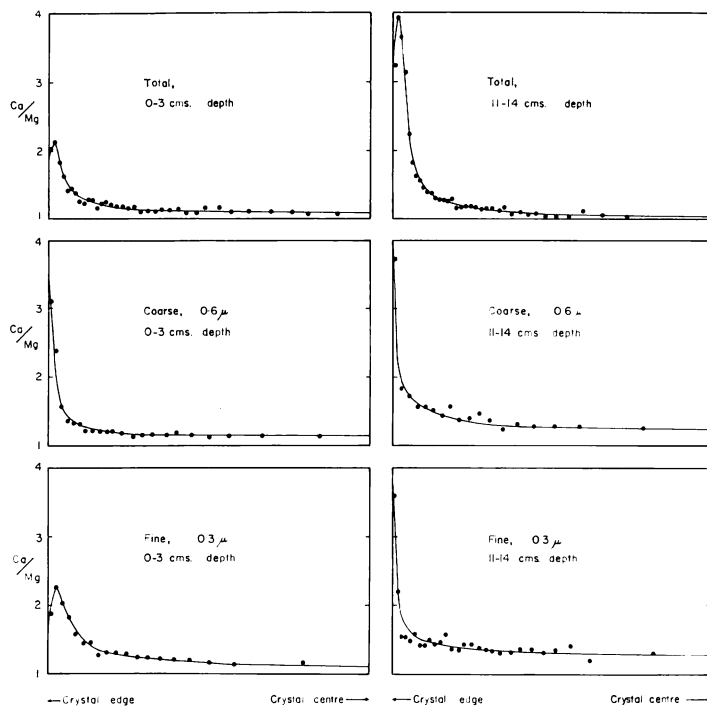


Fig. 4. Progressive leaching curves for two total samples (left, 0-3 cm; right, 11-14 cm) of dolomite from Deep Springs Lake and for coarse and fine crystal size fractions thereof. Each series is initially high in Ca, relative to the composition of dolomite. This effect is interpreted as a Ca-rich surface layer on the individual crystals of dolomite. The plots are normalized to a unit cube as an approximation to a rhombohedron and based on the amount of EDTA in titration.

tions common for sedimentary dolomites, somewhat higher in Ca than is appropriate for ideal dolomite. The highest Ca/Mg ratios obtained for the several series correspond to the extreme tail, shown by the arrows in figure 2, on the composition-sensitive X-ray diffraction maximum for the unleached sample. The correspondence of the composition of this early-leached material to the Ca-rich extreme of the composition spectrum shown by X-ray diffraction is additional evidence that it is part of a continuum of composition in the Ca-Mg carbonates and that it is not a contribution of a discrete phase, for example, of aragonite. This was previously argued on the basis of rates of solution, shown in figure 3. It was also argued that all the crystals must be leached uniformly. It is therefore concluded that this Ca-rich material must be a surface layer on the crystals of dolomite.

The characteristics of this surface layer may now be examined more closely. It should be emphasized that it appears to be a transitional phenomenon and that it approaches the composition of the main body of the crystal at its inner side, assuming that these leaching curves, which

are derived from a vast number of individual crystals, yield a reasonable representation of the variation in composition with regard to a single crystal. The leaching curves shown in figure 4 have been adjusted to a unit cube, as an approximation of a rhombohedron, and show variation in composition with respect to relative distance from the edge of the crystal to the center of the crystal. For the purpose of direct comparison of the surface layers, the  $0.3\mu$  and  $0.6\mu$  fractions of the 0 to 3 centimeter sample have been adjusted in figure 5 to show the leaching curve plotted with respect to the true distance from the surface of the crystal. These two lake-surface fractions were chosen for this purpose because they are the ones most easily compared and interpreted; the samples at depth were not used because, as will be shown, they are not the products of strictly modern precipitation or crystallization and probably have undergone some recrystallization. As can be seen, the composition profiles of the surface layers in these two size fractions are very much the same. One can only be arbitrary in naming a thickness for this layer, which is transitional at its inner surface, but, at a depth in the crystal corresponding to a composition of 10 percent excess Ca, at which some cation ordering might be possible, it is of the order of 100 Ångströms. This is about 15 times  $a_{rh}$ , or about 6 times  $C_0$ , cell constants for the rhombohedral carbonates (Graf, 1961).

#### TIME DEPENDENCE

It is now desirable to inquire, in detail, what might be the time dependence of growth of the entire crystal and of the surface layer. In order to do this, advantage was taken of the same leaching techniques used previously, except that the initial sample, of material identical to that of the "total" sample, was much larger. The successive leachings were carried out in a closed system, the entire purified sample being suspended in water and violently blended as the lithium acetate-buffered

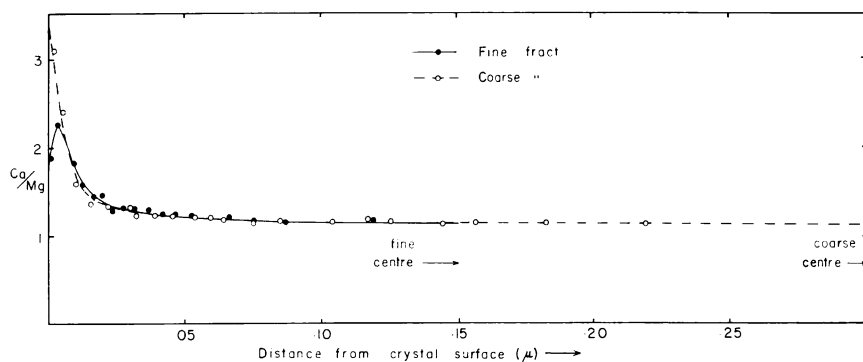


Fig. 5. Progressive leaching curves for the coarse and fine fractions from sample taken 0 to 3 centimeters in the sediment, plotted with respect to computed true distance from the surface of the crystals. Average size of crystals was determined from electron photomicrographs. The surface Ca-rich layers are very similar on both the coarse and fine fractions.

acetic acid was slowly added. The sample was swept of  $\text{CO}_2$  prior to leaching, and then, as  $\text{CO}_2$  evolved, it was continuously swept from the system and trapped in 1-normal  $\text{NaOH}$  saturated with  $\text{BaCl}_2$ . Each sample was subjected to 13 successive leachings before all the dolomite was dissolved. Apparent  $\text{C}^{14}$  ages obtained on the carbon thus extracted are shown in table 1.

In a volume of material, such as a dolomite crystal which has been growing for a long time, the apparent  $\text{C}^{14}$  age of the crystal is not the time since last growth nor is it the time since nucleation of the crystal, but rather it is the composite age of all the material in the crystal. By dividing the crystals into dissolution shell volume elements, the analytical methods of the integral calculus have been physically approximated.

It is desirable, however, to assign a position within each volume element that is equal in age to the average age of all the material in the volume element, because there are only thirteen, rather than an infinite number of such volume elements.

In a manner parallel to that used (Peterson, Bien, and Berner, 1963) to evaluate crystal growth rates from  $\text{C}^{14}$  ages of whole crystals:

$$\bar{t} \approx \frac{\int_{X'}^{X''} t(x) dV}{\int_{X'}^{X''} dV}$$

where

$x$  = edge length of the rhombohedral shell volume element  $dV$  at a given edge of growth.

$t$  = age of volume element.

$X'$  = rhombohedral edge length at any growth stage corresponding to time  $T'$ , and  $X''$  = rhombohedral edge length at some later growth stage.

$\bar{t}$  = age of a finite dissolution shell volume element.

If the rhombohedra are approximated by cubes, then:

$$dV = 3x^2 dx$$

In detail the growth of any single dolomite crystal must be somewhat complex and perhaps discontinuous; however, the data from this study indicates that the average growth, based on samples containing about  $5 \times 10^{15}$  crystals, is quite uniform. As a first approximation, two growth models can be proposed:

1. The date of growth of the rhombohedral (cube) *edge* is constant with time, for example,  $t = T - kx$ .

2. The rate of growth of the rhombohedral (cube) *volume* is constant with time, for example,  $t = T - kx^3$ .

The apparent ages of the surface brines and interstitial solutions from surficial sediments show that crystal growth has taken place very nearly in exchange equilibrium with the atmosphere. It is assumed that solid-state diffusion of carbon in the dolomite crystals is negligible; this also

appears to be true of the oxygen in the carbonate ion of dolomite (Degens and Epstein, 1964). From the first model:

$$\bar{t} \approx T' - \frac{\int_{X'}^{X''} 3kx^3 dx}{\int_{X'}^{X''} 3x^2 dx}$$

For the case of  $X' = 0$  and  $T' =$  total time since nucleation of the crystal and  $X'' =$  measured, present-day rhombohedral edge, then  $\bar{t}$  applies to

$$\bar{t} = T' - \frac{3}{4} kX''$$

Then, if  $x_t$  is the edge length of the rhombohedral surface, within the crystal, of the same age as the average age of the crystal

$$\bar{t} = T' - kx_t$$

and

$$x_t = \frac{3}{4} X''$$

A more general solution that applies to a growth (or dissolution) volume element is:

$$\bar{t} \approx T' - k \frac{3}{4} (X' - X'')$$

TABLE 1

Carbon-14 ages showing growth of dolomite crystals from Deep Springs Lake, California. Dates in series 1 and 2 are from leached volume elements, which are related in the table to the volume of a unit cube, as an approximation to a rhombohedron.

0-3 cm				11-14 cm			
LJ no.	series no.	Apparent* age, years B.P.	$\sqrt{\Sigma\%}$	LJ no.	series no.	Apparent* age, years B.P.	$\sqrt{\Sigma\%}$
1000	1-1	100 $\pm$ 150	4.64	1013	2-1	485 $\pm$ 150	4.64
1001	1-2	420 $\pm$ 150	4.56	1014	2-2	590 $\pm$ 150	4.59
1002	1-3	350 $\pm$ 150	4.51	1015	2-3	590 $\pm$ 150	4.53
1003	1-4	760 $\pm$ 150	4.45	1016	2-4	765 $\pm$ 150	4.38
1004	1-5	780 $\pm$ 150	4.36	1017	2-5	1050 $\pm$ 150	4.31
1005	1-6	1000 $\pm$ 150	4.16	1018	2-6	1060 $\pm$ 150	4.10
1006	1-7	1000 $\pm$ 150	4.02	1019	2-7	1040 $\pm$ 150	3.85
1007	1-8	1070 $\pm$ 150	3.87	1020	2-8	1040 $\pm$ 150	3.80
1008	1-9	1290 $\pm$ 150	3.56	1021	2-9	1250 $\pm$ 150	3.58
1009	1-10	1710 $\pm$ 150	3.14	1022	2-10	1230 $\pm$ 150	3.39
1010	1-11	2130 $\pm$ 150	2.52	1023	2-11	1550 $\pm$ 150	3.24
1011	1-12	2790 $\pm$ 150	1.82	1024	2-12	1740 $\pm$ 150	2.84
1012	1-13	3200 $\pm$ 150	1.00	1025	2-13	2340 $\pm$ 150	1.91
817**	—	-384 $\pm$ 50	—	818***	—	-184 $\pm$ 50	—

\* Relative to 1850 Sequoia Wood, corrected to 1950 as zero age, La Jolla Radio-carbon Laboratory.

\*\* Brine from surface of lake.

\*\*\* Interstitial brine from surface sediment.

If  $x_t$  is the increment over  $X'$  of edge length of the rhombohedral (cube) surface, within the volume element, of the same age as the average age of the volume element corresponding to  $(X' - X'')$ :

$$\bar{t} = T' - kx_t$$

then:

$$x_t = \frac{3}{4} (X' - X'')$$

Thus, the surface that is equal in age to the average age of all the dolomite in a crystal growth or dissolution volume element corresponding to  $(X' - X'')$  lies  $\approx$  one-fourth of the distance in from the outer surface of the volume element to the inner surface of the volume element. It is on this basis that the data in figure 6 were plotted. The first growth model fits the data sufficiently well so that the second model will not be considered further.

Individual volume elements have been plotted in figure 6 with respect to distance from the surface of the crystal to its center, adjusted to a unit cube, based on the cumulative amount of  $\text{CO}_2$  trapped for each volume element. Curves of compositional variation from surface inward are also shown.

The average growth in length of the rhombohedral crystal edge has been essentially constant with time. The slope of the curve showing age with respect to position within the crystal gives the growth rate of the crystals. For the surficial sediment, in which the average rhombohedral edge is about  $0.35\mu$ , the rate of growth of the rhombohedral edge is about 0.09 microns/ $10^3$  years. This is to be compared with growth rates of from 0.05 to 0.09 microns per thousand years for similar material (Peterson, Bien, and Berner, 1963), based on the entire crystal. Thus, two methods for determining rates of crystal growth of this dolomite, which though superficially similar are philosophically quite different, have yielded essentially the same slow crystal growth rates. The sample taken from 11 to 14 centimeters does not contain dolomite with the same age range as the 0 to 3 centimeter sample. This probably results from a narrower size distribution of the crystals, there being a lack of larger crystals with correspondingly older ages. It is futile to speculate on why this may be, except to suggest size sorting during the last episode of sedimentation of these crystals. In addition,  $\text{C}^{14}$  ages for the 11 to 14 centimeter sample do not extrapolate as close to zero age at the surface of the crystals as do those for the 0 to 3 centimeter sample, probably resulting from partial, if not complete, isolation from atmospheric  $\text{CO}_2$ .

The computed arithmetic mean age is 1260 years for the 0 to 3 centimeter sample and 1240 years for the 11 to 14 centimeter sample. Both these values fall very close (fig. 6) to a surface that is one-fourth of the distance in from the outside of the crystals. This surface, by model I, in the paper by Peterson, Bien, and Berner (1963) should be equal in age to the average age of the material in the growing crystals, thus confirming experimentally the arguments put forth in that growth model.

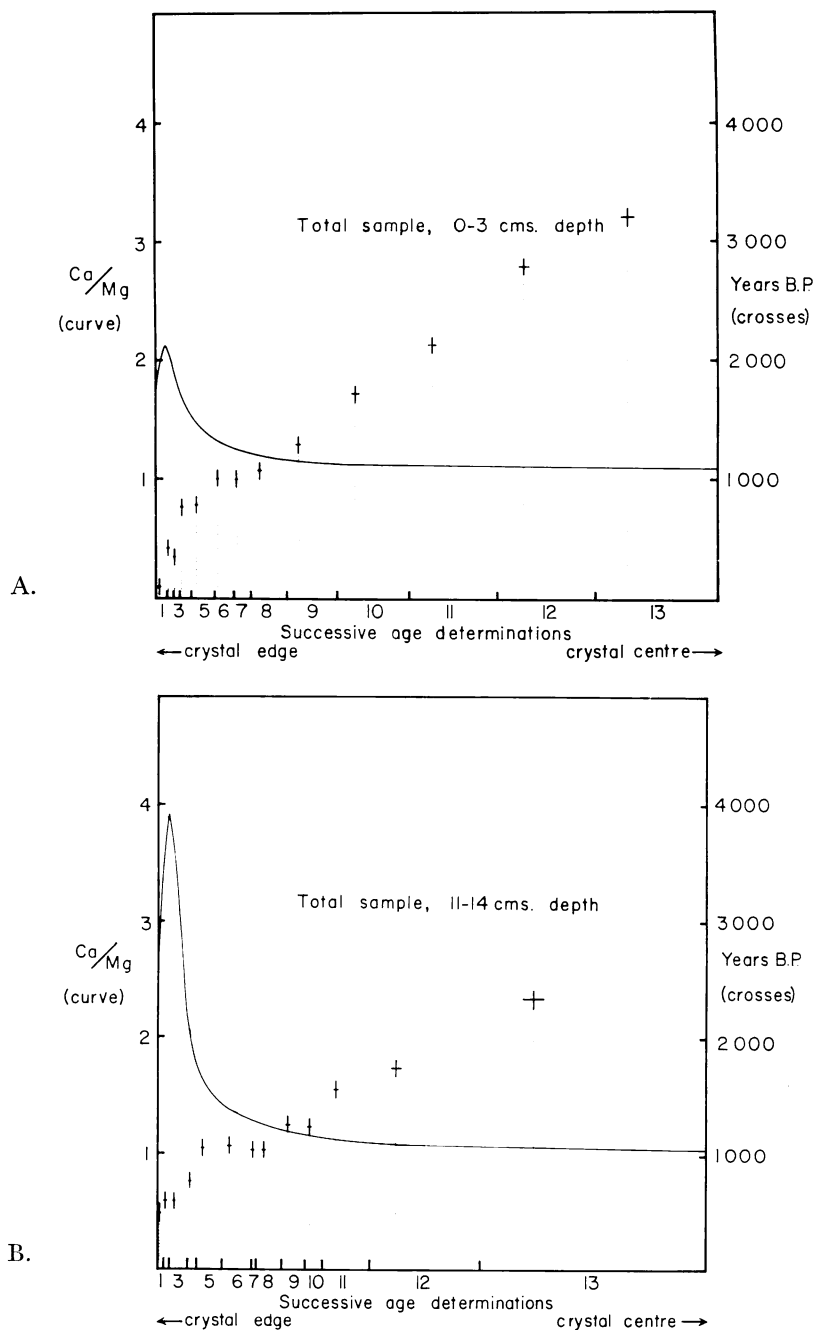


Fig. 6. Relation of age and composition to relative distance in from surface of growing crystals of dolomite from two samples from Deep Springs Lake, California.

The Ca-rich surface layer on these crystals also has a discernible growth history; its age, on the very outside, is virtually zero, for the 0 to 3 centimeter sample. It becomes progressively older inward. A similar history exists for the surface layer on the sample at depth in the sediment, although it is older both at its outside surface and at its innermost extent. Probably there has been some recrystallization of the smaller crystals. The small departures from linearity of the  $C^{14}$  ages plotted against position in the crystal, for both the surface sample and the sample at depth, lie not far outside the probable error ascribed to each point on the graph; thus there is doubt as to the reality of these departures.

It does not seem likely that this surface layer is an artifact of laboratory treatment; it was not possible to form it again on crystals from which it had been leached by allowing these crystals to remain in distilled water for times as long as the original laboratory treatment. These experiments do not preclude the possibility that a much thinner surface might form on crystals or fragments by the dolomite dissolving incongruently in distilled water. If such a layer were to form, it must be thinner than our techniques could perceive, and thus it is not to be confused with the growth layer we have studied.

#### DISCUSSION

The concept of a surface layer on *individual crystals* of dolomite growing at low temperatures lends a sense of unity to many of the conflicting aspects of the formation of this mineral.

This layer may be envisaged as a sort of moving boundary that surrounds the growing crystals (fig. 7). Without specifying in detail the nature of the very outside of the surface layer, it must be quite similar to that which exists on the growing crystals of rhombohedral carbonates, such as calcite, having the  $R\bar{3}c$  space group, and which are crystallizing in the unit rhombohedron. The body of the layer itself must be sufficient-

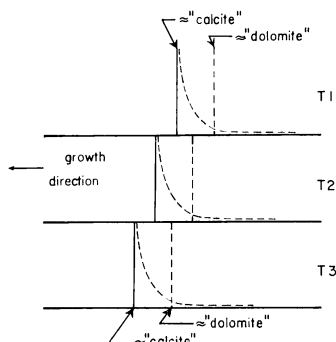


Fig. 7. The surface layer on growing dolomite crystals can be interpreted as a moving boundary. Growth is by solid-state diffusion through this surface layer. Three illustrative growth times are shown.

ly defect to permit the migration through short distances of both Ca and Mg.

Low-temperature dolomite is commonly non-stoichiometric, a characteristic that may result from the crystal structure no longer being sufficiently defect to permit additional diffusion of either Ca or Mg as its composition approaches that of dolomite. In the case of Deep Springs Lake, this surface layer, and also the dolomite itself, is Ca-rich; however, it may not be necessary for it to be Ca-rich. In the light of the reported formation of magnesite from some of the Coorong-associated lakes in South Australia (Alderman and von der Borch, 1961), it is tantalizing to speculate that in some instances the outside of this surface layer might bear strong resemblances to the surface on magnesite. In this case, it might be possible for dolomite to form by the diffusion of Ca into a Mg-rich surface layer. Such dolomite should be Mg-rich, being effectively trapped at this composition by the same mechanism that yields the Ca-rich dolomites, that is, the stabilization of the crystal structure at a composition that is not stoichiometric but will inhibit diffusion of Ca and Mg.

The growth rate of the dolomite crystals yields a time parameter for the introduction of Mg into the rhombohedral lattice. The outside of the surface layer is compositionally much closer to calcite than to dolomite. The actual rate of fixation of Mg, calculated on a basis of the crystal faces growing outward a distance equal to the thickness of the surface layer, 100 Å, in 200 years, is about  $1.5 \times 10^6$  atoms Mg/sec/cm<sup>2</sup> of crystal surface. This corresponds to about 4 atoms Mg/sec/10<sup>9</sup> unit cells exposed at the surface. If attention is focused on a particular surface in the structure, parallel to the crystal face, it is clear that the flux of Mg through it must drop to a very small value as all of the material on the crystal side of it approaches the configuration of dolomite. The flux of Mg, during steady-state growth, through such a surface, averaged through the time from when it would be on the very outside of the crystal to the time when it would be on the inside of the surface layer, is somewhat less than  $7 \times 10^5$  atoms Mg/cm<sup>2</sup>/sec. A concomitant migration of Ca also takes place in the opposite direction, and some mechanism of exchange jumps in this defect lattice seems likely.

At least partial ordering, with the formation of a rudimentary R $\bar{3}$  space group, must take place near the base of this surface layer. It was noted (Peterson, Bien, and Berner, 1963) that, after only a small amount of leaching, but still more than sufficient to strip this surface layer from the crystals, there was a noticeable change in the profile of the X-ray diffraction maxima corresponding to the superstructure reflections of dolomite; this indicates that at least some of the material removed was contributing to this superstructure reflection.

The diffusion must take place down a chemical potential gradient, even though Mg is clearly diffusing up a concentration gradient. The Ca/Mg profiles, from surface inward, represent a kind of steady state be-

tween diffusion, which would tend to bring Mg into the structure and minimize the thickness of the surface layer, and crystal growth, which continually renews the Ca-rich surface. These profiles would then depend on relative availability of ions and rates of growth. Throughout the surface layer, which is intrinsically metastable, as Mg-calcite at low temperatures (Goldsmith, 1956), a "microscopic reversibility" or "local equilibrium" may prevail (Thompson, 1959); there appear to be no abrupt changes in composition from surface inward. A sort of "micro-metasomatism" takes place in this very thin layer that surrounds the growing crystals. In another sense, the process is akin to exsolution of the transient Mg-calcite, taking place continuously in the surface layer, with Mg moving in one direction and Ca in the other. The origin of the gradient in chemical potential is to be found in the creation of a structure site for  $\text{Mg}^{++}$  in the rhombohedral crystal lattice, of which the basic architecture must be already available. This structure site can be thought of as having an activity coefficient for  $\text{Mg}^{++}$  that is different from what it would be in the outer part of the surface layer. For this reason also, the assumptions in Fick's laws of diffusion cannot be satisfied, except for a moving surface a constant depth in from the outside of the crystal.

The low-temperature formation of dolomite must involve a double nucleation. First must be formed crystals or domains of an  $R\bar{3}c$  rhombohedral carbonate, such as calcite or Mg-calcite, of a critical size perhaps related to some minimum thickness of the surface layer. Then, secondly, the configuration characteristic of dolomite would have to form at a depth within these domains sufficient to permit the different structure sites for  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$  to be characterized adequately in three dimensions. This, then, is presumably the critical step in the formation of dolomite. Until the  $R\bar{3}$  space group is at least incipiently present, the chemical potential gradients necessary for additional diffusive growth do not exist.

The apparent solubility of dolomite must be in some way dependent on this surface layer. Laboratory determinations of the solubility equilibrium constants for dolomite commonly utilize dolomite, usually of stoichiometric composition, or nearly so, which has been ground to a powder. Such material, in addition to having been deformed, would not necessarily present crystal faces appropriate for growth, nor would it have the appropriate surface layer which is apparently part of the growth process at low temperatures. Field studies of natural solutions in contact with dolomite would fall into two groups: (1) a constructional mode, in which dolomite is forming, such as in some of the modern dolomite-precipitating localities; and (2) a destructional mode, in which dolomite is dissolving, such as in some ground-water systems and aquifers. In this latter group, the surface layer might be missing, having been dissolved away. Thus, in these several types of solubility determinations, the solutions are in contact with different materials.

It is clear that dolomite, once formed, is relatively stable in conditions in which it does not form. For example, it is found in deep-sea sediments, but there is no evidence that dolomite is forming in the deep sea, even in times of the order of millions of years. Berner (1965) has suggested that the dolomite of coral atolls formed by downward migration of hypersaline solutions formed in evaporitic lagoons. We find considerable amounts of dolomite in some pelagic sediments far from continental sources, in sediments from which all other carbonate minerals commonly present, such as in foraminifera, have been dissolved. A most likely source of this dolomite is the coralline atolls and guyots. It may also be that some of this deep-sea dolomite formed in local and temporary "hot spots" in the sea floor, resulting perhaps from volcanism or hydrothermal activity. Reef debris carried to the deep sea would for the most part dissolve, but any dolomite that might be present apparently does not dissolve under conditions in which calcite and aragonite do dissolve. Mineral assemblages of ancient carbonate rocks can also be interpreted to indicate that dolomite persists where it cannot form (Peterson, 1962).

The outside of this surface layer, which must be comparable to that on the surface of growing calcite crystals, selects the isotopes during crystallization. Here, then, lies the explanation of the apparent inconsistency whereby dolomite appears to have formed, on the basis of oxygen isotope data, by solid-state replacement of calcite, and yet does not appear, texturally, in low-temperature rocks, ever to replace calcite in any form of crystallographic continuity. The replacement occurs only in this very thin transitional surface layer on the growing dolomite crystals. At high temperatures, both isotopic and chemical equilibrium would be achieved much more readily.

Slowness of growth which is necessitated by the formation of low-temperature dolomite through a solid-state diffusive process and slowness of deposition which is necessary in order that a very slowly forming mineral may be found at the surface of a depositional environment largely account for the rarity of this mineral in modern sediments. There must also be time for the evolution of conditions under which the complex nucleation of dolomite takes place. These requirements imply a stability that is not commonly to be found in modern sedimentary environments, largely because of recent changes in climate and relative sea level.

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## REFERENCES

- Alderman, A. R., and von der Borch, C. C., 1961, Occurrence of magnesite-dolomite sediments in South Australia: *Nature*, v. 192, p. 861.
- Barnes, Ivan, and Back, William, 1964, Dolomite solubility in ground water: U. S. Geol. Survey Prof. Paper 475-D, p. 179-180.
- Berner, R. A., 1965, Dolomitization of the Mid-Pacific atolls: *Science*, v. 147, p. 1297-1299.
- Clayton, R. N., and Epstein, Samuel, 1958, The relationship between  $O^{18}/O^{16}$  ratios in coexisting quartz, carbonate, and iron oxides from various geological environments: *Jour. Geology*, v. 66, p. 352-373.
- Degens, E. T., and Epstein, Samuel, 1964, Oxygen and carbon isotope ratios in coexisting calcites and dolomites from recent and ancient sediments: *Geochim. et Cosmochim. Acta*, v. 28, p. 23-44.
- Engel, A. E. J., Clayton, R. N., and Epstein, Samuel, 1958, Variations in the isotopic composition of oxygen and carbon in the Leadville limestone and in its hydrothermal and metamorphic phases: *Jour. Geology*, v. 66, p. 374-393.
- Epstein, Samuel, Graf, D. L., and Degens, E. T., 1964, Oxygen isotope studies on the origin of dolomites, in Craig, H., Miller, S. L., and Wasserburg, G. J., eds., *Isotopic and cosmic chemistry*: Amsterdam, North Holland Pub. Co., p. 169-180.
- Goldsmith, J. R., 1956, Exsolution of dolomite from calcite [abs.]: *Geol. Soc. America Bull.*, v. 67, p. 1699.
- Goldsmith, J. R., and Graf, D. L., 1958, Relation between lattice constants and composition of the Ca-Mg carbonates: *Am. Mineralogist*, v. 43, p. 84-101.
- Goldsmith, J. R., Graf, D. L., and Heard, H. C., 1961, Lattice constants of the calcium-magnesium carbonates: *Am. Mineralogist*, v. 46, p. 453-457.
- Graf, D. L., 1961, Crystallographic tables for the rhombohedral carbonates: *Am. Mineralogist*, v. 46, p. 1283-1316.
- Graf, D. L., and Goldsmith, J. R., 1956, Some hydrothermal syntheses of dolomite and protodolomite: *Jour. Geology*, v. 64, p. 173-186.
- Ingerson, Earl, 1962, Problems of the geochemistry of sedimentary carbonate rocks: *Geochim. et Cosmochim. Acta*, v. 26, p. 815-847.
- Peterson, M. N. A., 1962, The mineralogy and petrology of upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee: *Jour. Geology*, v. 70, p. 1-31.
- Peterson, M. N. A., Bien, G. S., and Berner, R. A., 1963, Radiocarbon studies of recent dolomite from Deep Springs Lake, California: *Jour. Geophys. Research*, v. 68, p. 6493-6505.
- Thompson, J. B., Jr., 1959, Local equilibrium in metasomatic processes, in Abelson, P. H., ed., *Researches in Geochemistry*: New York, John Wiley and Sons, p. 427-457.
- von der Borch, C. C., Rubin, Meyer, and Skinner, B. J., 1964, Modern dolomite from South Australia: *Am. Jour. Sci.*, v. 262, p. 1116-1118.