THE ROLE OF PRE-EXISTING GRAIN SURFACES IN THE RECRYSTALLIZATION OF THE MISSISSIPPIAN BAYPORT LIMESTONE

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ABSTRACT

THE ROLE OF PRE-EXISTING GRAIN SURFACES IN THE RECRYSTALLIZATION OF THE MISSISSIPPIAN BAYPORT LIMESTONE

BY

Carl Steinfurth

Textural variables have been used by igneous and metamorphic petrologists to determine reaction pathways and kinetics. The variables used in these studies differ from the customarily used textural variables, because they are quantitatively expressed, rather than qualitative descriptions. Some of these variables are grain neighborhoods, surface area per unit volume, grain size and shape, frequency of occurence and composition. The variation of these factors can frequently be explained as a function of surface free energy.

This study of the Bayport Limestone (a Mississippian sabkha-intertidal flat system) illustrates the usefulness of the above variables in an investigation of the role of pre-existing grain surfaces on recrystallization.

Nucleation of new grains first occurs at sites of high surface energy. In these rocks, the dolomite grains first nucleated at calcite triple points and quartz-calcite interfaces. Clay films inhibit the nucleation of dolomite on some quartz grains.

Dolomite grains adjacent to the quartz grains were found to be significantly larger than matrix dolomite, which had no quartz contacts. The calculated surface energy of the dolomite adjacent to the quartz was one half the surface energy for matrix dolomite. The dolomite size difference is a result of growth of the dolomite on the quartz as a mechanism to reduce the high surface energy calcite-quartz interface. The surface energy for this quartz-dolomite interface has been calculated to be seven times the surface energy of a dolomite-dolomite interface.

The recrystalization sequence of the matrix material begins with a micritic calcite. With continued recrystalization, the calcite grains grow to a microsparite calcite, and then to a sparry calcite. Within the sparry calcite phase micritic dolomite recrystalizes and the average grain size is reduced. Such an unexpected grain size reduction could be related to a lack of growth, and a preference to nucleation. This could be caused by a lack of energy necessary to break a grain size barrier, or threshold, as suggested by Folk (1968). This threshold could represent an optimum surface energy for each component and the environment in which recrystalization is occuring.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.	ii
LIST OF TABLES	iv
LIST OF FIGURES.	v
INTRODUCTION	1
THE GEOLOGIC SETTING	4
SAMPLING AND SAMPLE PREPARATION.	8
GENERAL RECRYSTALLIZATION AND SURFACE ENERGY TRENDS. . .	9
THE QUARTZ-DOLOMITE ASSOCIATION.	15
INHIBITED NUCLEATION BY CLAY FILMS	21
PREFERED ORIENTATION OF DOLOMITE ON QUARTZ	28
THE DOLOMITE SIZE-DISTANCE RELATIONSHIP.	31
DOLOMITE SURFACE AREA RELATIONSHIPS.	36
DISCUSSION AND CONCLUSIONS	40
Dolomite-dolomite-quartz relationship	40
Dolomite-calcite-quartz relationship.	43
Recrystallization sequence.	44
REFERENCES	45

LIST OF TABLES

Table Page

1. Contingency table illustrating the quartz-dolomite association. 19

2. Dolomite apparent long axis frequencies 32

3. Dolomite size-distance contingency table. 33

LIST OF FIGURES

Figure		Page
1.	Location of Wallace Stone Company quarry.	5
2.	The geologic column	6
3.	Photomicrograph of a quartz grain in micrite and microsparite matrix	10
4.	Photomicrograph of three quartz grains in a sparite matrix.	11
5.	Photomicrograph of quartz grains in a dolomite matrix	13
6.	Photomicrograph of quartz grains in a matrix of calcite and dolomite	14
7.	Photomicrograph of quartz grains with dolomite coating.	16
8.	Photomicrograph of quartz grains with dolomite coating	17
9.	Photomicrograph of quartz grains with dolomite coating and triple point dolomite	18
10.	Photomicrograph of a secondary electron image of quartz grains in a matrix of calcite and dolomite.	22
11.	Photomicrograph of silica x-ray fluorescence. . .	23
12.	Photomicrograph of magnesium x-ray fluorescence.	24
13.	Photomicrograph of aluminum x-ray fluorescence.	25
14.	Microprobe traverse of quartz grains with aluminum coating.	26
15.	Photomicrograph of quartz with oriented dolomite rhombohedrons.	29

16. Photomicrograph of quartz grains with oriented dolomite rhombohedrons 30

17. Histograms of significent dolomite size-distance relationships. 34

18. Equations and geometric relationships for the rhombohedron perimeter calculations 38

INTRODUCTION

Studies in the fields of igneous and metamorphic petrology have shown that the reaction pathways and the kinetics of recrystallized rocks can be determined by textural variables. (Devore 1959, Flinn 1969, Vernon 1970)

The variables measured in these studies differ from customary textural variables in that they are quantitatively expressed, rather than qualitative descriptions. Some of the variables used were grain neighborhoods, surface area per unit of volume, grain size and shape, frequency of occurence, and composition. The variation within these variables can frequently be explained as a function of surface free energy.

Surface free energy, surface energy, or interfacial energy is defined as the energy difference between the higher energy surface atoms, and the lower energy interior atoms of a grain. The total surface energy of a specific surface is defined as the surface energy times the surface area. The surface energy is therefore proportional to the area of the surface. (Spry 1969)

As the total surface energy of a rock varies, it affects the recrystallization of new grains. These surface energy changes can be observed in the rock texture.

Nucleation of new grains tends to favor high surface energy conditions which would be at grain boundaries, especially boundaries between like grains with a high dislocation angle between them, between unlike grains, (Spry, 1969), and at triple points. (Devore, 1959) This grain nucleation lowers the surface free energy at the boundary and reduces the total surface free energy of the rock.

Grain shape changes are produced as the grain boundaries tend toward an equilibrium configuration. The equalibrium shape is one which lowers the total surface free energy of the rock. (Devore, 1959) Shape changes involve the straightening of boundaries, with the reduction of surface area, or the development of a euhedral shape to reduce the surface energy. (Kretz, 1966)

The above mentioned textural changes have been studied by metallurgists, ceramists, and metamorphic and igneous petrologists. The processes, however, should apply to all recrystallized rocks.

In the study of the Bayport Limestone, these above mentioned textural variables were measured in order to investigate the role of pre-existing grain surfaces on the recrystallization of these rocks.

The Wallace Stone Company quarry provides an excellent location for a study of grain surfaces nad their role in recrystallization. In the well exposed rocks, the composition is highly variable. It ranges from a micritic limestone with little quartz, to a quartz sand with a carbonate cement.

These rocks have been well documented as Carboniferous marine and intertidal flat sediments, (Bacon, 1971), which will partly define the nature of diagenetic events which affected recrystallization.

THE GEOLOGIC SETTING

In the quarry at Bayport, Michigan, (Figure 1), the rocks represent a progressively inundated sabkha, intertidal flat system, (Figure 2), (Bacon, 1971). The environments represented range from the supratidal zone, where flooding occured monthly, or, even less frequently, to normal marine conditions.

The lowermost rock units are the most dolomitized, and contain dessication features, such as mud cracks, gypsum crystals, and molds. These represent the supratidal zone.

Upon this dolomite is a quartz sandstone, which contains varying percentages of quartz. The cementing material is both dolomite and calcite, in varying proportions. The sand also interfingers with and is overlain by algal mats. This sandy unit represents the foreshore region of the intertidal zone.

Resting upon the sandstone are algal limestones and chertified algal mats. This unit was formed in the middle intertidal zone.

The next higher unit is a sandstone, with varying quartz content. The cement grades from a high percentage of dolomite at the base to a high percent of calcite at the top. Upon this unit rests an algal mat. This unit also

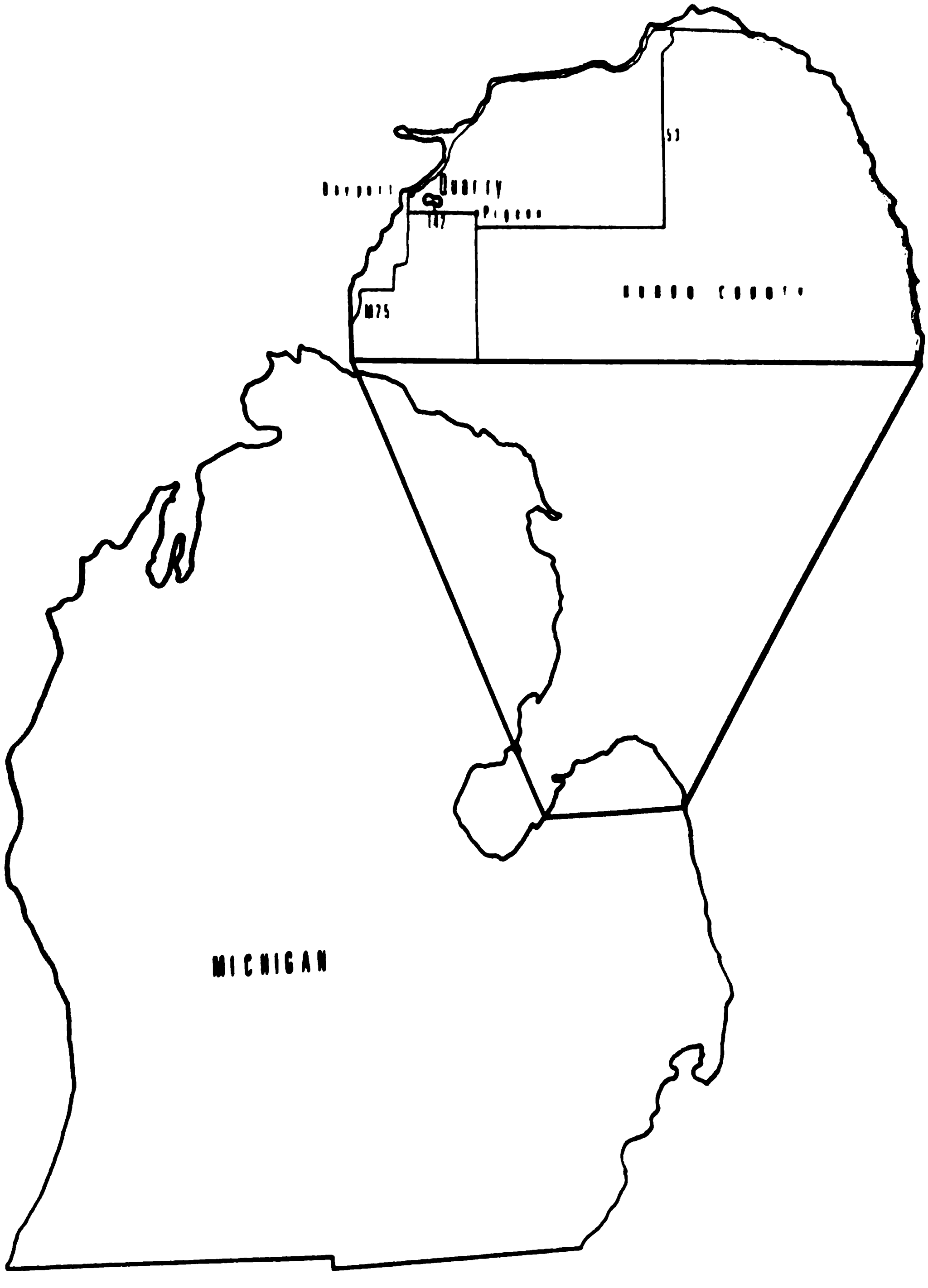


Figure 1. Location of Wallace Stone Company quarry (from Bacon, 1971).

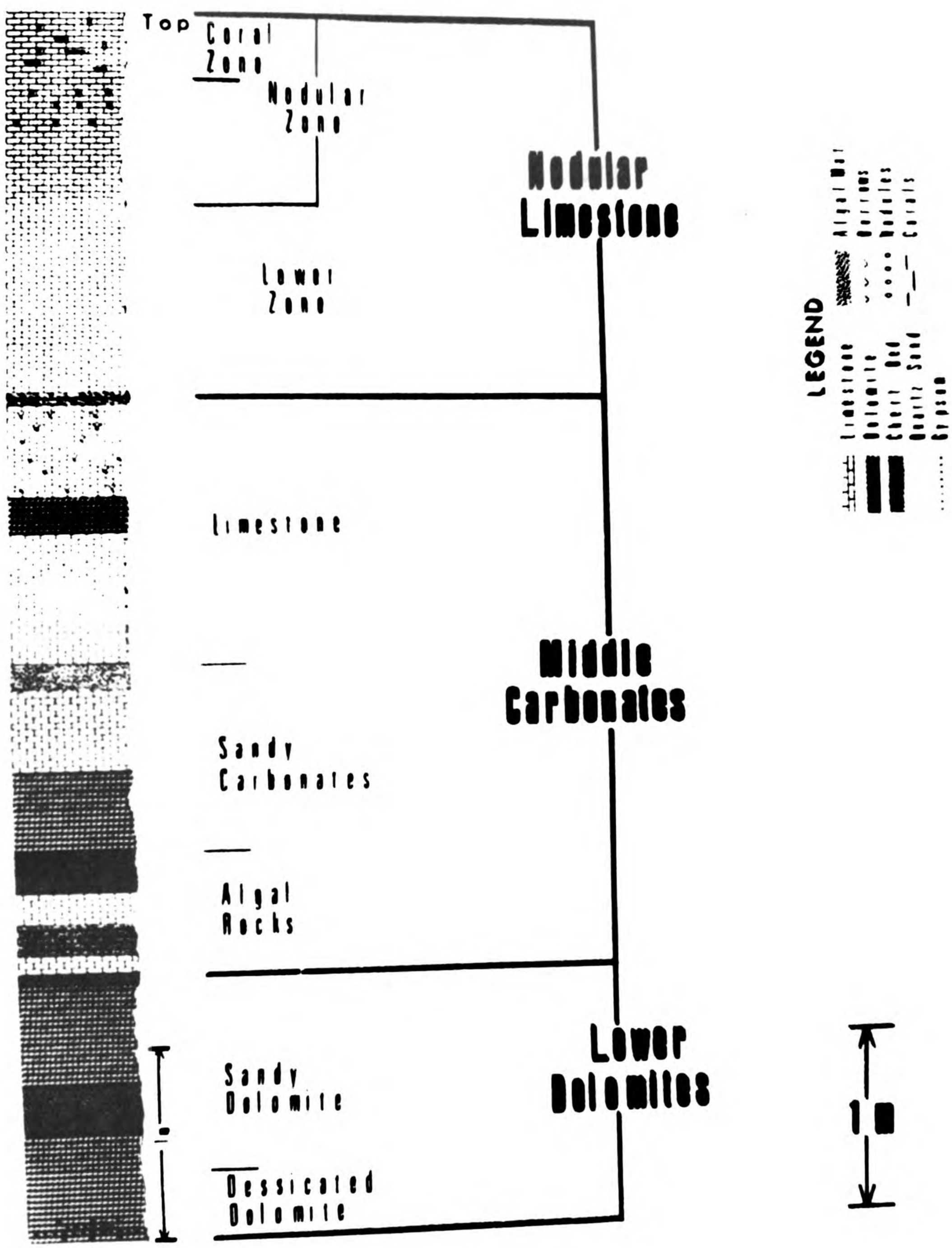


Figure 2. The geologic column of the lithologic units exposed in the Wallace Stone Company quarry, as discribed by Bacon (1971).

represents the middle intertidal zone deposits.

Upon this sandstone is a dark limestone which contains a zone of pyrite crystals along with lenses of quartz sand, fossil fragments, dolomite, and regions which have been heavily burrowed. This limestone represents a sheltered embayment within the lower intertidal zone.

The next unit is a fossiliferous limestone, ranging from fossil assemblages of shallow marine conditions, at the base, to those representing deeper water toward the top.

The rock record presents an environmental model of sabkha, intertidal flat system, which was progressively inundated. Using this model, we can hypothesize the nature of the pore fluids and the diagenetic processes which affected the texture and composition of the sediments.

SAMPLING AND SAMPLE PREPARATION

Samples were collected from the two sandstones within the quarry. The sampling goal was to obtain the complete spectrum of variation within the sands. The criteria used were macroscopic features, such as color and percent of quartz, based upon visual estimates; the type of cement, determined by response to hydrochloric acid; and the stratigraphic position. One or more samples were then collected from each variation of the sandstones. Thin sections were cut of each sample. Many of the rocks contained micron sized crystals. In order to observe these crystals the slides needed to be cut thinner than the "normal" thickness slide of .03mm. This was achieved by polishing a "normal" thickness slide for ten minutes on a Buehler polisher, using diamond paste and a cloth lap wheel, (Woodbury and Vogel, 1970). The final thickness was about ten microns. The slides were then etched with hydrochloric acid and the calcite stained red with Alizarin Red S, using a method modified from Friedman, (1959).

GENERAL RECRYSTALLIZATION AND SURFACE ENERGY TRENDS

The thin sections were petrographically examined. Three main components were observed: calcite, dolomite, and quartz. Small amounts of pyrite and muscovite were also present.

Based upon the characteristics of the matrix material three major stages of recrystallization were defined. The order of recrystallization of these stages was determined by the trend toward formation of larger grains with recrystallization, the introduction of new mineral phases, and grain relationships within the slides.

The stage with the least recrystallization consists of a quartz sand with a calcite matrix, (Figure 3). The calcite grains range in size from micrite (1μ to 4μ) to microsparite (5μ to 15μ). The micritic grains form an interlocking mosaic texture with highly irregular grain boundaries. Within the micrite are pockets of larger calcite grains, of the size defined as microspar, (Folk, 1959). These grains also form an interlocking texture, with the boundaries being less irregular than the micrite, and frequently gently curving. Also noted within these rocks is the common association of larger micrite and microsparite grains adjacent to the quartz.

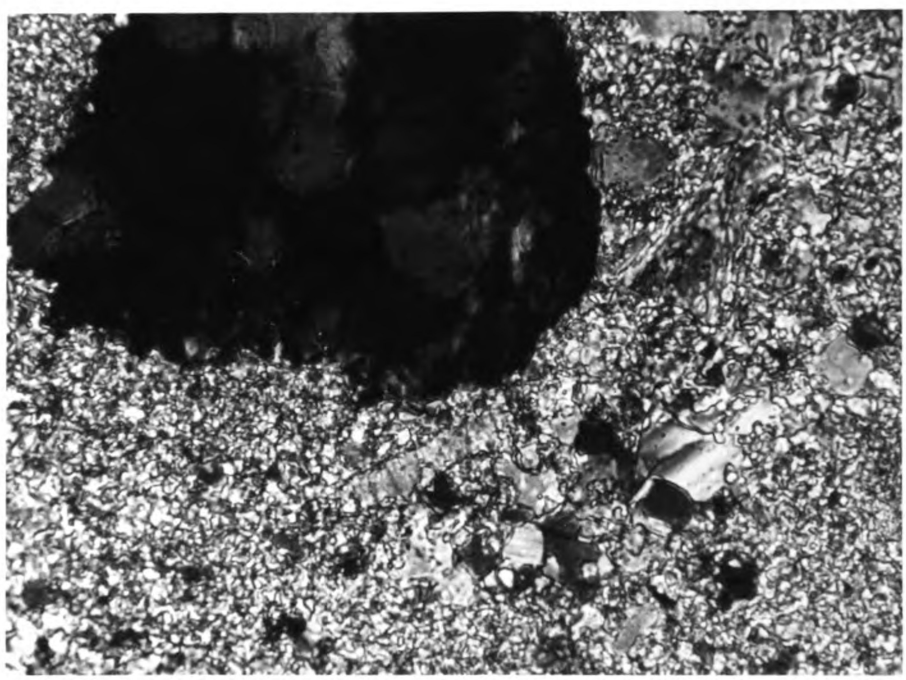


Figure 3. Photomicrograph of a quartz grain in a micrite and microsparite matrix, as viewed under crossed nicols. Magnification 100X.

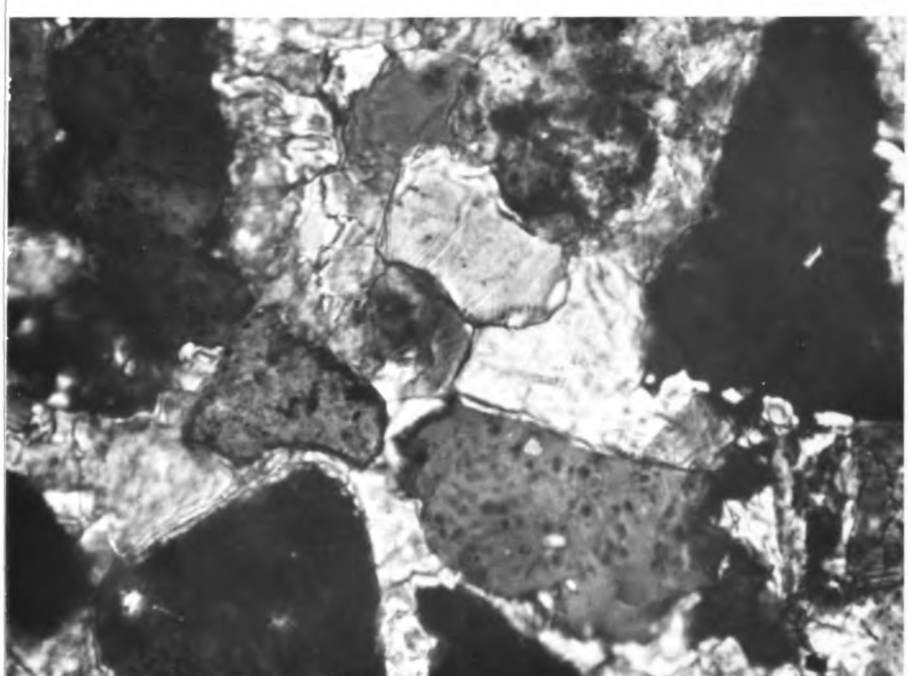


Figure 4. Photomicrograph of three quartz grains in a sparite matrix, as viewed under crossed nicols. Magnification 100X.

The second stage of recrystallization is characterized by the calcite cement consisting of large spar-sized grains, (greater than 15μ), (Figure 4). The grain boundaries are mostly gently curving; only a few boundaries are irregularly shaped.

The third recrystallization stage consists of the quartz sand, with a matrix of sparite calcite and the introduction of dolomite and pyrite phases to this matrix, (Figures 5 and 6). The percentage of dolomite ranges from a few percent to one hundred percent. The micro-crystalline dolomite grains have the shape of euhedral rhombehedrons.

In the above described rocks, we see a trend toward equilibrium conditions, with the lowering of the total surface free energy of the rocks.

The irregular grain boundaries within the micritic calcite indicate high surface energy. Recrystallization with grain growth and the straightening of grain boundaries reduces the total surface energy, as seen in the development of the pockets of microsparite sized calcite grains.

As recrystallization continues, the calcite grows, forming spar sized grains with curved boundaries. This process futher reduces the rocks' surface free energy.

The third stage is the final lowering of the total surface energy. The occurence of the dolomite phase, with euhedral grains, progressively lowers the surface energy until equilibrium is reached with a total matrix of dolomite.

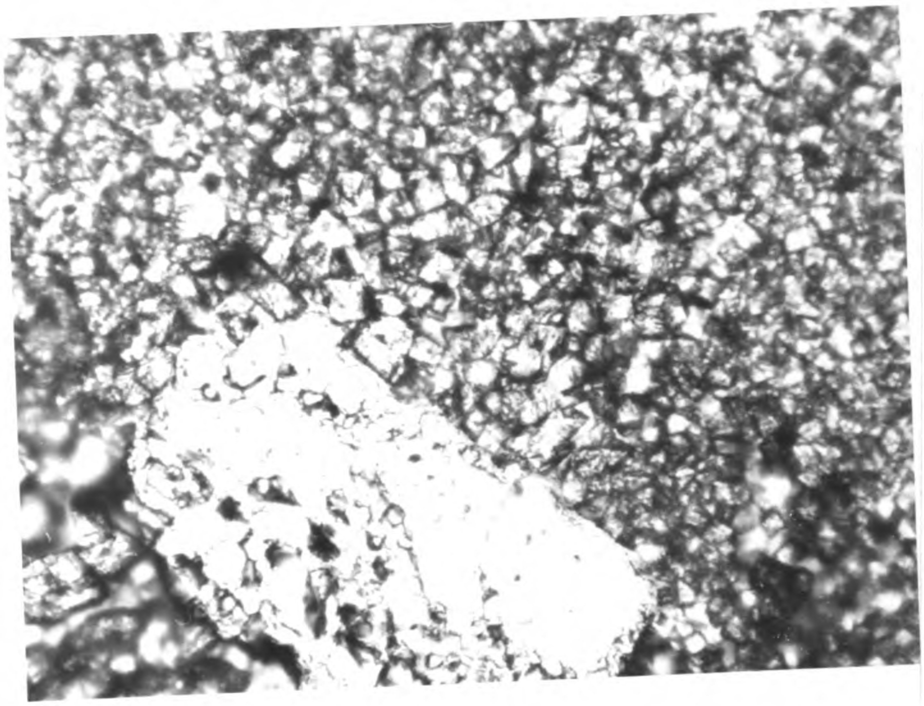


Figure 5. Photomicrograph of quartz grains in a dolomite matrix, as viewed under plane light. Magnification 100X.

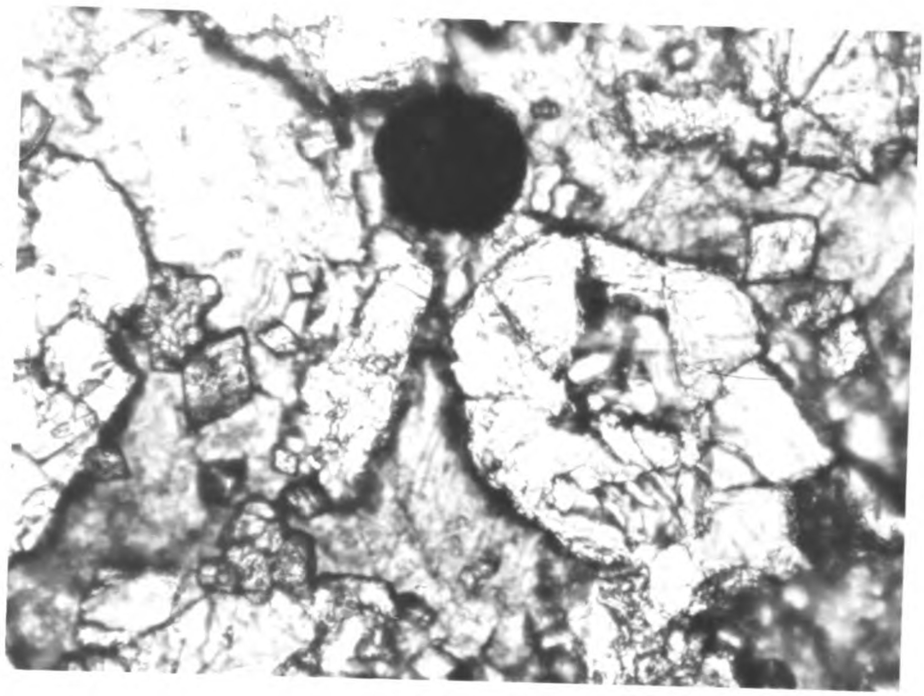


Figure 6. Photomicrograph of four quartz grains in a matrix of calcite, with dolomite rhombohedrons, as viewed in plane light. The opaque sphere is pyrite. Magnification is 250X.

THE QUARTZ-DOLOMITE ASSOCIATION

Within the rocks of the stage three recrystallization, the role of pre-existing grains in the recrystallization process can best be studied.

It was observed that the initial dolomite rhombohedrons tend to be located at two main sites: upon the quartz grains or at calcite triple points. These two sites of recrystallization must therefore be locations of high surface free energy, and prefered sites of nucleation. If this is true, the we would expect to find dolomite enveloping all quartz grains. As seen in figures 7, 8, and 9, most of the quartz grains do have a coating of dolomite. The sparry calcite, which fills the remaining space, contains few rhombohedrons.

The dolomite-quartz association was tested by noting the frequency of occurence of the dolomite and calcite phases with the quartz grains. The method involves superimposing a line, such as the cross hairs of the microscope objective, upon the thin section. As the slide is passed through the field of view, the calcite or dolomite phase in contact with the quartz grains, which are located along this line, are counted. The data was arranged in a contingency table, as seen in table 1 , and tested with a chi

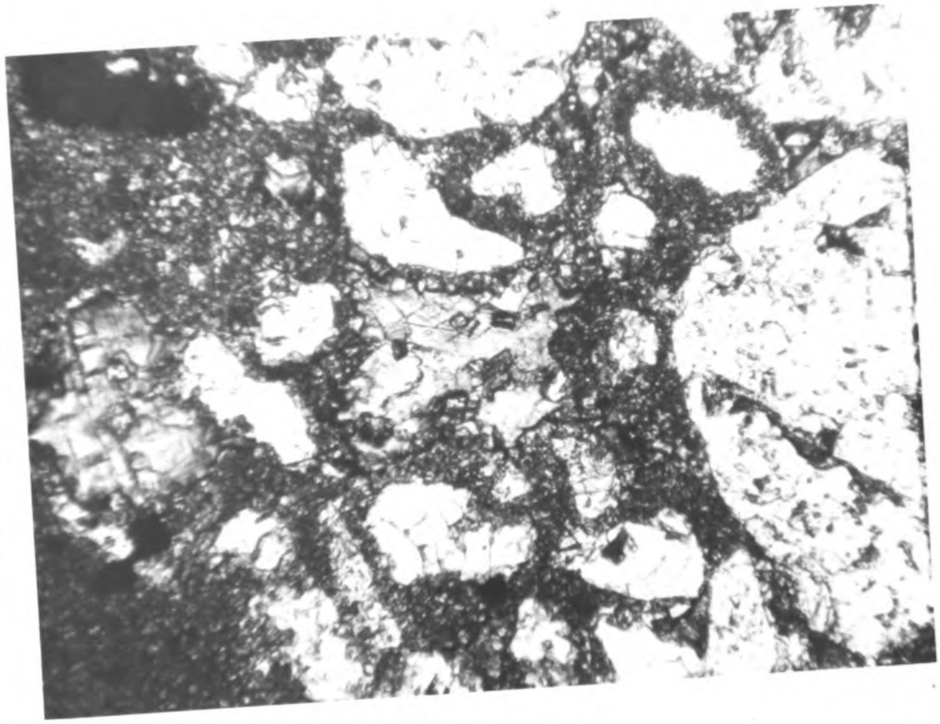


Figure 7. Quartz grains in a calcite and dolomite matrix illustrating the dolomite coating on the quartz grains. Viewed in plane light. Magnification 50X.

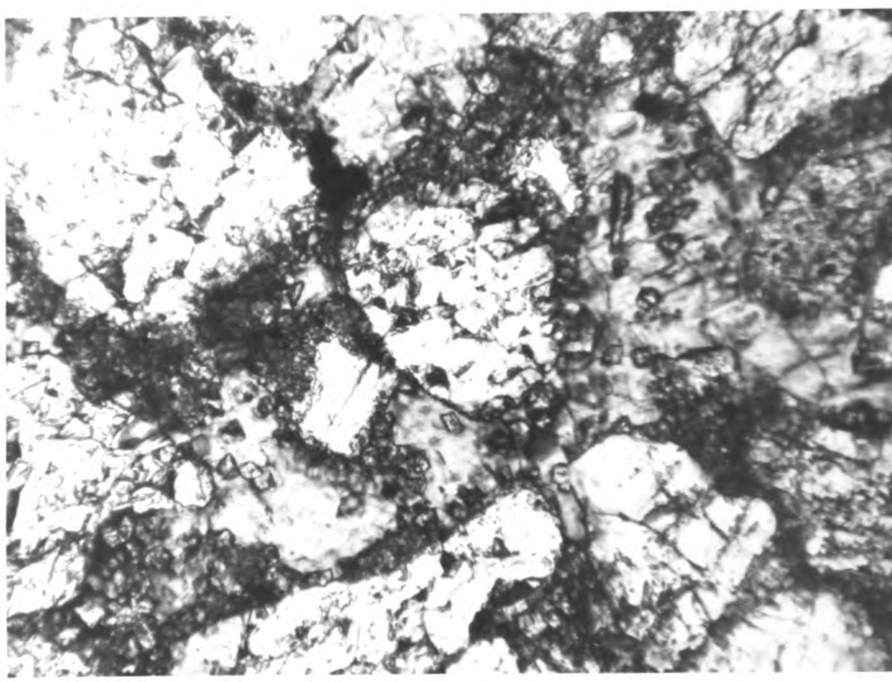


Figure 8. Quartz grains in a calcite and dolomite matrix. Notice the dolomite coating on the quartz grains. Viewed in plane light. Magnification 50X.

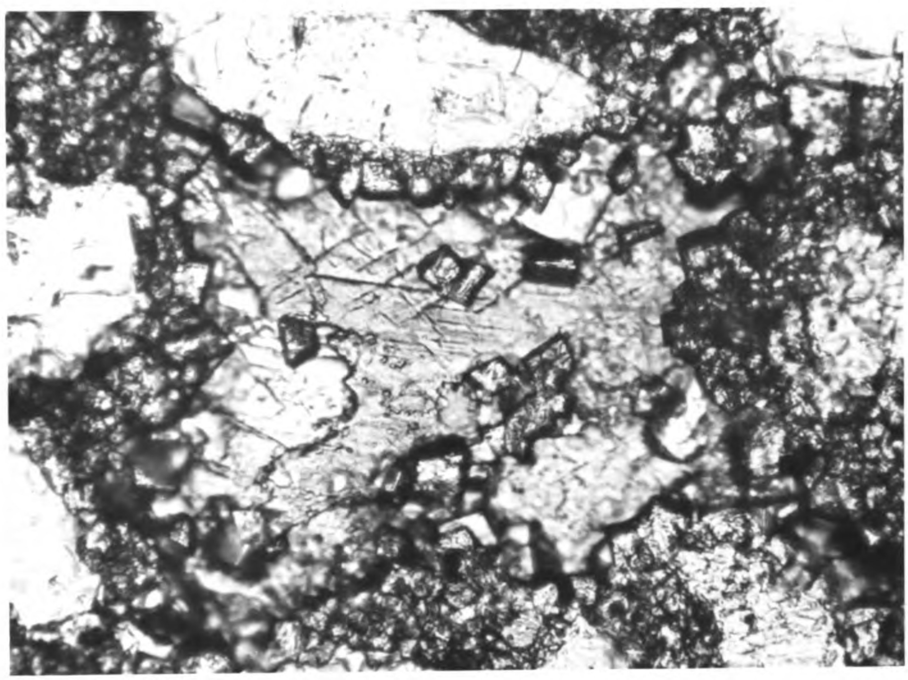


Figure 9. Quartz grains in calcite and dolomite matrix. Notice the dolomite coating on the quartz and the dolomite at calcite triple points. Viewed under plane light. Magnification 250X.

SLIDE NUMBER	DOLOMITE	CALCITE
C1c	203	49
C1b	164	96
BP7a	189	35
C2	171	24
BP22	84	56
C2a	221	75

Calculated $\chi^2 = 68.67$***

degrees of freedom = 5

Tabulated $\chi^2_{.05} = 11.070$

Table 1. Contingency table illustrating the quartz-dolomite association.

square statistic. The null hypothesis tested was that there is no difference between the frequency of occurence of either phase contact. The calculated chi-square value is highly significant, so the null hypothesis is rejected; the dolomite-quartz neighborhood is thus verified.

INHIBITED NUCLEATION BY CLAY FILMS

Many quartz grains were found to be only partly coated with dolomite; and some grains had no rhombohedrons upon them, though all nearby quartz grains had dolomite coatings. The reasons for this unexpected absence could not be seen petrographically, so a microprobe examination was conducted.

Quartz grains having no dolomite and those only partly coated with dolomite were studied. Microprobe traverses were taken across the calcite-quartz boundaries, observing the elements silica, calcium, magnesium, iron, and aluminum.

Upon the quartz grains which had no dolomite, high concentrations of aluminum were found, (Figures 10, 11, 12, and 13). Figure 10 is a secondary electron image photograph, while figures 11, 12, and 13 are X-ray flourescence photographs. All three photographs were taken in the same region, containing two quartz grains, as seen in figure 11, dolomite grains, figure 12, aluminum, represented by light areas in figure 13, and calcite, the remaining area of the photographs. Notice the absence of aluminum where the dolomite is in contact with the quartz grain, (bottom left side of figures 11, 12, and 13). Figure 14 is an electron trace across the large quartz grain.

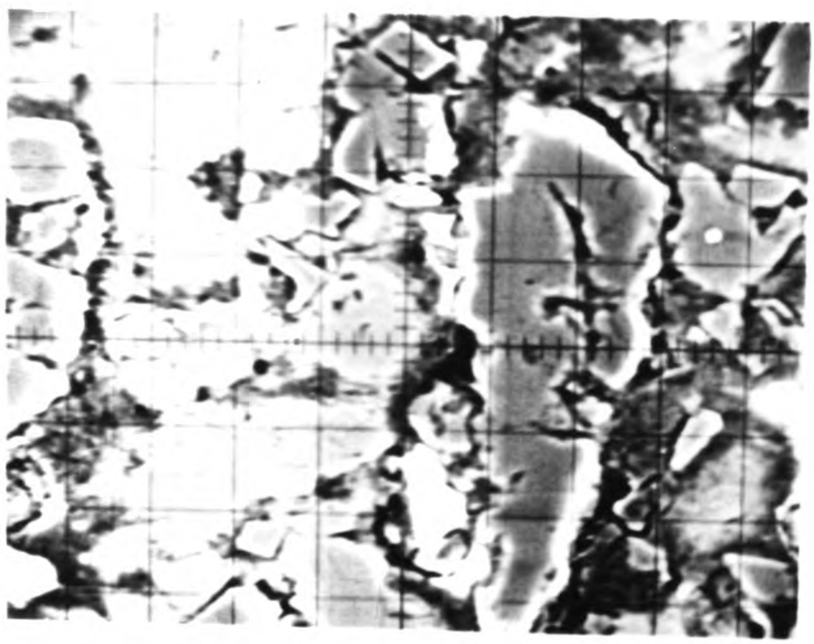


Figure 10. Secondary electron image of two quartz grains in a matrix of calcite containing dolomite rhombohedrons. Magnification 1000X.

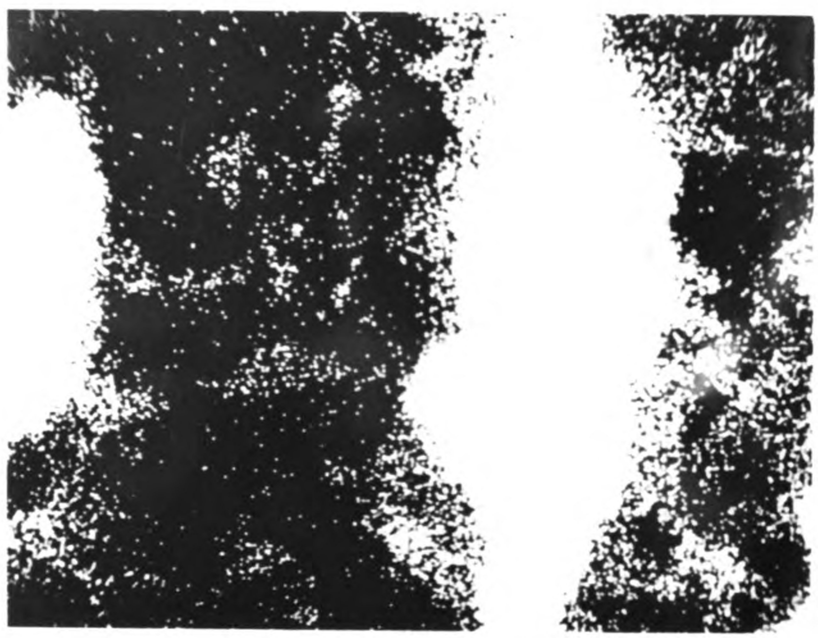


Figure 11. X-ray fluorescence of silica.
Magnification 1000X.

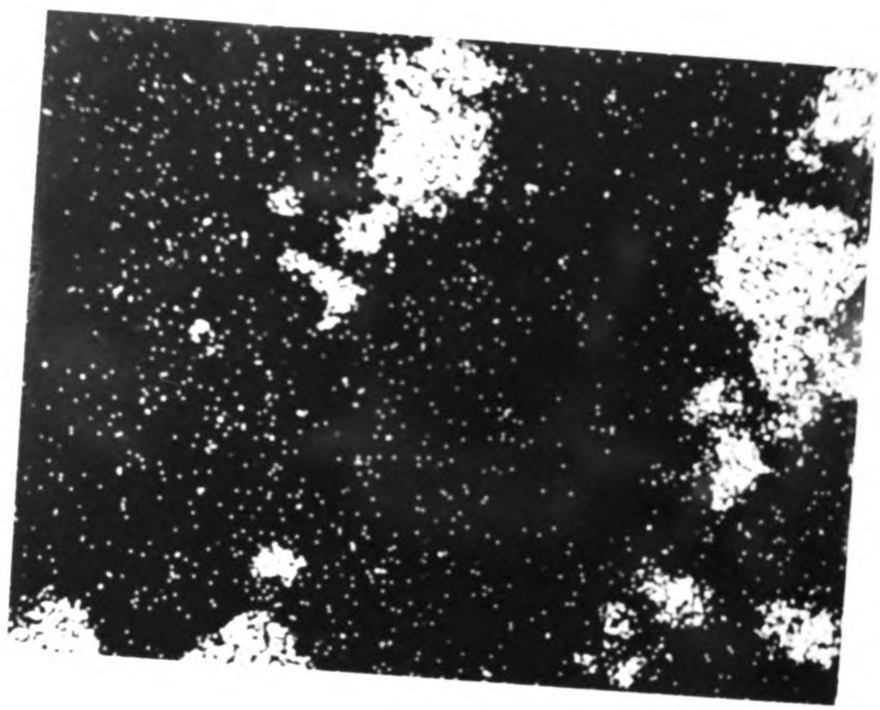


Figure 12. X-ray fluorescence of magnesium; magnification 1000X.

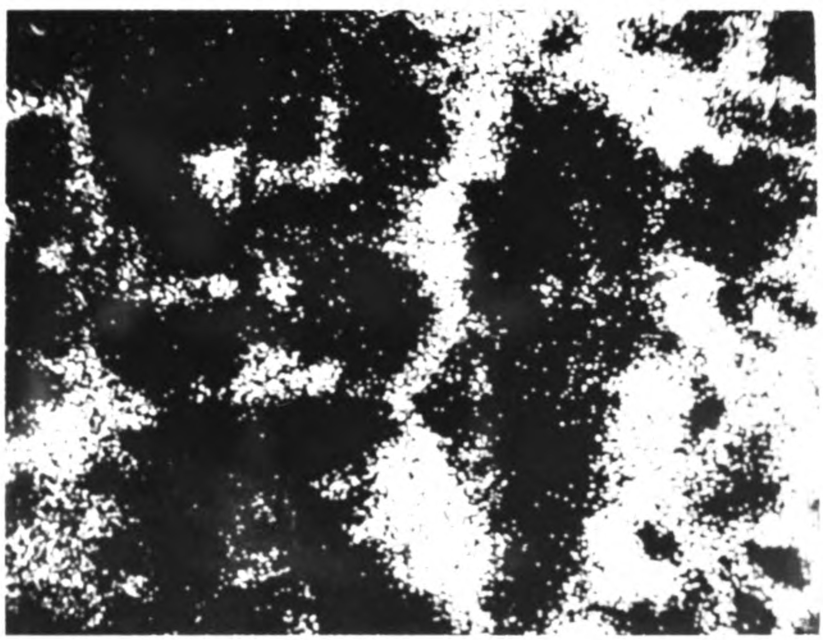


Figure 13. X-ray fluorescence of aluminum; magnification 1000X.

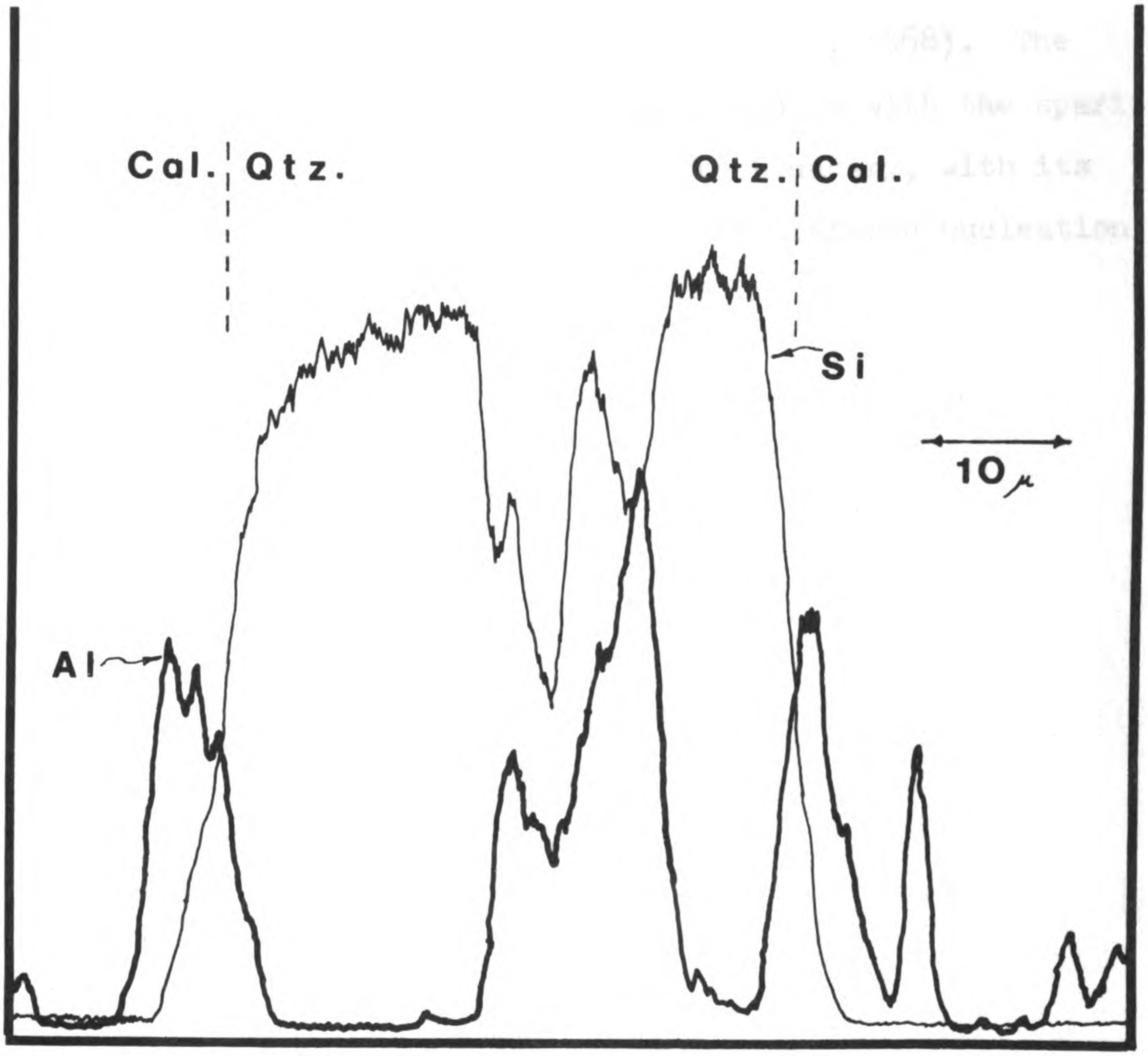


Figure 14. Microprobe traverse of a quartz grain, illustrating the aluminum coating on the quartz. Aluminum seting was 3,000 counts full scale, and the silica was 10,000 counts full scale.

These aluminum concentrations probably represent films of clay mineral, which seem to inhibit the nucleation of dolomite. This role of clay has been suggested by Bausch to explain why some rock units within a recrystallized limestone failed to recrystallize, (Bausch, 1968). The clay may form a low surface energy boundary with the sparite calcite. The quartz-sparite calcite boundary, with its high surface energy, will then be the prefered nucleation site.

PREFERRED ORIENTATION OF DOLOMITE ON QUARTZ

The dolomite rhombohedrons, when they were not inhibited by a lack of growing space, were observed to make contact with the quartz grains in two ways: with a rhombohedron face directly upon the quartz, and with the rhombohedron corner upon the quartz. This is seen in figures 6, 15, and 16. The corner contact represents a rhombohedron edge, as seen in end view, in contact with the quartz. Many of the "face" contacts are probably "edge" or "corner" contacts as viewed from the side.

This preferred orientation of the rhombohedron upon the quartz probably represents the lowest possible surface energy configuration between these grains.

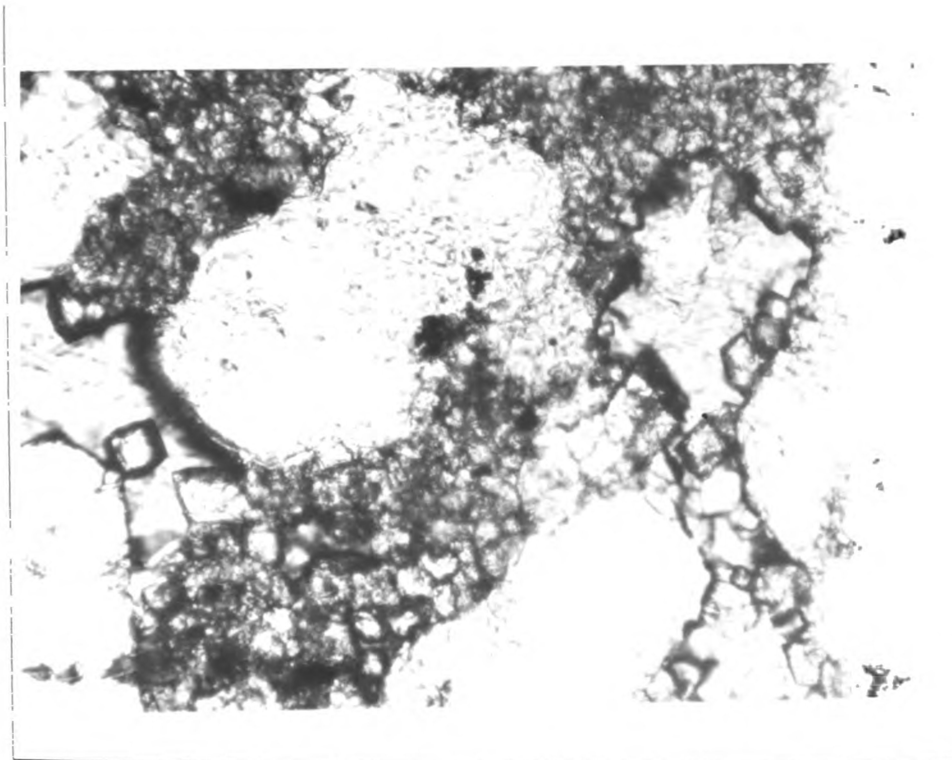


Figure 15. Quartz grains with oriented dolomite rhombohedrons, viewed under plane light. Magnification 250X.

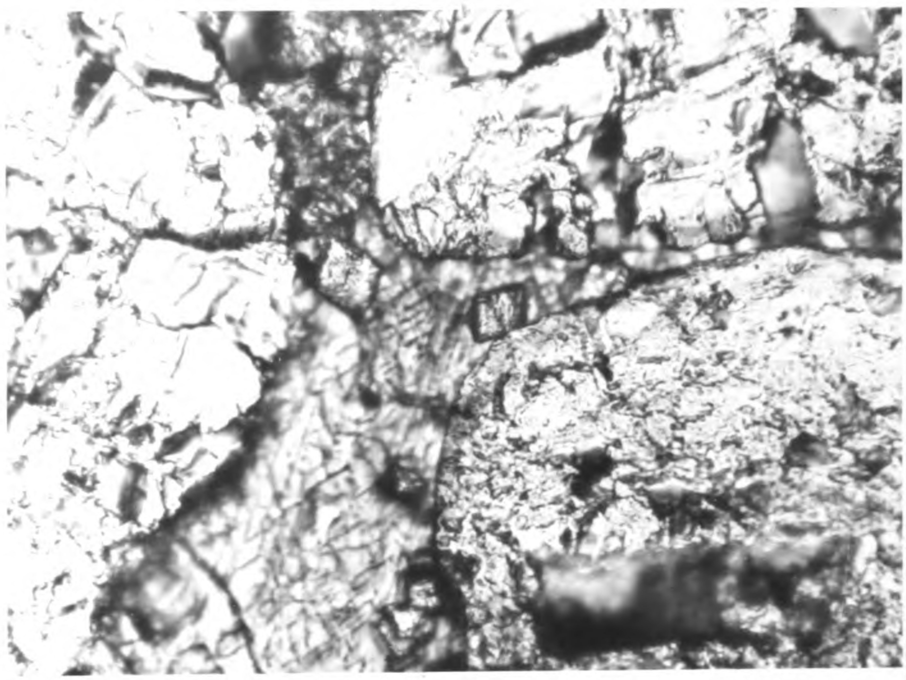


Figure 16. Quartz grains with oriented dolomite rhombohedrons, as viewed under plane light. Magnification 250X.

THE DOLOMITE SIZE-DISTANCE RELATIONSHIP

Another relationship, which was observed, indicated that the dolomite rhombohedrons upon the quartz grains were larger than those away from the quartz grains.

The petrographic method used to determine this rhombohedron size-distance relationship involved the measuring of the apparant long axis of the rhombohedron and its distance from the quartz grain, using a calibrated microscope or ocular. The data are found in table 2. This data was grouped, and then analyzed using chi-square contingency tables. In table 3 are the results of the partitioned contingency table, and in figure 17, histograms illustrate the significant grain-distance relationships.

The dolomite grains were divided into three distance classes: those in contact with the quartz grains, defined as "On", the grains within 0.0085mm of a quartz grain, defined as "Near", and the grains greater than 0.0085mm from a quartz grain, defined as "Far". In table 3 we see that the significant comparison is between the "On" distance class versus the "Near" plus the "Far" classes. This means that there is a significant size-distance relationship, with the larger dolomite grains upon the quartz, and the smaller grains away from the quartz. Notice also in table

CLASS LIMITS (microscope units)	0.1-2.0	2.1-4.0	4.1-6.0
MID-POINT " "	1.05	3.05	5.05
MID-POINT (mm)	0.0017	0.0051	0.0085
"ON" C1b FREQUENCY	1	9	3
"ON" BP22b FREQUENCY	0	2	9
"NEAR"+"FAR" FREQUENCY	1	19	21

C.L. (m.u.)	6.1-8.0	8.1-10.0	10.1-12.0	12.1-14.0
M.P. (m.u.)	7.05	9.05	11.05	13.05
M.P. (mm)	0.0119	0.0153	0.0187	0.0221
"ON" C1b	13	12	11	2
"ON" BP22b	7	15	11	14
"NEAR"+"FAR"	41	32	24	10

C.L. (m.u.)	14.1-16.0	16.1-18.0	18.1-20.0	20.1-22.0
M.P. (m.u.)	15.05	17.05	19.05	21.05
M.P. (mm)	0.0255	0.0289	0.0323	0.0357
"ON" C1b	6	2	2	0
"ON" BP22b	6	3	3	0
"NEAR"+"FAR"	13	3	1	0

C.L. (m.u.)	22.1-24.0	32.1-34.0
M.P. (m.u.)	23.05	33.05
M.P. (mm)	0.0391	0.0561
"ON" C1b	4	1
"ON" BP22b	0	0
"NEAR"+"FAR"	0	0

Table 2. Dolomite apparent long axis frequencies.

SOURSE OF VARIATION	CHI-SQUARE VALUE	DEGREES OF FREEDOM
TOTAL	35.341*	20
Between total	21.227*	8
Within total	14.114	12
Within "On"	9.488*	4
Within "Near"	3.314	4
Within "Far"	1.312	4
Between "On" verses "Near" plus "Far"	16.640*	4
Between "Near" verses "Far"	4.587	4

Table 3. Dolomite size-distance contingency table. One asterisk indicates .05 level of significence.

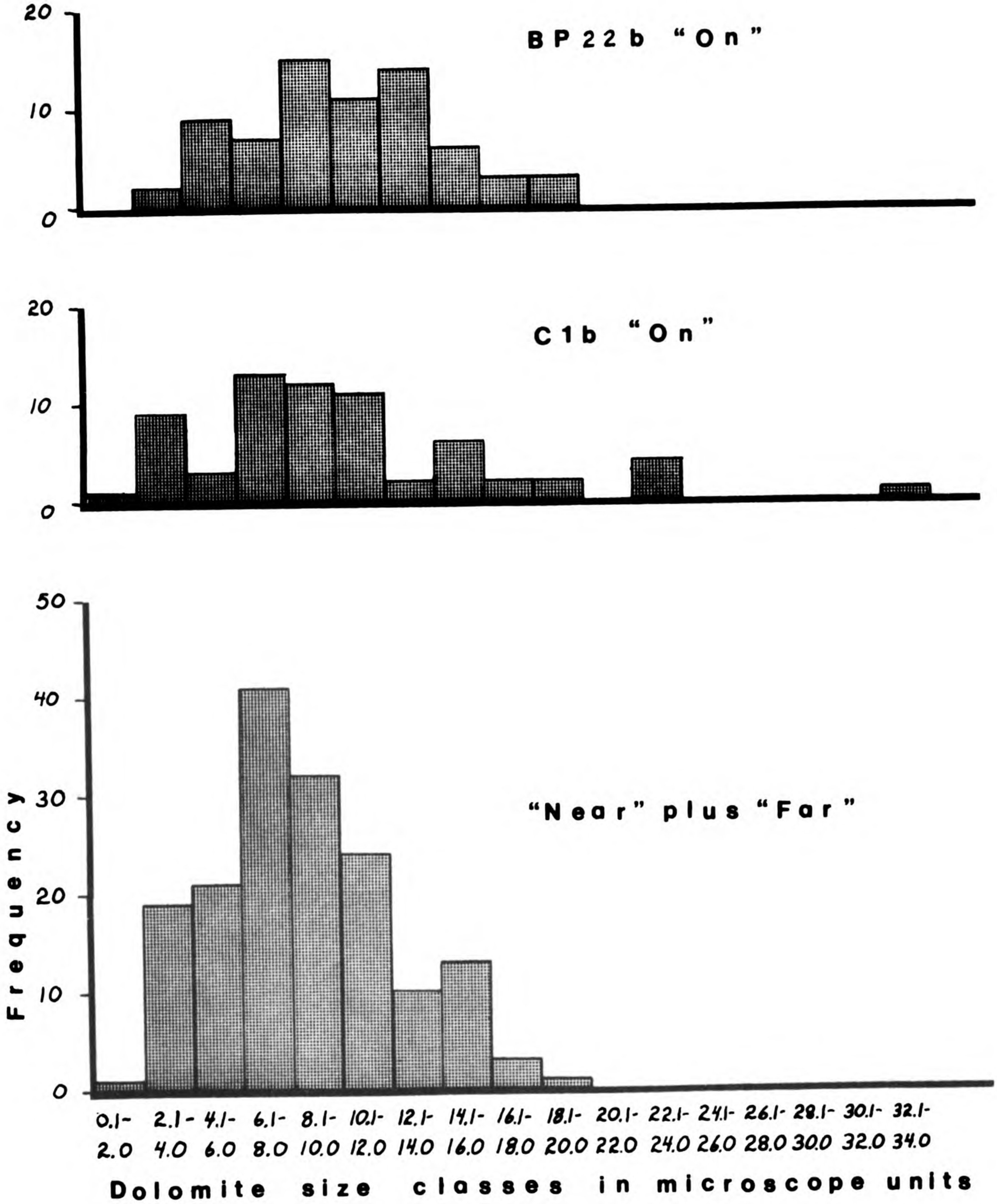


Figure 17. Histograms of significent dolomite size-distance relationships.

3 that the within chi-square value for both the "Near" and "Far" components are non-significant, meaning that the within variation could be due to chance alone. The comparison between the "Near" and "Far" components is also non-significant. These components can then be grouped and treated as one component.

The histograms in figure 17 indicate that the size of the rhombohedrons is unimodal for each distance class, and that each appears to symmetrically be distributed. Both the mean apparant long axis and the confidence limits for these measurements can be calculated from the data in table 2. The "On" class measured the mean size of 0.0174mm for slide C1b, with the .05 confidence limits of 0.0149mm to 0.0199mm. Slide BP22b had a mean size of 0.0179mm, with the .05 confidence limits of 0.0163mm to 0.0195mm. The "Near" plus "Far" class measured a mean grain size of 0.0144mm, with the .05 confidence limits of 0.0136mm to 0.0153mm.

The above calculated distance class comparisons, because they possess a symmetrical unimodal distribution, and with a significant "On" versus "Near" plus "Far" distance class comparison, permit us to examine the relative surface free energy of these distance classes.

DOLOMITE SURFACE AREA RELATIONSHIPS

As previously mentioned, recrystallization begins upon the quartz grains and at calcite triple points. With continued recrystallization we would expect the pre-existing grains to grow, and form a homogeneous interlocking texture of large rhombohedrons (Folk, 1965). An increase in size would lower the total surface free energy of the rock, and also lower the total surface area per unit volume (Spry, 1969). However, what we find are the largest rhombohedrons resting upon the quartz grains, and a matrix of smaller, unimodal, interlocking rhombohedrons. Figure 17 and table 3 illustrate this relationship. The larger dolomite grains and the fine grained matrix represents a grain size reduction with continued recrystallization, and the preferred nucleation of new grains over pre-existing grain growth. A grain size reduction , such as this, might represent an optimum surface energy which could be attained under the conditions at which recrystallization occurred.

Surface area calculations were based upon simple trigometric principles and a mathematical proof by Kendall and Moran (1963).

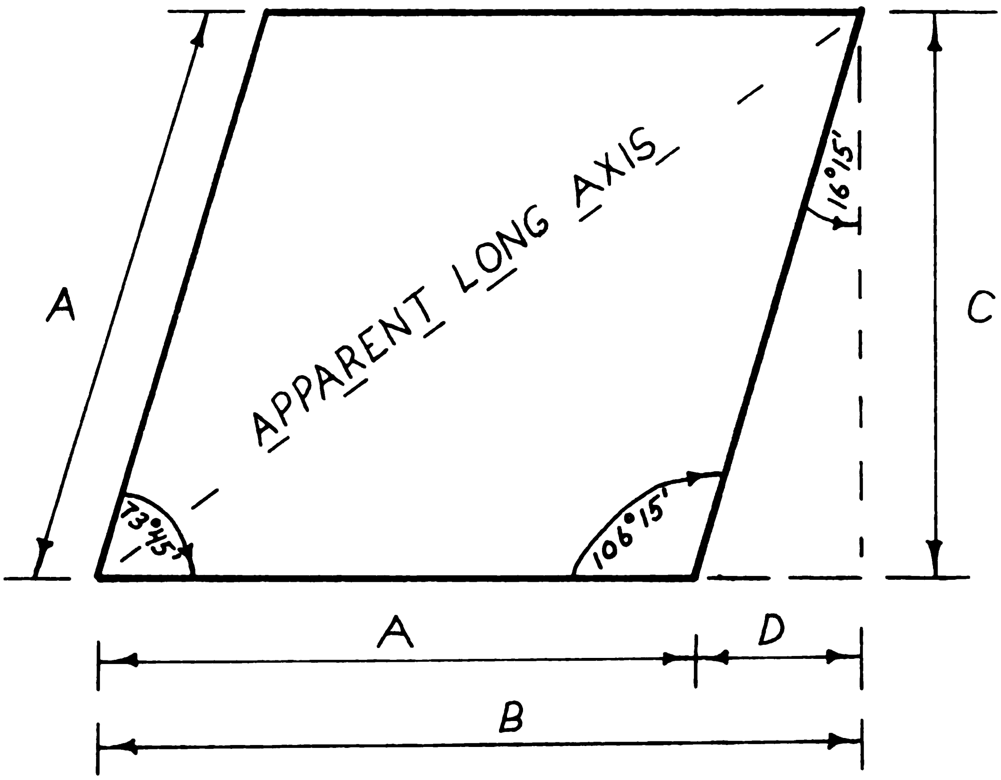
Kendall and Moran set up the proof for the simple relationships between thin section measurements along random lines, and the surface area per unit volume which can be calculated from these measurements.

> "Let λ_p, A_p, and L_p be the average number of intersections with a random plane per unit area, their average area, and their average perimeter, and similarily let λ_1, L_1 be the average number of intersections per unit length of a random line, and their average length.... Clearly,
>
> $$\lambda_p A_p = \lambda_1 L_1 = \lambda v,$$
>
> so that from either plane or line intersection we can estimate the proportion of the volume occupied by particles. $\lambda_p L_p$ will be the average sum of the perimeters of all intersections per unit area, and ... this will equal $2\pi^{-1}\lambda_1$ multiples of unit length. On the other hand, $4\lambda_1$ units of area will equal the average total surface area of the particles in unit volume..." (Kendall and Moran, 1963, p. 90).

The average sum of the perimeters could not be measured directly from the thin sections, because of the small rhombohedron size, and the difficulty of determining grain boundaries. The method used to determine the perimeters was based on the angles of a dolomite rhombohedron, and the length of the apparent long axis. These relationships are seen in figure 18. The perimeter of each size distribution class, of table 2 , was calculated and multiplied by each class n and summed, giving the average sum of the perimeters.

The surface area calculations provide a minimum estimate of the surface area per unit volume because a thin section does not orient all true long axis in the plane of the section. An accurate estimate of the relative surface area between the two size classes may still be calculated.

With a decrease in average grain size, we would expect an increase in surface area per unit volume. The surface



C = apparent long axis(sin $36^{o}52.5'$

D = C(ctn $73^{o}45'$)

B = apparent long axis(cos $36^{o}52.5'$)

A = B - D

4A= perimeter of rhombohedron

Figure 18. Equations and geometric relationships for the rhombohedron perimeter calculations.

area per unit volume was calculated to be $149.14mm^2/mm^3$ for the matrix material, and the surface area upon the quartz was $62.54mm^2/mm^3$ for slide Clb, and $68.99mm^2/mm^3$ for slide BP22b. Since surface area per unit volume is directly related to the surface free energy of the rock, we notice a trend toward a higher total surface energy with continuous recrystallization, in these rocks.

These calculations verify our predicted surface area increase, with the decrease in grain size, and an increase in surface energy of the matrix grains with continued recrystallization.

DISCUSSION AND CONCLUSIONS

Surface free energy can be used to explain reaction pathways and textural variations in recrystallized rocks. High temperature recrystallization has been explained by both ceramists and metallurgists. This study of the Bayport Limestone illustrates the validity of the concepts and principles resulting from their studies of rocks recrystallized at low temperatures.

Nucleation of new grains first occurs at sites of high surface energy. Nucleation of dolomite occured first at two sites: calcite triple points and calcite-quartz interfaces. This nucleation process tends to reduce the surface energy at these sites of high surface energy. In doing so, the total surface free energy of the rock is reduced.

Quartz grains, which were lacking the expected dolomite grains, were found to be coated with clay films. The clays have low surface tension and therefore low surface energy. The clay-calcite boundary would not be expected to act as a site for nucleation.

Dolomite-Dolomite-Quartz Relationship

It was observed that the dolomite rhombohedrons upon the quartz grains were significantly larger than the matrix rhombohedrons. If we assume the totally dolomitized rock to be in equilibrium, then this grain size difference can be explained as a function of the surface free energy of the quartz-dolomite boundary.

If we had a matrix composed of nothing but dolomite rhombohedrons, all of equal size, in equilibrium, then the surface energy would be equal everywhere, (assuming random orientation and equal composition of the rhombohedrons). When quartz grains are added to this matrix, the neighborhoods of some dolomite grains change, and so does the surface free energy. This change occurs because the dolomite-quartz interface is a higher surface energy boundary than the dolomite-dolomite boundary. Larger grains have smaller surface area per unit volume, and therefore have lower surface energy, (if all things are equal). Therefore the increase in size of the dolomite rhombohedrons adjacent to the quartz grain is seen as a mechanism to reduce the surface energy of dolomite grains. This growth then compensates for the increased interfacial energy resulting from the quartz-dolomite boundary. The crystal size of the dolomite on the quartz is great enough such that this neighborhood's total surface energy is equal to the matrix surface energy.

As seen, the calculated matrix surface area is twice the surface area calculated for the rhombohedrons of the size found on the quartz grains.

If we have a matrix of only larger dolomite grains, then the total surface energy will be only one half of the smaller grained matrix. If this texture is in equilibrium, then the surface energy should be about equal in all regions. With the addition of quartz to these larger grains, we can assume that the large dolomite-quartz interface increases the larger grain's surface energy by 100 percent.

The total surface energy of the large dolomite rhombohedrons is then a function of its neighborhood and the surface energy of each boundary. Four of the six rhombohedron faces would be in contact with other large rhombohedrons. One face will be in contact with the quartz grain and one face will be bounded by several of the smaller dolomite grains of the matrix.

The large-dolomite matrix-dolomite interfaces will account for a portion of the neighborhood's total surface free energy. However, the amount would probably be very small, as the grain size difference is not great and they are like phases. Some surface energy would be contained in the large-dolomite large-dolomite contacts, but probably even less than the large-dolomite matrix-dolomite surface energy. The large rhombohedrons have a preferred orientation, which probably gives their boundaries the lowest possible surface free energy. The largest amount of surface energy would then be held in the dolomite-quartz contact, the unlike phase contact.

If one were to assume equal surface energy for all of the dolomite-dolomite faces of one rhombohedron, and an unequal surface energy for the dolomite-quartz face, then an approximate contribution of the dolomite-quartz surface energy to the total surface energy can be calculated.

If: X = the total surface energy for a large dolomite grain.

$\frac{X}{2}$ = the total surface energy of a matrix grain.

K = Surface energy of one dolomite-dolomite boundary.

Q = Surface energy of a dolomite-quartz boundary.

$$\frac{X}{2} = 6K$$

Then:

$$X = 12K$$

$$X = 5K + Q$$

$$Q = 7K$$

We see that the quartz-dolomite boundary is responsible for seven times the surface energy of any other grain interface.

Dolomite-Calcite-Quartz Relationship

If a dolomite rhombohedron were growing upon the quartz at a sparry calcite-quartz boundary, then the above reasoning also applies. Growth of the dolomite rhombohedron will stop when the growing conditions are unfavorable for further growth and the surface free energy for the conditions is at a minimum. The total surface energy for the grain will be equal to the calcite; but the dolomite-calcite surface energy will be only a small portion of the total, as the lattice differences between dolomite and calcite are not great. The dolomite-quartz interface will have a high surface energy because of the unlike boundary.

Recrystallization Sequence

The matrix recrystallization sequence begins with micritic calcite. With continued recrystallization, the micritic calcite is crystallized to microsparite calcite. This recrystallizes to sparry calcite matrix. At this stage a micritic dolomite phase recrystallizes, first at high energy sites, and then it continues to form a micritic dolomite matrix.

Within the micritic dolomite matrix we see a unimodal grain size population with small confidence limits. With continued recrystallization, one would expect to find an increase in grain size and a decrease in nucleation, in an attempt to lower the total rock surface energy. This is not the case in the dolomitic stage of recrystallization. If the grain size of these recrystallized grains reflects the energy conditions of the environment, then we might explain this lack of growth by a lack of the necessary energy to break a grain size barrier or threshold, as suggested by Folk, (Folk, 1968). This threshold could represent an optimum surface energy for each of the components and the environment in which recrystallization is occurring. To break the threshold would require increased energy, resulting in larger grains and a decrease in surface energy.

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