A MODEL FOR SURFACE AREA, MINERALOGY, AND METAMORPHIC GRADE IN CARBONATES

Dissertation for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

GARY R. BYERLY

1974

This is to certify that the

thesis entitled

A MODEL FOR SURFACE AREA, MINERALOGY,
AND METAMORPHIC GRADE IN CARBONATES

presented by

GARY R. BYERLY

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Geology

Thomas A. Vogel
Major professor

Date 9/11/74

O-7639

ABSTRACT

A MODEL FOR SURFACE AREA, MINERALOGY, AND METAMORPHIC GRADE IN CARBONATES

By

Gary R. Byerly

In meta-carbonates ranging from greenschist to middle amphibolite grade, total and partitioned components of surface area demonstrate highly significant variation as a function of both metamorphic grade and percentage of coexisting phases (calcite, dolomite, quartz, and phlogopite). Total surface area is a positive linear function of modal percent second phases (dolomite + quartz + phlogopite), whereas, calcite-calcite surface area is a negative linear function at greenschist grade and a very flat second order function at amphibolite grades. All surface area components decrease with increasing metamorphic grade. Second phases control surface area by inhibiting grain boundary migration and thus grain growth. At low grades, strain induced recrystallization and grain boundary migration result in a high surface area aggregate. At higher grades, grain boundary migration, driven by surface energy differences, becomes dominant and results in a very low surface area aggregate.

A MODEL FOR SURFACE AREA, MINERALOGY, AND METAMORPHIC GRADE IN CARBONATES

By

Gary R. Byerly

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geology

1974

ACKNOWLEDGMENTS

Tom Vogel, for his encouragement and support these last four years. A good friend and competent teacher.

Bob Ehrlich, for getting me involved with research as an undergraduate, and making me aware of the philosophy of science.

Sam Upchurch, Bob Anstey, Bill Cambray, and Charles Spooner, for their work on my committee.

Kevin, Bruce, Lee, Graham, Steve, and many others, for their friendship, and their valuable discussions on this research.

The Coffee-room Gang, including Jean, Jeanne, Larry, Wendy, Vivian, Stoney, Sue, Jeff, and Duncan, for just being around.

My Parents, for accepting me as the strange person I am growing into.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Textures have received much attention for their relationship to deformation, recrystallization, grain growth, and phase transformations in metamorphic petrology (Pitcher and Flynn, 1965; Spry, 1969). Ehrlich and others (1972) have shown that in the progressive regional metamorphism of a granodiorite textural variables are more responsive to pressure and temperature changes than mineralogical or chemical variables. Total rock surface area and plagioclase surface area as a function of metamorphic grade seem to be the most responsive variables.

Quantitative work on phase distributions in metamorphic rocks has been noticeably lacking although theoretical (for example American Society of Metals, 1966; Fulrath and Pask, 1968) and empirical (Underwood, 1968; and DeHoff and Rhines, 1970) basis for such work does exist. The importance of phase distributions or textures has long been discussed in the geological sciences but in general in a very qualitative fashion.

This paper is concerned with the textural response of impure carbonates to progressive regional metamorphism. By studying a range of modal compositions within each suite of metamorphic samples, the effects of second phase particles are also evaluated. Two techniques are used for studying the phase distributions. Surface area is partitioned between the possible grain boundary types and from these grain transition probabilities are derived. The following section first gives the reader a review of current models relating textures to the processes which affect crystalline aggregates.

DISCUSSION OF MODELS

The importance of surfaces in controlling many properties of crystalline aggregates is well documented in the literature of ceramics and metallurgy. Smith's (1948) discussion of the role of surface energy in controlling textures is a classic work. Surface energy forces move the various boundaries in an aggregate to a state of balancing forces, that is, an equilibrium configuration. White (1966) has quantitatively demonstrated the surface energy controls on textures, specifically on preferred phase distributions in two and three phase aggregates, and with small impurity additions. He uses parameters similar to the grain transition probabilities of this paper in addition to grain size distributions. White observes that total surface area is maximized at specific modal compositions. His work supports the concept that second phases exert strong controls on surface area. With increasing modal percent of a second phase the grain size of both phases decreases significantly. He further finds that unlike boundaries occur significantly more frequently than boundaries between like phases. DeVore (1955, 1959) and Voll (1960) conclude that surface energy effects should be of major importance in controlling phase distributions in petrological systems. DeVore (1955) speculates that even modal percentages could be a function of surface energy controls where slight differences in chemical potentials were driving reactions, such as in metasomatism.

Recrystallization and grain growth are the solid state processes responsible for major changes in the texture of a crystalline aggregate. These processes are a function of temperature, strain, and dispersed second phase particles. Recrystallization, Grain Growth, and Textures (American Society for Metals, 1966) and more recently Aust (1972) review the relationship of these variables to recrystallization and grain growth. The following discussion is derived largely from these sources.

The major effect of increasing temperature is to overcome thermal barriers to diffusion, which enhances migration of defects, dislocations, and grain boundaries. Strain increases the free energy of the crystal, thus enhancing recrystallization. Variation in strain rates and temperature can result in two fundamentally different forms of grain boundary migration. At low temperatures and high strains grain boundary migration is driven by the increased free energy of the strained crystal and small recrystallized grains will grow at the expense of larger, more highly strained grains. At high temperatures and low strain rates grain boundary migration is driven by differences in surface energy, resulting in large grains growing at the expense of small grains. A coarse grained, low surface area aggregate is formed.

The distribution of a second phase in an aggregate effects the properties and resultant texture in several ways. Grain growth is limited by the inhibition of grain boundary migration. As sites for recrystallization mucleii, rapid recrystallization is promoted as a response to increasing temperature and strain.

Previous textural work in geology has focused primarily on the effects of temperature and strain, with little on phase distributions. Indeed, most of the studies have been done on single phase aggregates such as carbonates, quartzites and dunites. DeVore has attempted to develop models for preferred phase distributions as a function of stress orientation and elastic compliance anisotropies in crystals (1969), and surface chemistry and surface energy (1955, 1959). Vistelius (1972) has developed a stochastic model for phase distributions in granitic rocks as a function of crystallization pathways.

Much of the experimental work in geology has been with carbonates due to their relative ease of recrystallization at times, pressures and temperatures possible in the laboratory. Heard and Raleigh (1972), Wenk and others (1973), and Rutter (1974) are recent investigators. Their experiments and those reviewed by them indicate that above 350°C recrystallization and grain growth in strained calcite aggregates becomes dominant over mechanisms such as twinning, translation, and kinking. This first becomes noticeable with development of calcite porphroblasts in a fine matrix. With complete recrystallization at higher temperatures a coarse equidimensional aggregate is formed. Steady-state flow is possible at temperatures in excess of 250°C for geological strain rates ($\sim 10^{-14}$ sec^{-1}).

PHASE DISTRIBUTIONS IN META-CARBONATES

Marbles from the Grenville Province of southeastern Ontario were collected for variation in mineralogy and metamorphic grade. Metamorphic grade, as determined by mineralogy of adjacent pelitic units, ranges from greenschist near Madoc to middle amphibolite near Fernleigh (Moore and Thompson, 1972).

The sample units for modal and surface area analyses were defined on the basis of homogeneity of mineralogy and grain size to minimize sample variance (Ehrlich, 1964). At lowest grades these homogeneous units range in thickness from 0.5 to 2 cm and probably represent primary sedimentary lamella. At higher grades the homogeneous units thicken to sizes from 1 to 10 cm and may represent some metamorphic effect on the primary sedimentary lamella.

Sample suites were collected at greenschist, lower amphibolite, and middle amphibolite grades. Dolomite, quartz, phlogopite, and calcite are stable in the sample suites from greenschist and lower amphibolite grades, with dolomite absent in the middle amphibolite grade suite. At lower metamorphic grades the samples range from nearly pure quartzites to nearly pure marbles. The highest grade sample suite had no samples with less than 60% calcite.

Sixteen sample units were chosen from each of the three metamorphic sample suites. A uniform distribution of sample units between 50 and 100 percent calcite was attempted. Surface area analyses were performed using the method of Kendall and Moran (1963). An unbiased estimate of surface area is simply twice the number of intersected boundaries per unit length of transect line. Grain boundaries were counted on transects perpendicular and parallel to the planar direction of the sampling units. Three transects counting 100 boundaries each were run in both directions. Parallel surface components were always 5 to 15 percent lower than equivalent perpendicular components, but conform to similar trends. For this reason all six traverses were averaged in each sample. The unbiased estimate of surface area should be made by random transects through the sample volume. The above technique gives an average of the minimum (parallel) and maximum (perpendicular) surface area.

This same data can then be used for estimates of grain transition probabilities. These variables are the probability of encountering a specified phase at the next boundary along a traverse, given only the current phase of the traverse. This simply amounts to division of the partitioned surface area by the total surface area for each sample unit. These parameters are only a different way of analyzing the surface area data and actually contain less information than the absolute values of partitioned and total surface area. Vistelius (1972), Flinn (1970), and Kretz (1969) have used grain transition probabilities to characterize phase distributions in igneous and metamorphic rocks. The use of the entire transition probability matrix is operationally difficult and the statistical tests ambiguous, therefore, only selected probabilities will be examined.

Surface Area Variation

In order to demonstrate the strong controls which both metamorphic grade and mineralogy have on surface area, total and calcite-calcite surface area are plotted as a function of modal percent second phases for each of the three sample suites (Figure 1). In all cases the functional relationship is statistically significant. Statistics for both first order and second order regression models are shown in Tables 1 and 2.

At all three grades the total surface area versus modal percent second phases has highly significant, positive, first order correlations. That is, with increasing impurities in the meta-carbonate the surface area increases linearly. Variation in calcite-calcite surface area is also highly correlated with modal percent second phases. The greenschist trend is negative first order, whereas the amphibolite trends are negative second order. Photomicrographs of representative samples from each suite are shown Figure 2.

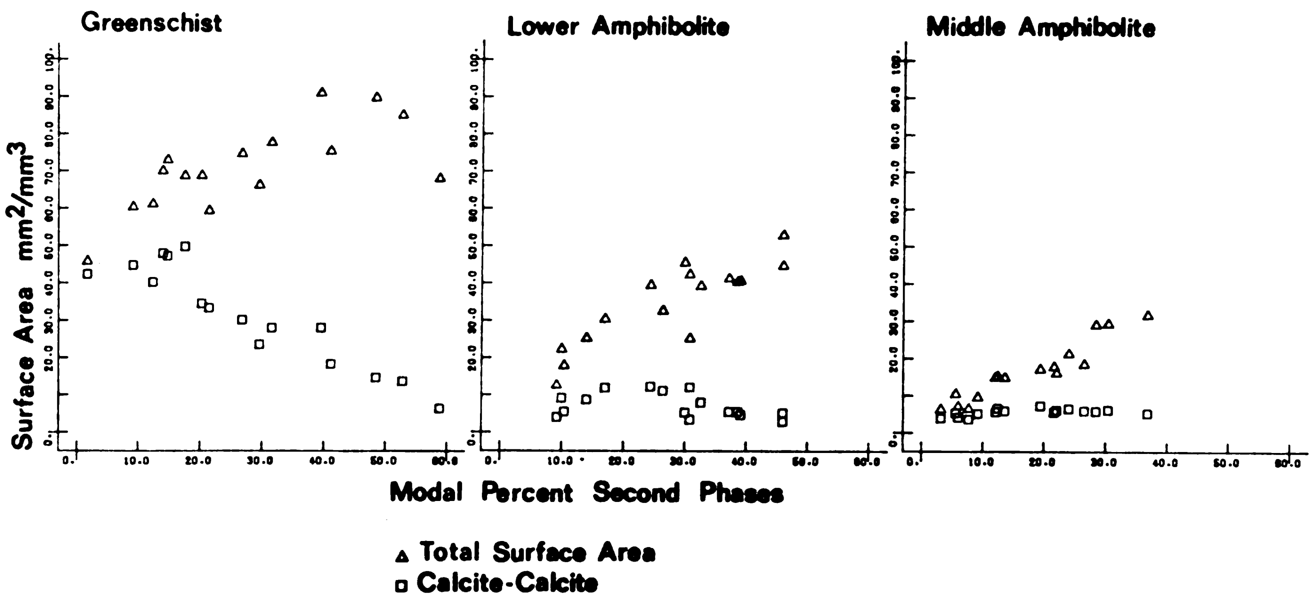

Figure 1.--Relationship of total and calcite-calcite surface area to modal percent second phases (dolomite + quartz + phlogopite) for the three metamorphic sampling suites. Regression statistics are summarized in Tables 1 and 2.

TABLE 1. REGRESSION STATISTICS FOR FIRST ORDER MODELS.

	Multiple correlation coeff., R^2	F-test on total regression	Regression coeff. for constant	F-test for constant	Regression coeff. for (100-C)	F-test for (100-C)
Greenschist						
Total surface area	.5016	**	57.1257	***	.4989	**
C-C surface area	.8616	***	51.9392	***	-.7488	***
C-C transition probabilities	.9453	***	.8637	***	-.0143	***
Lower amphibolite						
Total surface area	.7646	***	12.7212	**	.7917	***
C-C surface area	.1218	N S	9.7735	***	-.0916	N S
C-C transition probabilities	.7682	***	.6888	***	-.0122	***
Middle amphibolite						
Total surface area	.8959	***	3.4385	*	.7523	***
C-C surface area	.2784	*	4.6232	***	.0515	*
C-C transition probabilities	.8828	***	.9376	***	-.0196	***

* Significant at .1

** Significant at .01

*** Significant at .001

N S Nonsignificant at .1

TABLE 2. REGRESSION STATISTICS FOR SECOND ORDER MODELS.

	Multiple correlation coeff., R^2	F-test on total regression	Regression coeff. for constant	F-test for constant	Regression coeff. for (100-C)	F-test for (100-C)	Regression coeff. for $(100-C)^2$	F-test for $(100-C)^2$
Greenschist								
Total surface area	.6589	***	45.0703	***	1.5954	**	-.0178	*
C-C surface area	.8682	***	49.1074	***	-.4912	NS	-.0042	NS
C-C transition probabilities	.9619	***	.9455	***	-.0218	***	-.0001	*
Lower amphibolite								
Total surface area	.7820	***	6.4366	NS	1.3845	*	-.0111	NS
C-C surface area	.3789	*	2.7806	NS	.5680	*	-.0124	*
C-C transition probabilities	.7800	***	.6089	***	-.0047	NS	-.0001	NS
Middle amphibolite								
Total surface area	.9012	***	5.0528	*	.5143	NS	.0063	NS
C-C surface area	.6342	***	2.9754	***	.2946	***	-.0065	**
C-C transition probabilities	.8873	***	.9766	***	-.0254	**	.0002	NS

* Significant at .1
** Significant at .01
*** Significant at .001
NS Nonsignificant at .1

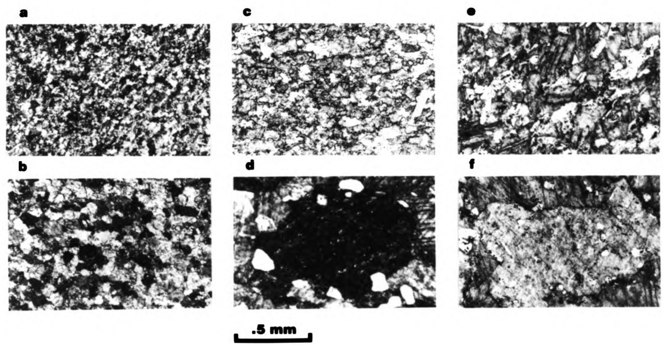

Figure 2.--Photomicrographs of representative samples. Greenschist grade, a--1.7% second phases, 46.3 mm^2/mm^3 total surface area; b--31.2% second phases, 76.2 mm^2/mm^3 total surface area. Lower amphibolite; c--9.2% second phases, 12.5 mm^2/mm^3 total surface area; d--27.2% second phases, 41.5 mm^2/mm^3 total surface area. Middle amphibolite, e--5.6% second phases, 10.5 mm^2/mm^3 total surface area; f--26.8% second phases, 19.2 mm^2/mm^3 total surface area.

Surface area progressively decreases with increasing metamorphic grade, with the major adjustment occurring between the greenschist and lower amphibolite grades. Probably the most interesting trend found in the partitioned surface area is that of the calcite-calcite surface area with increasing metamorphic grade. In the greenschist grade suite the calcite-calcite surface area increases linearly with increasing modal percent calcite. Geometrically this would indicate the addition of relatively constant sized calcite grains to the aggregate. At amphibolite grades the calcite-calcite surface area flattens out to a broad negative parabola with a maximum value of calcite-calcite surface area at approximately 20% second phases. This trend has no simple geometrical explanation, however, it is apparent that increasingly larger sized calcite grains must be added to the aggregate to explain the near zero slope.

Grain Transition Probabilities

Figure 3 demonstrates the functional relationship of calcite-calcite transition probabilities to modal percent second phases. All three grades show similar trends. The greenschist grade trend has an extremely high correlation with modal percent second phases, again indicating a simpler relationship than at amphibolite grades. It should be evident, however, that grain transition probabilities contain less information than absolute surface area

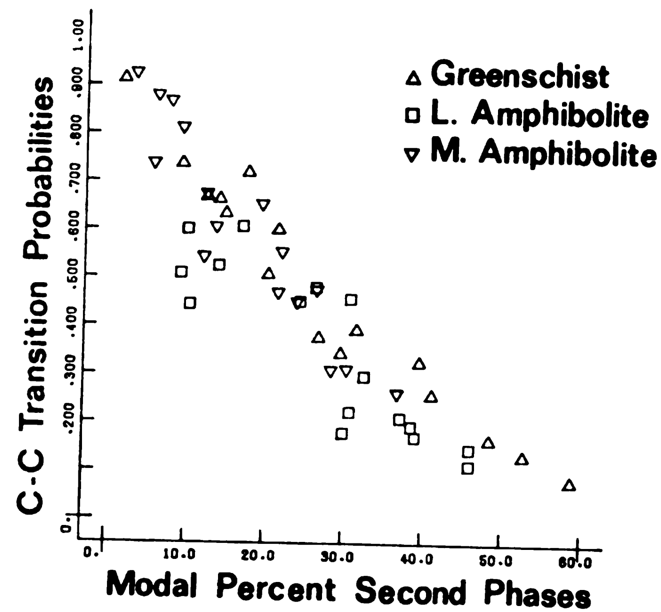

Figure 3.--Relationship of grain transition probabilities to modal percent second phases for the three metamorphic sampling suites. Regression statistics are summarized in Tables 1 and 2.

parameters. Variation of grain transition probabilities with metamorphic grade is not easily recognized.

DISCUSSION OF RESULTS

Several important observations on the phase distributions of progressively metamorphosed carbonates can be related to the processes of recrystallization and grain growth. These observations are:

1. Total surface area is highly correlated to modal percent second phases at all conditions studies in this paper (greenschist through middle amphibolite grades). With increasing second phases surface area increases linearly.

2. Calcite-calcite surface area is negatively correlated with modal percent second phases at greenschist grade, but is a very flat second order function at higher grades.

3. Total and calcite-calcite surface area decrease with increasing metamorphic grade.

4. Increase in surface area with metamorphic grade may be discontinuous. With only three metamorphic sample suites this is difficult to evaluate. However, all three suites have distinct surface area to modal composition trends.

Variation of surface area with mineralogy is in response to one or both of the following mechanisms.

Nucleation may be highly favored at boundaries of second phase particles. Alternatively, if recrystallization occurs from random nucleii, second phase particles will inhibit grain boundary migration and thus limit grain growth. Either mechanism would explain the direct relationship between modal percent second phases and total surface area. However, experiments in ceramic systems indicate the dominant role of second phase particles is to limit grain growth (American Society for Metals, 1966).

With increasing metamorphism several mechanisms may be responsible for the decrease in total surface area. Reactions which remove or coalesce second phase particles would allow increased grain growth. In these rocks, this process may contribute to the surface area pattern, but cannot be a major factor since reactions of this type (e.g. disappearance of dolomite) occur primarily between the lower and middle amphibolite grades where the surface area changes are least dramatic. With increasing temperature of metamorphism, diffusional processes become dominant. Progressively less strain build up can occur in the crystals and consequently less recrystallization takes place. The driving force of grain boundary migration changes from the free energy differences between strained and unstrained crystals (at lower temperatures) to the much smaller surface energy associated with curvature and orientation differences (at higher temperatures).

This last model explains the change in slope of calcite-calcite partitioned surface area versus modal composition. At greenschist grade recrystallization and strain-induced grain boundary migration favor smaller calcite crystals, and with increasing modal percent calcite an increase in calcite-calcite surface area can be expected. At amphibolite grades recrystallization becomes less important and grain boundary migration is driven by surface energy differences. Second phase particles thus control the limiting grain size and calcite-calcite surface area shows no increase with increasing calcite modal percent.

The possibility that decreases in surface area with metamorphic grade are discontinuous has some justification. Secondary recrystallization in metals and ceramics often occurs when an aggregate is stabilized from further growth by second phase particles or development of a highly oriented fabric from primary recrystallization. This results in quantum decreases in surface area from the recrystallized texture to the secondary recrystallized texture.

In summary, both metamorphic grade and mineralogy control significantly the total surface area and partitioned components of surface area within carbonates ranging from greenschist to middle amphibolite grade metamorphism. Second phase particles control the surface area by inhibiting grain boundary migration and thus grain growth at all metamorphic grades studied. The response of surface area to metamorphism is controlled by the relative contributions of recrystallization and grain growth. At low grades strain induced recrystallization and grain boundary migration result in a fine-grained aggregate of high surface area. At higher grades increased lattice diffusion results in much less strain build up in the crystal lattices. Grain boundary migration, driven by surface energy differences, becomes dominant and results in a coarse aggregate of very low surface area.

REFERENCES

REFERENCES

American Society for Metals (Eds.), Recrystallization, Grain Growth, and Textures, 617 p., American Society for Metals, Metals Park, Ohio, 1966.

Aust, K. T., Principles of crystal growth from the solid state in relation to the preparation of large single crystals, J. Crystal Growth, 13/14, 57-61, 1972.

DeHoff, R. T., and F. N. Rhines, Quantitative Microscopy, 422 p., McGraw-Hill, New York, 1968.

DeVore, G. W., Surface chemistry as a chemical control on mineral association, J. Geology, 54, 31-55, 1955.

DeVore, G. W., Role of minimum interfacial free energy in determining the macroscopic features of mineral assemblages: I. The model, J. Geology, 57, 211-226, 1959.

DeVore, G. W., Preferred mineral distributions of polymineralic rocks related to non-hydrostatic stresses as expressions of mechanical equilibria, J. Geology, 77, 26-38, 1969.

Ehrlich, R., The role of the homogeneous unit in sampling plans for sediments, J. Sed. Pet., 34, 437-439, 1964.

Ehrlich, R., T. A. Vogel, B. Weinberg, D. C. Kamilli, G. Byerly, and H. Richter, Textural variation in petrogenetic analyses, Geol. Soc. Amer. Bull., 83, 665-676, 1972.

Flinn, D., Grain contacts in crystalline rocks, Lithos, 3, 361-370, 1969.

Fulrath, R. M., and J. A. Pask (Eds.), Ceramic Microstructures, 1008 p., John Wiley and Sons, New York, 1968.

Heard, H. C., and C. B. Raleigh, Steady-state flow in marble at 500° to 800°C, Geol. Soc. Amer. Bull., 83, 935-956, 1972.

Kendall, M. G., and P. A. P. Moran, Geometrical Probability, 125 p., Charles Griffin and Company, London, 1963.

Kretz, R., On the spatial distribution of crystals in rocks, Lithos, 2, 39-66, 1969.

Moore, J. M. Jr., and P. H. Thompson, The Flinton Group, Grenville Province, eastern Ontario, Canada, Twenty-fourth International Geological Congress, Section 1, 221-229, 1972.

Pitcher, W. S., and G. W. Flinn (Eds.), Controls of Metamorphism, 368 p., John Wiley and Sons, New York, 1965.

Rutter, E. H., The influence of temperature, strain rate, and interstitial water in the experimental deformation of calcite rocks, Tectonophysics, 22, 311-334, 1974.

Smith, C. S., Grains, phases, and interfaces: an interpretation of microstructure, Trans. Amer. Inst. Min. metall. Engrs., 173, 15-51, 1948.

Spry, A., Metamorphic Textures, 350 p., Pergamon Press, Oxford, 1969.

Underwood, E., Quantitative Sterology, 274 p., Addison-Wesley, Reading, Mass., 1970.

Vistelius, A. B., Ideal granite and its properties. I. The stochastic model, Math. Geol., 4, 89-102, 1972.

Voll, G., New work on petrofabrics, Liverpool and Manchester Geol. J., 2, 503-567, 1960.

Wenk, H. R., C. S. Venkitasubramanyan, and D. W. Baker, Preferred orientation in experimentally deformed limestone, Contrib. Mineral. Petrol., 38, 88-114, 1973.

White, J., Phase distributions in ceramics, in Ceramic Microstructures, edited by R. M. Fulrath and J. A. Pask, pp. 728-762, John Wiley and Sons, New York, 1968.