

**1084.** *An Attempt to Determine the Mechanism of a Natural Mineral-forming Reaction from Examination of the Products.*

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A detailed examination has been made of the size distribution of well-developed garnet crystals present in calcium carbonate-aluminosilicate rocks close to dolerite which had been intruded in the molten state. It was found that there was no trend of garnet size distribution or of unit-cell edge of the crystal with distance from the intrusion. The crystal-size distributions obeyed the equation  $\log [N/(100 - N)] = kr$ , where  $N$  was the number of crystals in the class of average radius  $r$  added to the number in all classes of radius greater than  $r$ . Furthermore, the product  $kr_1$  was equal to  $3.4 \pm 0.3$  for all three samples studied, where  $r_1$  was the radius for which  $d^2N/dr^2 = 0$ . Comparison of these results with similar results for other systems suggests that these distribution functions may be of more general applicability. Two, alternative, models are suggested to account for the crystal-size distribution.

IN the study of the kinetics of chemical reactions, information about the course of the reaction is usually derived from measurements of the amount of product and/or reactant, or of some factor determined by these quantities, at known intervals of time. Work of this type has led to the wide acceptance of kinetic laws which are applicable to a large number of chemical processes. It is not always possible, however, to follow the variation in amount of reaction with time. In the present work an attempt has been made to account for the relative frequency of occurrence of crystals of different sizes in the solid products of a reaction which occurred during the metamorphism of certain samples of rock. The system examined consisted of crystals of garnet embedded in a calcium carbonate-aluminosilicate matrix close to intrusions of dolerite which entered the limestone as a silicate melt. It appeared likely that the garnet was formed at the time of the intrusion of this melt and this, therefore, appeared to be a simple chemical system for detailed examination. The relative frequency of occurrence of garnet crystals (the product) having mean radii in classes defined by successive equal increments of radii were measured, and the resultant distribution was examined to see whether it could be accounted for by a reasonable model based on the kinetics of nucleation and growth of this new phase. The laws of nucleation and growth of product in the decomposition of pure solids, giving at least one gaseous product, have been reviewed by Jacobs and Tompkins.<sup>1</sup> A review of reactions between solids which do not involve gases (as is probable in the present system) has been given by Welch,<sup>2</sup> but experimental work in this field is often difficult. The object of the present work was to gain information about the kinetics and mechanism of a reaction solely from examination of the final products.

The comparatively easy separation of the components of the assemblage studied permitted investigation of whether the size of crystals in a solid could be deduced from measurement of the distribution of diameters of random cross-sections of these crystals. This problem has received some attention in metallurgy and is of importance in the study of solid products of reactions in the solid state.<sup>3,4</sup>

#### EXPERIMENTAL AND RESULTS

*Specimens Selected for Study.*—Samples were collected from a small limestone outcrop on the sea shore half a mile east of Portnoo harbour, Portnoo, Co. Donegal, Ireland. Garnet

<sup>1</sup> Jacobs and Tompkins, in "Chemistry of the Solid State," ed. Garner, Butterworths, London 1955, Ch. 7.

<sup>2</sup> Welch, ref. 1, Ch. 12.

<sup>3</sup> Scheil, *Z. Metallkunde*, 1935, **27**, 199.

<sup>4</sup> Rutherford, Aborn, and McBain, *Metals and Alloys*, 1937, **8**, 345.

crystals in the form of well-developed rhombododecahedra have grown in the limestone matrix in regions of the rock close to junctions between the limestone and the numerous dolerite intrusions. Examination of the rocks *in situ* showed no obvious systematic variation of garnet crystal size with distance from a neighbouring intrusion. Three samples were selected for detailed study; all were obtained from rock in the immediate vicinity of the limestone-dolerite interface, samples A and B actually including the interface. Samples A and B contained crystals up to 5 mm. radius; sample C contained a relatively larger number of smaller crystals.

*Samples A and B.*—The limestone matrix was dissolved in stages with acid, and the position of each crystal in each specimen, as defined by reference to three mutually perpendicular axes, was measured ( $x$  giving the perpendicular distance of the crystal from the intrusion interface,  $y$  and  $z$  being defined by the original surfaces of the specimen). The size of each, approximately spherical, crystal was measured on a gauge which consisted of a series of holes of equal increment of radius. 341 crystals from sample A and 154 crystals in sample B were studied. The distribution of relative numbers of crystals in size divisions defined by equal increments of

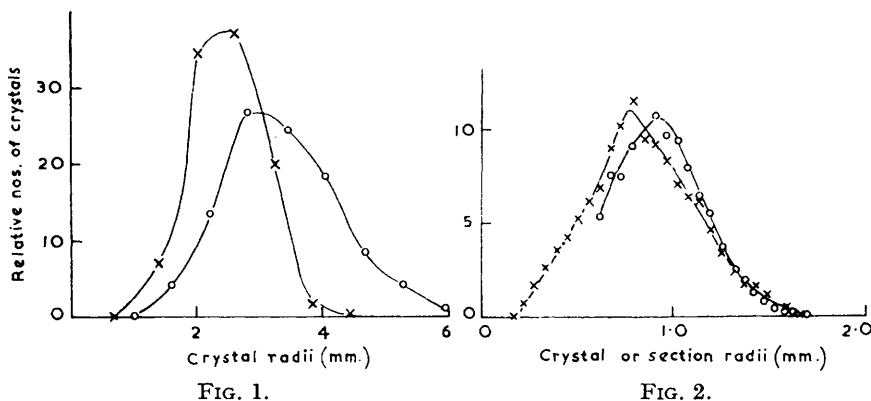


FIG. 1. Plot of relative numbers of crystals observed in groups of constant increase of radius plotted against radius for samples A (O) and B (X).

FIG. 2. Plot of relative numbers of crystals (O) and random cross-sections of crystals (X) observed in groups of constant increase of radius plotted against radius for sample C.

radius is shown in Fig. 1 (both sets of results scaled to total 100). A plot of the radius of each crystal against  $x$  gave a random scatter of points from which no trend of variation of crystal radius with  $x$  could be discerned.

*Sample C.*—With this sample the measured distribution of radii of random cross-sections of the crystals was compared with the actual distribution of radii. The original sample was cut into six specimens, each some 2 cm. thick, and the ten faces so exposed were ground flat and painted with lacquer, and photographic enlargements were made. The approximately circular cross-sections of the crystals appearing in the photographic enlargements, 2864 in all, were each fitted to the nearest-size hole of the gauge mentioned above and a radius distribution curve was constructed (Fig. 2).

Each specimen was then dissolved in acid and the single crystals of garnet obtained. 8291 crystals were measured in a gauge which consisted of two square-sectioned steel plates bolted on a firm base at an angle of about  $3^\circ$  and touching at one end. Each crystal was lightly pressed in the direction of the closed end and the crystal radius could then be read from a scale attached to one arm of the gauge. Fragmented crystals, and those sectioned crystals for which the radius could not be determined, were rejected. The smallest crystals in the specimen, which apparently occurred in small numbers only, could not be measured in this way and readings were extended only to the minimum radius at which reproducible results could be obtained. All six specimens gave very similar measured distributions, results obtained by both authors being closely comparable. Frequency-distribution curves for sections and for actual measurements of whole crystals are shown in Fig. 2.

*Composition of Garnets.*—X-Ray rotation photographs, with nickel-filtered  $\text{Cu-K}_\alpha$  radiation,

were taken of small fragments ( $\sim 0.5$  mm. edge cubes) of garnet crystal. From each sample (A, B, and C) a series of specimens was selected from the centre and the outside edges of individual crystals of different sizes, occurring at different distances from the limestone-basalt interface. The position of the  $h^2 + k^2 + l^2 = 216$  line on the photographs obtained from 78 different garnet fragments gave unit-cell edges of 11.890–11.915 Å. It is seen, therefore, that the cell edge of garnet is constant ( $11.90 \pm 0.01$  Å) throughout the system studied.

*Comparison of Random-section Radii Distribution with Directly Measured Crystal-radius Distribution.*—Measurement of the size of crystals in a solid is often difficult since the particles cannot be separated. Quantitative calculations for the determination of grain sizes from cross-sections have been discussed.<sup>3,4</sup> The system studied in the present rock was particularly favourable for comparison of a distribution calculated from cross-section measurements and that measured directly (see Fig. 2).

In the calculation the garnet crystals were treated as spheres. It was also assumed that the probability of cutting a crystal of unit radius, so that the section radius lies between  $a_1$  and  $a_2$ , is directly proportional to the perpendicular distance between two parallel planes cutting the crystal to give section radii of  $a_1$  and  $a_2$ . From the results in Fig. 2 it was found that the

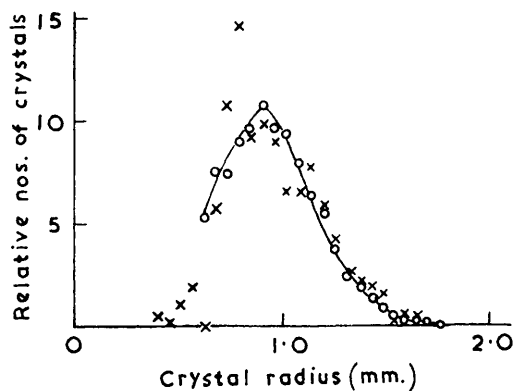


FIG. 3. Plot of relative numbers of crystals in groups of constant increase of radius plotted against radius, (x) as calculated (see text) from random cross-sections values in Fig. 2 and (o) as directly measured.

crystals in the largest-radius class contributed to 29 classes in all. On the above assumption, the fraction of these contributing to the largest-radius class may be calculated and compared with the value observed. It is then possible to calculate the contribution of this class to all classes of smaller radius. This calculation may then be repeated for the next lower class, after due allowance for contributions from the next-larger class. Successive somewhat extended calculations can thus be made to cover the complete range of sizes.

Each value thus found corresponds to the relative numbers of crystals with centres contained in a volume up to the distance equal to the radius of the group ( $r$ ) on each side of the plane; the relative numbers of crystals in each size class in unit volume of rock are found by division of each value by the corresponding value of  $r$ . Figures obtained in this way from the results in Fig. 2 are shown as crosses in Fig. 3 (direct measurement values are included on this plot). For the crystals of larger diameter, where the correction terms are small compared with the number of crystals in the group, reasonably good agreement is found between calculated and actual crystal-size distribution, in spite of the assumptions made in the calculations. At smaller diameters, however, the scatter of calculated results increases, probably owing to increase in importance of the correction terms for contributions from crystals of groups having large radii. It is seen from Fig. 3, however, that cross-section measurements show that there were comparatively few crystals in the classes considered (see above) too small for direct measurement.

The two curves in Fig. 2 are strikingly similar, the only significant difference being the slight change of the maximum to a smaller diameter in the sectioned crystals.

#### DISCUSSION

*Garnet Formation.*—The chemical composition of garnet is not uniquely defined by the unit-cell edge, but the almost constant value observed (11.90 Å) was between values

listed <sup>5</sup> for the calcium-rich garnet species, andradite (12.048 Å) and grossular (11.851 Å), which are end members of a solid-solution series. The absence of systematic variation of unit-cell edge with  $x$ , and of any variation in crystal-size distribution with  $x$ , in all three samples leads us to conclude that garnet was possibly formed by reaction of the elements present in the reactant matrix before the dolerite was intruded. It was considered that if diffusion of elements from the intruded material into the limestone were responsible for garnet formation this would result in systematic variation in numbers and composition of garnet crystals with distance from the interface. It is concluded that garnet was formed by reactions in the matrix under such influences as high temperature or partial pressures of water vapour or carbon dioxide at the time of the basalt intrusion.

Two alternative models can be proposed to account for the observations.

(1) *Probability model.* The result shown in Figs. 1 and 2, when plotted in the appropriate manner (see Waugh <sup>6</sup>), gave straight lines expected for normal distribution curves. This may be interpreted as showing that heating caused formation of garnet nuclei in a random manner throughout the reactant matrix. Each nucleus grew until completion of reaction by incorporation of the elements from the original matrix into the nearest growing crystal. On this model the ultimate size attained by each crystal on completion of reaction was controlled by the volume of the original reactant which provided elements for its growth (an approximately homogeneous reactant mixture is assumed). The radius of the domain that provides elements for the growth of any crystal is controlled by the mean distance to all nearest neighbours. It follows, therefore, that there will be a most probable value of domain radius, determined by nucleation density, and a preferred final crystal size. The probability of domains larger or smaller (and hence of crystal sizes larger or smaller) than average decreases rapidly with increasing deviation from the preferred value, so resulting in the observed crystal-size distribution which gives linear probability plots.

(2) *Nucleation and growth model.* In this section we attempt to account for the distribution of garnet size by a model based on reasonable assumptions concerning the laws of nucleation and growth. It is assumed that the rate of growth of a crystal is determined by temperature and concentration of reactants, but is independent of the size of the crystal. It follows, for crystals growing in an environment where diffusion of reactants is fast compared with the rate of consumption of reactant, that the final size of the crystal is a measure of the time during which it grew. The largest crystals were therefore nucleated early in the reaction and the smaller later, so that the relative numbers of crystals in the different size groups are interpreted as providing information about the course of the nucleation process.

On the above assumption the results shown in Figs. 1 and 2 lead us to conclude that nucleation was acceleratory in the early stages since greater numbers of nuclei are observed on going from larger to smaller crystals. It can reasonably be assumed also that during the early stages of reaction the concentration of reactant can be regarded as approximately constant. We suggest that this acceleratory behaviour is due to increase in temperature during the nucleation process. Each successive division of groups of crystals, therefore, represents nucleation which has occurred during decreasing time intervals. In order to simplify the equations which result from general consideration of the effect of increasing temperature on nucleation the assumption is made that the rate of increase in radius at any time during the reaction is proportional to a power of the reciprocal of the time interval since the first nuclei appeared in the system,  $dr/dt = k_1/t^\alpha$ . This conversion is intended to "correct" the system for the effect of increasing temperature, so that nucleation may be treated as a pseudo-isothermal reaction, by reduction of the

<sup>5</sup> Deer, Howie, and Zussman, "Rock Forming Minerals," Longmans, London, 1962, Vol. I, pp. 77—112.

<sup>6</sup> Waugh, "Elements of Statistical Method," McGraw-Hill, New York, 3rd edn., 1952, pp. 172—175.

“rate” by a factor which increases as reaction proceeds and offsets the effect of rising temperature. “*t*” is to be regarded as a measure of time intervals, but its magnitude is not determined in the present work.

The fraction of the total number of crystals which appear in each division of radius may be expressed under the corrected “isothermal” reaction as

$$\frac{dN}{dr} = \frac{dN}{dt} \cdot \frac{dt}{dr} = \frac{dN}{dt} \cdot k_2 t^\alpha,$$

where *dN* is the number of crystals occurring in any division *dr*, and *N* is the sum of all crystals in this division and divisions of greater value of *r*. *dN/dt* may be expected to depend on the concentration of reactant, which is a function of (100 - *N*), nucleation being treated as a rate process, and  $\sum_{r=0}^{\infty} N = 100$ . Isothermal nucleation in solids has been seen to fit an equation of the form  $N = k_3 t^\beta$ . Hence the nucleation equation may be written

$$dN/dr = k_4(100 - N)^x N^y,$$

where *x* and *y* are constants. Plots of  $\log [N/(100 - N)]$  against *r* give good straight lines (Fig. 4); hence it is experimentally found that for the present system *x* = *y* = 1. It is, therefore, concluded that under isothermal conditions the rate of nucleation was constant

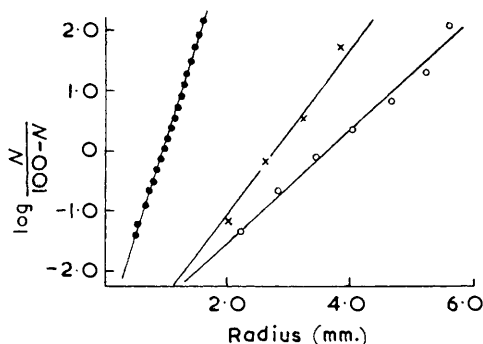


FIG. 4. Plot of  $\log_{10} [N/(100 - N)]$  against radius for samples A (○), B (×), and C (○); see text for definition of *N*.

(or possibly even deceleratory) on the “corrected” time scale. Reaction, however, represents a balance between nucleation and growth processes and the (100 - *N*) term is associated with a dependence of nucleation on a (100 - *N*) term greater than the rate of growth of existing nuclei.

The function,  $100k_4$  multiplied by radius at which  $d^2N/dr^2 = 0$  is defined as *K*. Values of *K* for the samples of the present system were nearly constant, results being (A) 3.4, (B) 3.7, and (C) 3.1, with a mean value of 3.4. This quantitative relation between the mean crystal radius and distribution about that radius shows that there is a high degree of order throughout the samples studied.

*Comparison with Other Systems.*—We have been unable to find quantitative information about the distribution of crystal sizes of naturally occurring minerals. A number of studies were undertaken, therefore, on rocks from different localities (to be published elsewhere). The results conformed to the same general pattern as the system discussed above and are briefly summarised in the annexed Table (some slight differences in technique

Locality	Type of rock	Distance from intrusion	No. of samples studied	Limiting values of <i>K</i>
Ardara (Ireland) .....	Al-Fe-Mg-Ca silicates	400 m.	6	2.44—2.82
Mallaig (Scotland) .....	“ ”	None near	10	1.00—1.50
Streamstown Bay (Ireland) ...	Limestone	200 m.	2	2.14—2.26
Portnoo (Ireland) .....	System discussed above	<10 cm.	3	3.1—3.7

were necessarily employed for the different systems). It is clear that the reactions forming garnet in these very different rock types result in similar size-frequency distributions. Furthermore, values of  $K$  are constant for different samples from the same small locality but vary for different localities.

It is suggested that the different values of  $K$  from different localities may be due to different rates of heating, so that the balance of reaction between the two processes has been changed in favour of the reaction having the greater energy of activation (*i.e.*, possibly nucleation) in rocks which were heated more rapidly, if it is supposed that both nucleation and growth obey the Arrhenius law with different energies of activation.

*Conclusions.*—While it is not possible to decide yet which model is correct, it is believed that the nucleation-and-growth model provides a more complete description of the reaction. The similarity of results found for the three samples of the present work and those for very different reactant systems suggests that some common factor influences the nucleation and growth of garnet in a number of widely different rocks. Further work may lead to a more detailed theory of the type here outlined, based on chemical principles. Chemical laws, particularly equilibrium and phase-rule studies have found extensive application in geological systems: the present work represents an attempt to apply the principles of chemical kinetics to the study of the micro-structure of rocks.

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