

# METAMORPHISM OF MINERALS<sup>1</sup>

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## ABSTRACT

The sources of the energy which drives metamorphism are discussed. It is pointed out that an important source of energy which is almost universally overlooked by the geologist is the strain energy which arises from plastic deformation of crystals. Theoretically, this energy ought to be capable of causing metamorphism when released either by annealing or by contact with solvent fluids. The remainder of the paper is devoted to demonstrating experimentally that metamorphism can be caused by this means, and to deriving the laws governing the process. An important feature is that no recrystallization occurs unless a critical temperature, which is characteristic of the particular crystal species, and which varies with the intensity of plastic deformation, is exceeded. Experiments are also cited in which recrystallization following plastic deformation is caused to occur with the aid of solvent fluids.

## THEORETICAL BACKGROUND

The fact that something changes to something else in any kind of metamorphism shows that the new system has lower energy than the old. For the present discussion, let us exclude the kinds of metamorphism which are concerned with a change of over-all composition of the metamorphosed material. Then the energy drop which drives the metamorphic process must come from a difference in the free energy of the old set of crystals and the free energy of a new set. This energy drop can be realized in an obvious way for polymineralic aggregates. For such instances, metamorphism implies that under the conditions of the metamorphic environment a new set of minerals,  $U, V, W, \dots$  has a lower net energy than the old set of minerals,  $A, B, C, \dots$ .

But metamorphism also takes place in monomineralic aggregates. In this case, the new collection of minerals is the same as the old collection. What drives the metamorphic process in such instances? At least two forms of energy are available to differentiate the beginning from the end aggregates: surface energy and strain energy. Thus, a fine-grained aggregate could be metamorphosed into a coarse-grained one, with a reduction of the net surface energy of the aggregate. Or, a strained aggregate could be metamorphosed into an unstrained one, with a net reduction in the strain energy of the aggregate.

The latter scheme is of particular importance because strain is an inevitable consequence of plastic deformation. This has been known since some of the earliest work on the plastic deformation of single crystals. For example, Johnson customarily determined the planes along which

<sup>1</sup> Read at the annual meeting of The Mineralogical Society, Pittsburgh, December 27, 1945.

translation-gliding took place in the transparent crystals he investigated, by observing the strain-anisotropism which arose from the deformation.<sup>2</sup> The strain is localized in the immediate neighborhood of the functional planes along which the gliding takes place. As early as 1930 one of us suggested that these strains were part of the cause of the recrystallization which accompanies metamorphism.<sup>3</sup>

It is thus evident that a plastically deformed mineral aggregate contains strain energy. The strain has the form of bending and other kinds of distortion of the crystal structure, especially in the neighborhood of the functional gliding planes. If a mineral which is so deformed is subjected to conditions under which a transfer of its matter is possible, it will distill, or dissolve, so that its matter comes to be added to a strain-free crystal or crystals. To have this transfer take place, it is only necessary to heat the strained mineral until its vapor pressure gives rise to an appreciable transfer of material from strained to unstrained crystals. Alternatively, the transfer may be accomplished by placing the strained mineral in a fluid in which it is slightly soluble. Either means provides the vehicle for transfer of matter from strained to unstrained crystal, and hence induces recrystallization.

#### EXPERIMENTAL MATERIAL

Guided by this reasoning, extensive experimental work has been undertaken in artificially metamorphosing monomineralic aggregates. For the first trials, minerals were selected which were known to be rather plastic, and whose subsequent heating would not be complicated by chemical decomposition to any appreciable extent. The minerals fluorite, periclase, and anhydrite appeared well suited in these properties. (Lists of the plastic characteristics of minerals are available.)<sup>4</sup> Thus fluorite has 3 planes and 6 directions of translation-gliding; periclase has 6 planes and 6 directions; while anhydrite has 3 planes and 2 directions. The planes of anhydrite are known to visibly crinkle when the mineral is plastically deformed.

#### GENERAL EXPERIMENTAL PROCEDURE

Since it is easier to plastically deform small crystals than large ones, deformation is readily accomplished with powders. For this purpose,

<sup>2</sup> Johsen, A., Biegungen und Translationen: *Neues Jahrb. f. Min., Geol., u. Pal.*, II, 148-150 (1902).

<sup>3</sup> Buerger, M. J., Translation-gliding in crystals: *Am. Mineral.*, 15, 46 (1930).

<sup>4</sup> Characteristics of crystals which undergo translation-gliding are given in: M. J. Buerger, Translation-gliding in crystals. *Am. Mineral.*, 15, 61-64 (1930).

A compilation of the characteristics of crystals which undergo twin gliding was also prepared by M. J. Buerger, and was published by Bell: *HANDBOOK OF PHYSICAL CONSTANTS*, G. S. A. *Special paper* No. 36, pp. 120-121 (1942).

powders finer than 170 mesh proved to be suitable. When compressed in a piston and cylinder device at pressures which can easily be obtained by commercial presses (about 5000 atmospheres) plastic deformation is induced throughout the smallest grains and is also induced in at least the corners and edges of the larger grains.

The aggregate so treated now possesses strain energy. To release this energy it is merely necessary to raise the temperature to such a level that atoms or groups of atoms can migrate from one crystal to another. This permits differential migration in the direction of unstrained crystals. A few hours proved sufficient to make the migration appreciable.

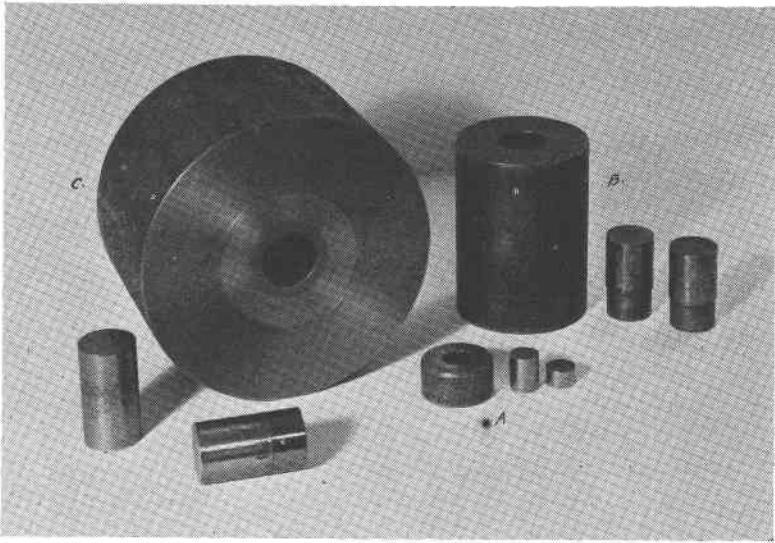


FIG. 1

## EXPERIMENTAL EQUIPMENT

Experimental metamorphism can be produced with the aid of rather simple laboratory equipment. To produce the plastic deformation of the original powder, simple piston and cylinder sets are used, Fig. 1. Ordinary high chrome, high carbon steel cylinders, 5/8 inch I. D., Fig. 1A, are satisfactory for deforming rather plastic materials such as anhydrite, fluorite and periclase. When the material is to be deformed at elevated temperatures, nitrided steel cylinders, Fig. 1B, are required, since the surface of this material retains its hardness at elevated temperatures. For plastically deforming powders of hard minerals such as corundum, it was found necessary to use dies made of tungsten carbide, Fig. 1C. All surfaces of the dies which come in contact with the material to be deformed are lapped and polished to nearly a mirror finish.

The required pressures using the 5/8 inch diameter die are easily obtained with a simple hydraulic press of 20 tons capacity, equipped with a gauge indicating the total pressure on the piston, Fig. 2. The platens of the press can be protected from damage by the die by means of two surface-hardened steel plates about three inches square.

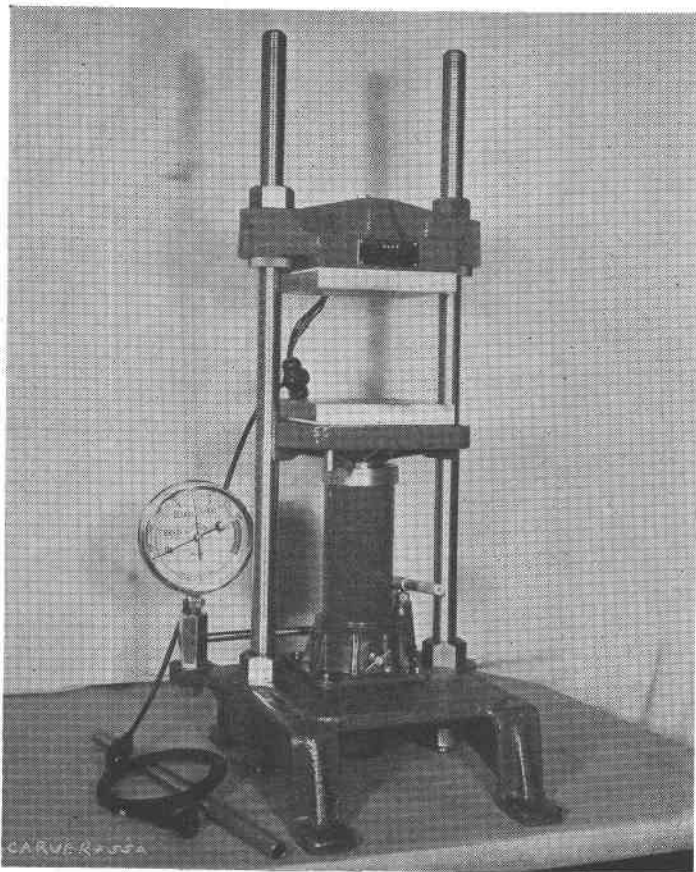


FIG. 2

The annealing is conveniently carried out in an ordinary muffle furnace. In our experiments a globar muffle furnace was used, with temperature indicated by a platinum-13% rhodium thermocouple.

#### PRELIMINARY EXPERIMENTS

It has already been pointed out that anhydrite is plastic. Furthermore some earlier work by one of us had indicated that anhydrite had an ap-

preciable vapor pressure in the neighborhood of 1200° C. Thus anhydrite was known to have characteristics favorable to a preliminary experiment in artificial metamorphism, and accordingly the first experiments were carried out with anhydrite.

Some finely powdered anhydrite was plastically deformed by compressing it at 40 tons per square inch. When ejected from the die the compressed powder was in the form of a coherent slug. This was annealed at 1200° C. for two hours. Ordinary visual examination of the slug then revealed that it had undergone a thorough recrystallization, and this observation was abundantly confirmed by an examination of a thin section.

We do not labor the details of this preliminary experiment. It is easy to duplicate simple thermal metamorphism experimentally.

The qualitative success of this preliminary experiment, which was based strictly on the ratiocination outlined in the first section, suggested a further investigation of the process of recrystallization, with emphasis on some of the quantitative aspects of the phenomenon.

For the next set of experiments, fluorite was selected as the appropriate crystal material. The reasons for this change of material were as follows: Anhydrite had shown a tendency to decompose on annealing. It might be expected to decompose to a greater extent at higher temperatures and longer annealing times. To avoid any complications imposed by possible decomposition while annealing, another mineral was selected which was known not to decompose. The selection of the particular material was further guided by the knowledge that isometric substances, if plastic, are very plastic because of the large number of symmetrically equivalent planes and directions of gliding. Among the several plastic isometric substances,<sup>4</sup> fluorite was known to be reasonably stable at temperatures approaching the melting point, so it appeared to be a natural choice for the experiments. It is true that fluorite deposits of metamorphic origin are apparently not known, but this was not regarded as a drawback for the material since we were seeking to find some of the general laws of this kind of metamorphism, and not trying merely to produce something to artificially duplicate a natural occurrence.

#### FLUORITE

*Preliminary Investigation.*—Preliminary experiments, following the lines of the original experiment with anhydrite, made it clear that fluorite could be caused to recrystallize in the same way, Fig. 3. In these and subsequent experiments hand-picked fluorite from Rosiclare, Illinois, was used. This was reduced to pass 170 mesh.

We first wished to get some quantitative idea of the rate at which the

recrystallization takes place with change of annealing temperature. To this end we plastically deformed a number of slugs of fluorite powder by pressing them all at 40 tons per square inch. These were all heated for the same time, namely 10 hours, but each was annealed at a different temperature. The temperature range from 1600° F. to 2200° F. was covered in steps of approximately 100° F. In a general way it was visually evident that increasing temperature of annealing brought about increasing grain size in the recrystallized product. We now sought to measure this grain size.

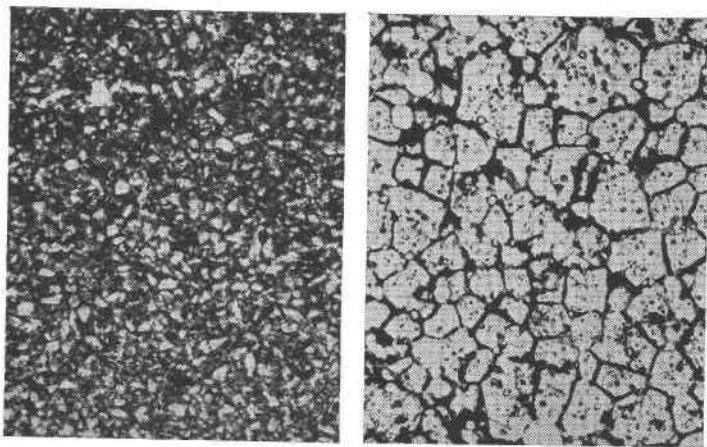


FIG. 3. The recrystallization of fluorite. Left: thin section of specimen made by pressing powder at 40 tons per square inch. Right: thin section of similar material after recrystallization caused by annealing (both  $\times 25$ ).

We first thought that thin sections would permit us to measure the dimensions of the grains. It turned out that, while thin sections were of some aid in studying specimens annealed at 2000° F. and higher, they were not very helpful for specimens annealed at lower temperatures. This was because the unrecrystallized material constituted a dust-like interstitial cement between the recrystallized grains, and such fine material is not easy to study in thin section.

We then turned to polished sections and sought an appropriate etch to reveal the grain boundaries. After considerable experimentation it was found that the grain boundaries could be brought out by immersing the polished section for 5 seconds in hot concentrated sulfuric acid. In Fig. 4 is shown a series of photographs of typical sections etched in this way. The course of recrystallization is made apparent by this series. The low-

est temperature sections are characterized by the angular grains of the original plastically deformed slug with fine interstitial flour. At increasing temperatures the angularity decreases and the flour vanishes until the section shows a mosaic texture of equant grains.

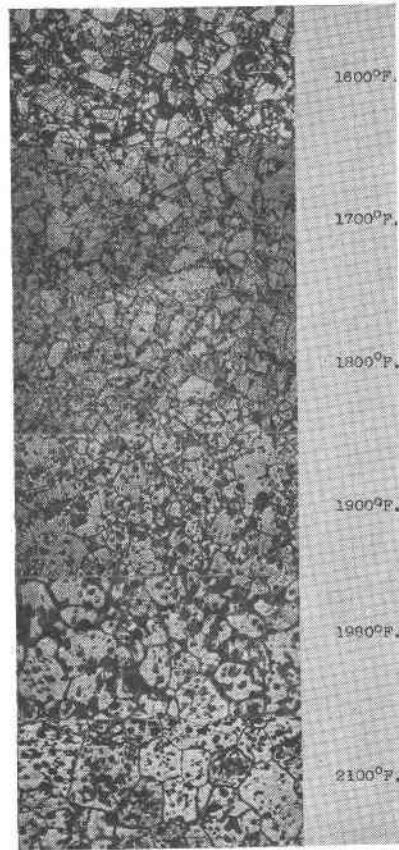


FIG. 4. The effect of temperature on recrystallization. Polished sections of fluorite etched with hot concentrated sulfuric acid to bring out grains. All samples were deformed at 40 tons per square inch and subsequently annealed 10 hours at the temperatures indicated ( $\times 50$ ).

It is not an easy matter to make grain-size measurements in mixtures of angular grains and interstitial flour. For this reason we do not regard our measurements as very accurate, but they do give an indication of the trend of recrystallization. They are shown in graphical form in Fig. 5.

*Determination of the Onset of Recrystallization.*—A neat way was developed for investigating certain aspects of grain growth. This consisted in studying the *x*-ray powder photograph of the recrystallized aggregate

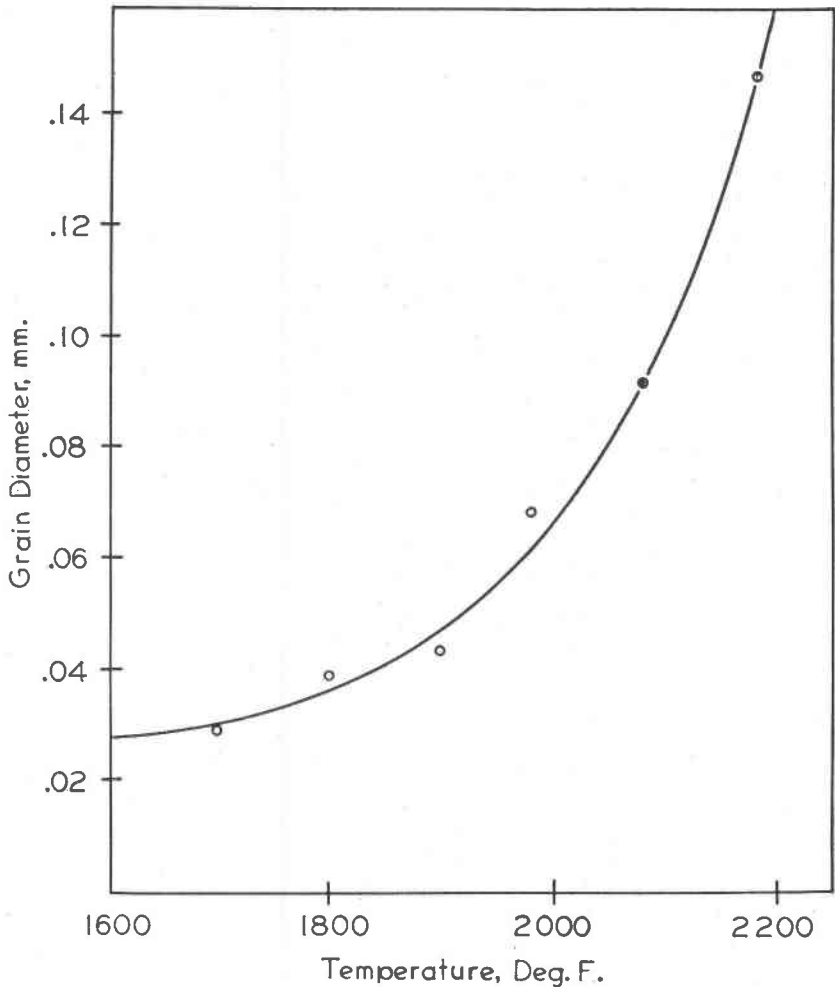


FIG. 5. Grain diameter as a function of annealing temperature. (Fluorite powder pressed at 40 tons per square inch; annealing time, 10 hours.)

according to the features discussed in the next paragraph. For this purpose the entire sample was made in the form of a small pin of such dimensions as to constitute a suitable sample for direct insertion into a standard *x*-ray powder camera.



The white component of the characteristic  $x$ -radiation produces Laue spots in the ordinary powder photograph provided that the specimen is not rotated.<sup>5</sup> If the crystals are strained, Laue spots are known to display asterism,<sup>6</sup> i.e., they are elongated into streaks. This is due to a bending of the Bragg reflecting planes, which is a manifestation of the strain in the crystal. When the strain is relieved, the asterism disappears from the spots and they assume normal appearance. Thus, by heating the specimen to various temperatures and watching the Laue-spot aspect of the powder photograph of the resulting sample, the temperature at which the strain becomes relieved can be determined.

The monochromatic component of the  $x$ -radiation produces the ordinary Debye lines. As the crystal grains of the sample grow by recrystallization, the number of crystals in the sample decreases. This causes the lines to become discontinuous and to break up into a series of beads. Each bead represents the reflection of a single crystal. As recrystallization continues, these beads increase in size, but decrease in number, indicating that the crystal size of the aggregate is increasing.

A part of such a sequence for fluorite powder pressed at 40 tons per square inch and annealed at various temperatures for three hours is shown in Fig. 6. It will be observed that the specimen annealed at 1600° F. shows asterism of the Laue spots near the center of the photograph, while for specimens annealed at temperatures higher than 1700° F. the asterism has disappeared. Furthermore, grain growth, as indicated by the disappearance of continuous Debye lines, is marked in specimens annealed above temperatures of 1800° F. in this series. This information is consistent with that shown in Figs 4 and 5.

*Effect of Time on Recrystallization.*—From the experiments just described one concludes that there is a definite temperature above which a deformed mineral aggregate must be heated before its strain begins to be relieved. The question naturally arises whether a longer time of annealing at a lower temperature would not bring about the same result. To test this question, specimens were deformed by the same amount and annealed at different times for each of a series of temperatures. It was found that annealing below 1700° F. for as long as 24 hours produced no apparent recrystallization of fluorite deformed at 40 tons per square inch.

These experiments confirm the conclusion that for a given amount of plastic deformation there is a critical temperature above which the material must be heated for any recrystallization to take place. To antic-

<sup>5</sup> Buerger, M. J., The design of  $x$ -ray powder cameras: *Jour. Appl. Phys.*, **16**, 508, Fig. 6C (1945).

<sup>6</sup> Schiebold, E., Die Verfestigungsfrage vom Standpunkt der Röntgenforschung: *Zeit. Metallk.*, **16**, 417-425 (1924).

ipate, it has been found that this temperature differs from mineral to mineral and is characteristic of a species. It is easy to rationalize this. The critical temperature is that which just supplies the energy to move material from one crystal to another over the potential barrier provided by its attachment to the crystal structure. It is therefore characteristic of the structure.

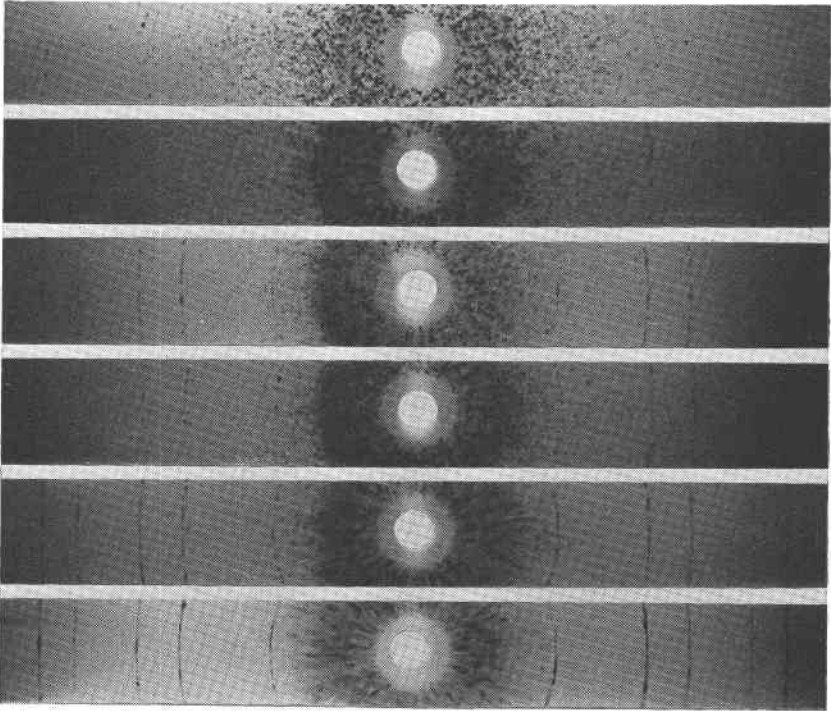


FIG. 6. Series of x-ray powder photographs of fluorite samples annealed at 1500°, 1600°, 1700°, 1800°, 1900°, and 2000° F. (from bottom to top).

*Effect of Intensity of Plastic Deformation.*—The above discussion suggests that the critical temperature might be varied with the severity of plastic deformation because the barrier energy is a function of the crystal structure energy. The latter should be lower for severely deformed structure.

That this is indeed the case is evident from Fig. 7, which graphically shows the results of a series of experiments designed to investigate the change of the strain relief point with intensity of deformation. It will be observed that the higher the pressure of deformation (and therefore the

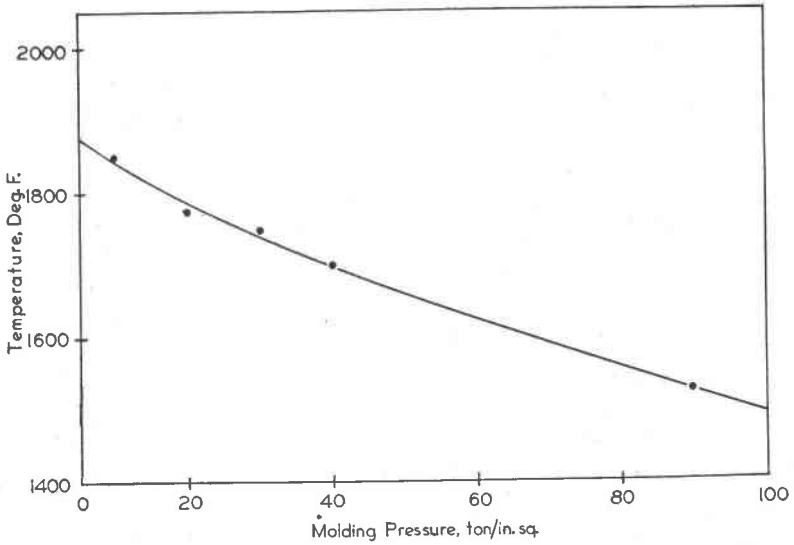


FIG. 7. The reduction of the critical temperature with the intensity of plastic deformation for fluorite.

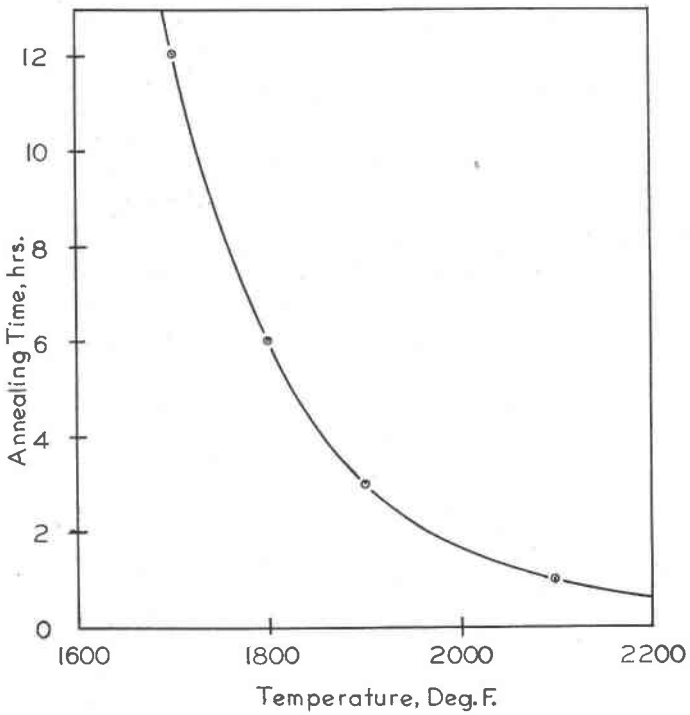


FIG. 8. The time necessary to relieve all traces of strain caused by plastic deformation. (Fluorite powder pressed at 40 tons per square inch.)

more severe the plastic deformation), the lower the critical temperature.

*Time Necessary to Relieve Strain.*—It is interesting to inquire into the time of annealing necessary to remove all traces of strain from the deformed specimen. This can be judged by the vanishing of the last traces of asterism of the Laue spots on the powder photograph of the specimen. Data obtained from fluorite powder pressed at 40 tons per square inch is plotted in Fig. 8. It will be noted that the curve of time of complete relief of stress trends more or less asymptotically toward about 1650° F. This is consistent to the finding that approximately 1700° F. is the critical temperature for this pressure.

#### PERICLASE

Periclase is another isometric mineral which is known to be plastic.<sup>4</sup> Since it is harder than fluorite it was expected that it would be more

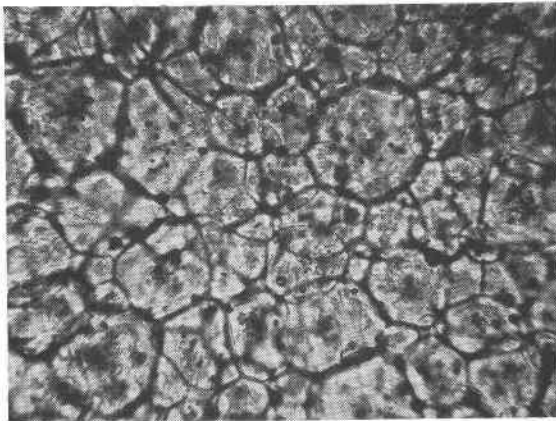


FIG. 9. Thin section of recrystallized periclase ( $\times 260$ ). The plastic deformation was furnished by pressing powder at 40 tons per square inch; the recrystallization occurred on annealing for 6 hours at 1500° C.

difficult to deform than fluorite and this proved to be the case. It was not found possible to obtain a large supply of natural periclase so artificial material made by the Norton Company in Worcester, Massachusetts, was used. The material used was a powder which passed 170 mesh.

The experimentation on periclase was not so extensive as that on fluorite, but followed the same general lines. It will suffice here to state that the critical temperature was determined to lie in the neighborhood of 2200° F. for deformations resulting from pressures of 40 tons per square inch. Figure 9 is a photograph of a thin section of recrystallized MgO.

## OTHER MATERIALS AND EXPERIMENTAL VARIATIONS

In addition to the minerals anhydrite, fluorite, and periclase, above discussed, we have also successfully recrystallized corundum, BeO, and certain other materials. Corundum, though very hard, was known to be plastic.<sup>4</sup> Because of the abrasive quality of such hard material, tungsten carbide dies are used.

We have also performed the plastic deformation part of the metamorphic scheme at temperatures up to 500° C. using nitrided dies. The resistance to deformation falls off very quickly with increasing temperature. Furthermore we have performed the recrystallization part of metamorphism with the aid of solvent fluids at greatly reduced temperatures. In later contributions we plan to give further information on the experimental results.

## CONCLUSIONS

The following general conclusions can be drawn from the experimental work on artificial metamorphism:

(1) A mineral will not recrystallize in the absence of solvents unless it is heated to at least a critical temperature.

(2) For the same initial conditions, this critical temperature varies with the mineral, and is characteristic of it.

(3) The critical temperature of recrystallization decreases for increasing initial deformation.

(4) Time does not affect the critical temperature of recrystallization within the limits studied.

(5) Time does affect the extent of crystal growth, the crystal dimensions increasing with time provided that the critical temperature is exceeded.

(6) Provided that the critical temperature is exceeded, rapidity of crystal growth increases with temperature, other factors being equal.