

75 percent of the annual heating load (9). By comparing the availability of solar energy with total heating requirements on a daily basis, we then computed the daily backup energy requirements for the solar heating systems. The resulting load duration curves (cumulative frequency distributions) of daily backup energy requirements are shown for the four sites in Fig. 2, a through d. The curve labeled "0 percent" corresponds to the conventional (nonsolar) case; the other three curves correspond to solar systems sized to meet 25, 50, and 75 percent of the annual heating load.

In Fig. 2, the backup energy requirement is normalized to the maximum daily heating load observed over the SOLMET period of record (usually the point corresponding to 1 day in 23 years). Although the assumption of no day-to-day storage carry-over, used in the calculation of solar output, is strictly accurate only for the subset of coldest days, the dashed portions of the curves have been included to show the results of a continuation of the same calculation procedure over all days with a positive heating load. The logarithmic scale along the horizontal axis provides greater detail over the period of coldest days.

Except for the Albuquerque site, there is little reduction in backup requirements of the solar systems relative to the power requirements of the conventional (nonsolar) system. Even for solar systems sized to supply 75 percent of the annual space heating load, backup requirements are usually in excess of 85 percent of the peak day requirement for the nonsolar system. For Albuquerque, the capacity reductions were approximately 10, 18, and 25 percent for solar systems sized to supply 25, 50, and 75 percent of the annual heating load, respectively.

J. G. ASBURY
C. MASLOWSKI
R. O. MUELLER

*Energy and Environmental Systems
Division, Argonne National Laboratory,
Argonne, Illinois 60439*

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Experimental Coarsening of Antiphase Domains in a Silicate Mineral

Abstract. Combined annealing experiments and observations by transmission electron microscopy show that in natural pigeonite crystals antiphase domains coarsen approximately according to a rate law in which the tenth power of the average domain size is proportional to time. This result suggests that certain cations (possibly Ca^{2+}) were segregated preferentially onto the antiphase boundaries. The domain size in samples quenched from above the high-low transformation temperature is large and apparently independent of annealing time and temperature. It appears that large domains can be generated either by very fast or by very slow cooling; thus the estimation of geological cooling rates from the sizes of antiphase domains in natural samples becomes rather difficult.

The low-calcium clinopyroxene pigeonite has been of interest to mineralogists both because of its transformation behavior and because of its potential as an indicator of thermal history for many lunar and terrestrial rocks. Optical and electron optical studies have revealed a variety of fine-scale structures in natural specimens (1). Exsolution of augite (a calcium-rich clinopyroxene) is commonly found and may occur by spinodal decomposition or nucleation and growth (2). During very slow cooling pigeonite may transform to the low-temperature orthopyroxene structure, but, if this reconstructive transformation fails to occur, then an alternative, displacive transformation takes place which results in a symmetry change from $C2/c$ (high pigeonite) to $P2_1/c$ (low pigeonite) (3, 4). The temperature of this high-low transformation is composition-dependent (5), and it gives rise to antiphase domains (APD's) related by $1/2(\mathbf{a} + \mathbf{b})$ (3) which have frequently been observed by transmission electron microscopy (6).

Attempts have been made to use the size of APD's as a measure of the relative cooling rates of natural rocks (7). Rapid cooling is expected to give the smallest domains because the nucleation rates are higher and the time available for coarsening is less than under conditions of slow cooling. There are, however, several complicating factors. Heterogeneous nucleation of APD's at suitable high-energy sites such as host-precipitate interfaces can give deceptive-

ly large domain sizes (8). The transformation temperatures vary with composition so that APD sizes may also be composition-dependent. Furthermore, it has been postulated that segregation of Ca^{2+} onto the antiphase boundaries (APB's) may occur (3); such a preferential segregation would affect the domain growth kinetics and hence the observed APD sizes. This certainly appears to be the case in slowly cooled specimens (9).

I present here the early results of an experimental study that was undertaken in an attempt to shed some light on these problems and to establish a quantitative relationship between thermal history and APD size. There are wider implications, however, in that the kinetics of APD coarsening in ordered metallic alloys have been extensively studied and a simple rate law has been determined (10-13), but the same law has not been tested for silicate minerals.

Theoretically, APD's should coarsen according to the relation (10):

$$\delta^n - \delta_0^n = nK_0 e^{-(Q/RT)} t \quad (1)$$

where δ is the average domain diameter, δ_0 is the initial domain diameter, K_0 is a constant, Q is the activation energy for domain coarsening, R is the universal gas constant, T is the absolute temperature, t is time, and n is a constant, ideally equal to 2.

Domain boundaries are effectively defects with an associated excess free energy. The driving force for coarsening arises from the decrease in energy

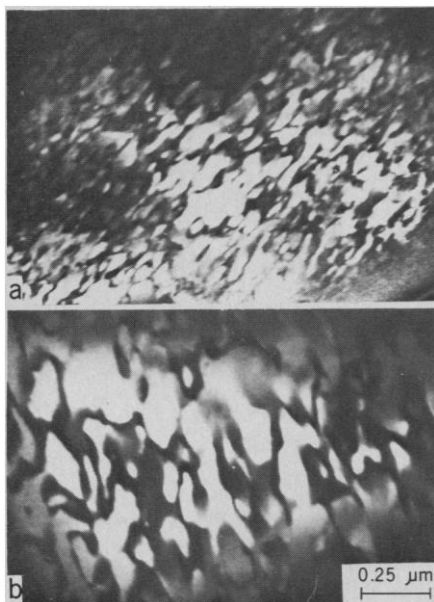


Fig. 1. Antiphase domains in Weiselberg pigeonite (imaged in dark field using an $h + k$ odd reflection): (a) before heat treatment and (b) after annealing at 750°C for 30 days.

achieved by the reduction in the total APB surface area. This areal dependence results in an ideal value of $n = 2$, independent of the material in which the APD's exist. For small initial domain sizes, isothermal coarsening fits $\delta^2\alpha t$, as in Cu_3Au (10, 11), Ni_3Fe (12), and Fe-Co-2V (13). Deviations from $n = 2$ have been ascribed to the concentration of excess or impurity atoms at the APB's (14, 15).

Pigeonite crystals for the experiments were separated from a porphyritic andesite from Weiselberg, Germany (16). Their compositions were determined by electron probe microanalysis and fell in the range $\text{En}_{41}\text{Fs}_{50}\text{Wo}_9$ to $\text{En}_{46}\text{Fs}_{46}\text{Wo}_8$ (where En is enstatite, Fs is ferrosilite, and Wo is wollastonite). Chemical zoning was minimal. Batches of crystals (~ 20 mg) were wrapped in platinum foil and sealed in evacuated silica tubes to which some powdered graphite was added to ensure a low oxygen fugacity. These charges were annealed at $745^\circ \pm 5^\circ\text{C}$ (CP75), $854^\circ \pm 5^\circ\text{C}$ (CP85), or $950^\circ \pm 5^\circ\text{C}$ (CP95) in vertical platinum or kanthal-wound furnaces for up to 32 days; they were quenched by being raised out of the furnaces and then dropped into cold water. The crystals invariably emerged as clean as they had been before heat treatment, and no sign of any reaction between them and their platinum envelopes was detected. They were mounted in epoxy resin and thinned by the action of an ion beam (titanium grids were used for support) before being examined with an electron microscope (AEI model EM6G) operating at 100 kV.

The average domain size (δ) was taken as the arithmetic mean of 300 to 500 APD's in a total of between two and five crystals, each domain length and width being taken as the distance between intercepts of APB's on straight lines approximately parallel and perpendicular to the c axis. The parent material contained APD's with an average size of 500 by 850 Å, with the long dimension approximately parallel to c . Exsolution was not found in the unheated crystals, and the only effect of annealing was to coarsen the APD's (Fig. 1).

The experimental results are given in Fig. 2. The slopes of straight-line fits to the 750°C and 850°C data are between 0.08 and 0.13 for both the long and the short dimensions (Fig. 2a); this result suggests that isothermal coarsening follows a rate law with $\delta^n\alpha t$ and $n \approx 10$. It also fits Eq. 1 because δ_0^{10} is small relative to δ^{10} . This behavior represents a considerable deviation from the ideal behavior and implies that there is some impediment to coarsening. In view of earlier discussions (3, 9), segregation of Ca^{2+} onto the APB's seems to be the most obvious explanation. The activation energy obtained from an Arrhenius plot is between 100 and 120 kcal mole $^{-1}$ but cannot be treated too seriously because of the limited data (two points only). It is, however, comparable to the activation energy reported by McCallister (17) which may arise from the diffusion of Ca^{2+} in iron-free clinopyroxene (99 ± 2 kcal mole $^{-1}$) and to the value for Ca self-diffusion in wollastonite (αCaSiO_3 , which has a similar type of structure), 112 kcal mole $^{-1}$ (18).

The magnitude of possible experimental errors is illustrated in Fig. 2b for the 750°C data. The size distribution in individual crystals is log-normal in character, as in Cu_3Au (19), and the difference in APD size measured from different areas in a single crystal is minimal as compared with the variation between crystals. This scatter is probably due to slight variations in composition and is carried through from the starting material. The errors as shown may be exaggerated in that a separate series of measurements at $\sim 750^\circ\text{C}$ led to essentially the same coarsening law. In any case, the important conclusion is not so much the precise value of n in Eq. 1 as that it differs significantly from 2, which it does even if the most extreme interpretation of the errors is used.

The APD sizes in pigeonites annealed at 950°C are large (~ 1300 by 2600 Å) and, within experimental error, independent of annealing time. Two heat treatments, at $1000^\circ \pm 10^\circ\text{C}$ for 7 days

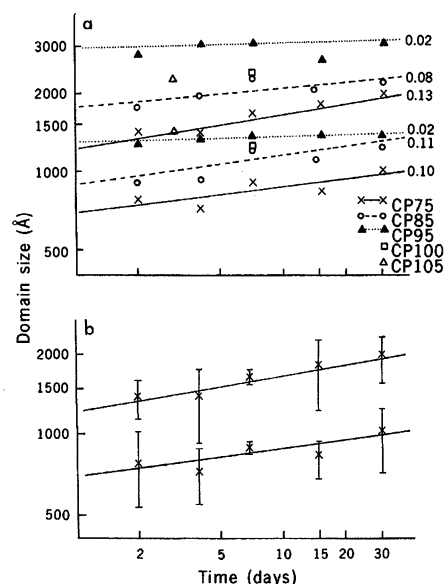


Fig. 2. (a) A log-log plot of the variation of domain size with time. The large dimension for each sample is the average length (approximately parallel to the c axis), and the smaller dimension is the average width. Slopes of straight lines fitted by the least-squares technique are given on the right. Heat treatments of samples CP75, CP85, CP95, CP100, and CP105 were made at $\sim 750^\circ$, 850° , 950° , 1000° , and 1050°C , respectively. (b) Data at $\sim 750^\circ\text{C}$ plotted to illustrate possible errors. The error bars represent two standard deviations for the average domain size averaged between different crystals. The starting material and all the experimental products showed similar standard deviations.

and $1050^\circ \pm 10^\circ\text{C}$ for 3 days, gave similar domain sizes. The high-low transformation temperature must be close to that determined for Mull pigeonite, $930^\circ \pm 30^\circ\text{C}$ (4), which has almost identical composition ($\text{En}_{38}\text{Fs}_{52}\text{Wo}_9$). It therefore seems that the final size of APD's in the crystals heated close to or above this value is independent both of annealing time and temperature and the observed large domains must form during quenching. X-ray studies of pigeonites experimentally quenched from high temperatures indicate the same effect as $h + k$ odd reflections from them are found to be sharp (20) whereas for crystals with small APD's they are diffuse (3).

Morimoto (1) suggested that during rapid quenching there is insufficient time for Ca^{2+} to segregate onto APB's and so there is easy boundary mobility. Extension of this argument leads to the suggestion that large domains can develop either by extremely fast cooling or by coarsening during slow cooling. Intermediate cooling rates, leading to glassy or fine-grained rocks in geological situations, result in small domain sizes because of the restriction imposed on APB motion by segregated Ca^{2+} ions. A geological example of extremely rapid cool-

ing could be the lunar sample described by Brown and Wechsler (21) who, to explain the large apparent APD size, suggested that a period of reheating had occurred although this reheating is now clearly not essential.

The isothermal coarsening kinetics of APD's in pigeonite provide good evidence of impurity segregations onto APB's. In metallic alloys, such segregations have given values of n between 2 and 4 (15). The higher value for pigeonite implies a more severe restriction of APB mobility. There is a fundamental difference between metals, in which the domains arise by atomic ordering, and pigeonite, in which they arise from a displacive transformation. Structural distortions at APB's in pigeonite may provide more suitable sites for the location of particular cations. Ions other than Ca^{2+} , however, may also restrict APB mobility in pigeonite. During heat treatments without graphite, some crystals became slightly oxidized and had smaller domain sizes than those heated for the same time and at the same temperature in the presence of graphite. The slower growth rate could be due to the segregation of Fe^{3+} or vacancies onto the APB's.

Unfortunately, it is not likely that any simple quantitative relationship between domain size and cooling rate can be established on the basis of the results presented here. There appear to be too many variables, particularly relating to the behavior of Ca^{2+} . Even on a qualitative basis, it may be difficult to interpret APD sizes in terms of thermal history without substantial additional evidence.

MICHAEL A. CARPENTER*

Department of Mineralogy and Petrology, Cambridge University, Cambridge, England

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* Present address: Department of Geological Sciences, Harvard University, Cambridge, Mass.

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Carbon-14 Dating of Small Samples by Proportional Counting

Abstract. Conventional carbon-14 dating by means of gas proportional counters has been extended to samples containing as little as 10 milligrams of carbon. The accuracy of the dating procedure has been checked by dating sequoia tree-ring samples of the 1st century A.D. and B.C. and an oak tree-ring sample of the 19th century A.D.

The advantages of small sample size in carbon-14 dating are evident. In the authentication of works of art, for example, milligram sampling might be permissible in many cases where the removal of as much as a gram of sample would not. In archeological dating it often happens that only small samples are available, which must be totally consumed in order to obtain the data.

Recently a series of studies have demonstrated the feasibility of ^{14}C dating of small samples by means of a procedure consisting of the production of carbon ions in a specially designed source, acceleration of these ions in a Van de Graaff electrostatic accelerator (1-3) or a

cyclotron (4, 5), reversal of the ion charge (in the Van de Graaff) to provide an effective decontamination from ^{14}N , magnetic and electrostatic selection, and finally direct counting. The method has been used for trial dating studies (2, 5) and would appear to be of enormous potential, especially for the dating of very old or very small samples. On the other hand, this method does require a machine which is expensive both to purchase [about \$500,000 (3)] and to operate; for best results it would appear that such a machine should be "dedicated," that is, designed, built, and used for no other purpose (3).

We describe here some new develop-

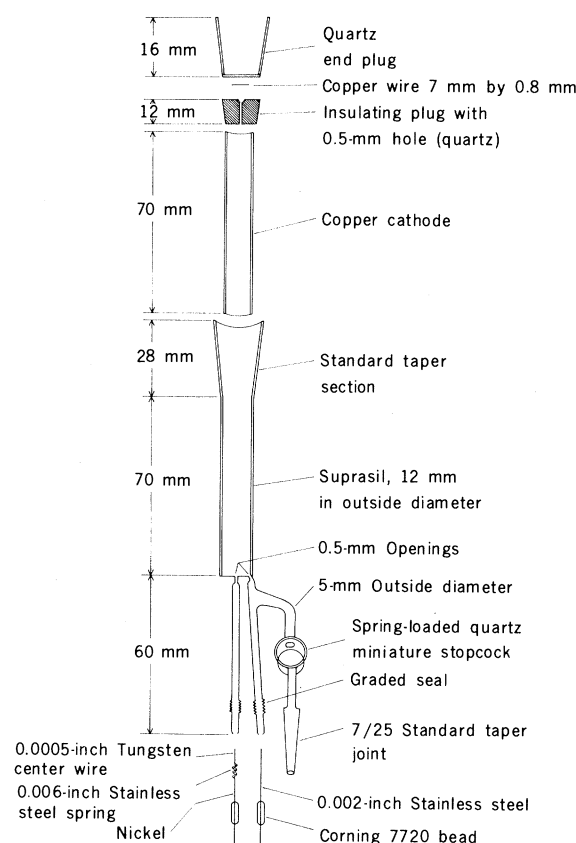


Fig. 1. Construction details for the 5-cm² counter for ^{14}C .