carbonate dissolution is slow, and because low pH facilitates carbonate dissolution, it appears logical to suppose that the major part of apparent oxygen utilization takes place first and that in turn favors carbonate dissolution. In addition, R. M. Pytkowicz and D. N. Connors [*Science* **144**, 840 (1964)] showed that high hydrostatic pressure (500 atm) near the sea floor increases the apparent solubility product of calcium carbonate by twice that at sea surface. Their study supports that carbonate dissolution is favored even after seawater sinks down to the depth whereas apparent oxygen utilization goes on while the water is sinking.

4. The fundamental equation used to obtain Eq. 1 is

$\Sigma\ CO_2 = [H^2 + HK_1' + K_1'K_2'/$
$\qquad\qquad (H + K_2')\ K_1']Alk$

where H is hydrogen ion concentration, K_1' and K_2' are the first and second apparent dissociation constants of carbonic acid in seawater. Its derivation is given by K. Park [*J. Oceanogr. Soc. Japan* **21**, 54 (1965)]. The term (106/138) in Eq. 2 is from the model by F. A. Richards [in *Chemical Oceanography*, J. P. Riley and G. Skirrow, Eds. (Academic Press, London, 1965), vol. 1, p. 624] of biochemical oxidation of organic matter; that is, $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \rightarrow$ $106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4$. Here, we see that an oxygen depletion of 138 molecules is accompanied by the increase of 106 molecules of carbon dioxide in seawater.
5. The apparent dissociation constants used are those of K. Buch [*Havsforsk. Inst. Skr. Helsing.* **151**, 6 (1951)], at 19 parts per thousand chlorinity and 25°C (shipboard temperature for the pH determination).
6. Changes in specific alkalinity and ratio of alkalinity to chlorinity provide an estimate of the extent of carbonate dissolution. Dissolution of 0.1 mmole/liter of carbonate mineral increases specific alkalinity by 0.1. At my hydrographic station, the surface specific alkalinity was 0.128, while at 4000 m it was 0.133. Therefore, when we take the surface condition as our reference, the deep water dissolution of carbonate is 0.05 mmole/liter.
7. R. M. Pytkowicz [*Geochim. Cosmochim. Acta* **31**, 63 (1967)] pointed out that, within a seawater turnover time of 1000 years, the carbonate cycle rather than the silicate cycle is the primary pH buffering agent in the ocean.
8. Supported by NSF grants GA-1281 and GP-5317 and by ONR contract Nonr 286(10).

5 August 1968

Orientation of Nuclei Produced under Nonhydrostatic Stress

Abstract. *Recrystallization of a material involves two distinct processes: critical nuclei are produced; these then grow into much larger crystallites. The present theory predicts the distribution of nuclei in orientation and the effect of growth on this initial distribution. The results are in good qualitative agreement with experiments.*

In most cases, the recrystallization of a material occurs through heterogeneous nucleation. The size of the critical nuclei depends on the conditions under which nucleation takes place. In the present report we are concerned with the *orientation* of the nuclei and not with their size and concentration, which are assumed known.

As usual, we assume that the stress in the material has the same value at every point and that the temperature is uniform and constant during nucleation. [It was pointed out by Kamb (*1*) that for such an imposed stress field, a body of arbitrary shape and orientation and arbitrary elastic properties is always in stable equilibrium.] A nucleus can be considered as a macromolecule; its orientation distribution is then given by a generalized Boltzmann's law (for an ensemble with given temperature and stress field). From a macroscopic point of view the same distribution is easily obtained from fluctuation theory (*2*). Let us call W the minimum work required to create a nucleus of a given orientation from the host (material within which nucleation occurs). The probability of having such an orientation is proportional to (*2*) $\exp - W/kT$. In general, W includes a surface term which represents the work of formation of the surface. We neglect the influence of this term on orientation in the pres-

ent theory: we can properly do so if the host is isotropic. (In practice, the host often behaves like an isotropic material if it is composed of many crystals randomly oriented.) Furthermore, we shall see that for *nonhydrostatic* stress, terms proportional to the volume of the nucleus enter W. In that case, the interaction with the host, which is only proportional to the surface of the nucleus, may have a negligible effect on orientation (for large enough nuclei) even if the host is a monocrystal. Notice that for hydrostatic stress the orientation of nuclei must be random if the interaction with the host plays no role. Notice also that, by definition, isotropic nuclei cannot have a preferred orientation.

We define a system of coordinates (S) fixed with respect to the host and call $\overline{\sigma_{mn}}$ the stress tensor measured in this system of coordinates. Since $\overline{\sigma_{mn}}$ has the same value at every point of the material (independently of the nucleus orientation), the principal axes of the stress tensor can always be taken as the (S) axes. Normally the three principal stresses are negative, that is, they are three compressions. We also define another system of coordinates (Σ) attached to each nucleus. The orientation of a nucleus is then defined by the usual Euler angles (*3*) (θ, ϕ, ψ) of the system (Σ) attached to that nucleus, with respect to the system (S). We call s_{ijkl} the

fourth-order tensor of the compliance coefficients measured in the (Σ) frame of reference. This tensor is then the same for each nucleus independently of its orientation. We denote by σ_{mn} and e_{mn} the stress and strain tensors also measured in system (Σ) (they depend on the nucleus orientation). If we call u_{ij} the cosine of the angle formed by the ith and jth axes of the (Σ) and (S) systems, respectively, then

$$\sigma_{mn} = u_{mp}\ \overline{\sigma_{pq}}\ u_{nq} \qquad (1)$$

With these notations the strain energy F, per unit volume of nucleus, is

$$2F = s_{ijkl}\ \sigma_{ij}\ \sigma_{kl} \qquad (2)$$

which can be expressed in terms of the fixed stress tensor $\overline{\sigma_{pq}}$ and the nucleus orientation through Eq. 1. As the molecules, originally part of the host, take the orientation of the nucleus, the corresponding change in strain energy gives a first term contributing to W. A second term represents the work performed by the fixed stress field as the change in orientation takes place (*2*). If the change in orientation leads to an increase (decrease) in volume this last term is minimum, since W must be minimum, if only the smallest (largest) of the applied compressions performs work. Call $(-\ \overline{\sigma})$ this compression (in either case) and define the Gibbs potential per unit volume, G

$$2G = e_{ij}\ [\sigma_{ij} - \overline{\sigma}\ \delta_{ij}] \qquad (3)$$

G is obviously related to one of Kamb's chemical potentials. Notice that $\overline{\sigma}$, which in Kamb's case can be any of the principal stresses, is exactly defined in the present theory. If G_0 is the Gibbs potential per unit volume for the host and V the volume of the nucleus, then

$$W = V\ [G - G_0] \qquad (4)$$

Then the probability density ρ for a nucleus to have the orientation (θ, ϕ, ψ) is

$$\rho\ (\theta, \phi, \psi) = A\ [\exp - W/kT] \qquad (5)$$

A is a normalization constant given by

$$A^{-1} = \iiint [\exp - W/kT]$$
$$\sin\theta\ d\theta\ d\phi\ d\psi \qquad (6)$$

the element of "volume" in the (θ, ϕ, ψ) space being $\sin\theta\ d\theta\ d\phi\ d\psi$. It is checked at once from the foregoing equations that, as expected, ρ is a constant when the stress is hydrostatic or the embryo isotropic. Notice that the *maxima* of ρ (most probable orientations) correspond

to *minima* of the Gibbs (or chemical) potential.

There exist no experimental data as yet on the orientation of nuclei, with which the theory can be compared directly. After nucleation, nuclei grow into much larger crystallites. The final orientation distribution of crystallites depends on the initial distribution of nuclei, the growth law, and the time during which growth is allowed to proceed. The kinetic transformation of nucleus into a crystallite is not completely understood. Kamb (*1, 4*; see also *5*) was able to predict that the preferred growth orientation corresponds to a *minimum* of the Gibbs potential, that is, it coincides with one of the most probable orientations of the nuclei. We can describe qualitatively the effect of growth on the initial nucleus distribution. If the Gibbs potential is minimum for only one orientation, the initial and final distributions remain similar. The only effect of growth is to sharpen the distribution (that is, the standard deviation decreases), since the most probable nucleus orientation is favored even further by growth. If the Gibbs potential has several minima, one minimum corresponding to the fastest growing orientation wil be selected at the expense of the others. (The process described above will then be repeated for that minimum.)

For instance, consider the case of α-quartz being recrystallized into β-quartz. For simplicity take $\overline{\sigma_{xx}} = \overline{\sigma_{yy}}$, $\overline{\sigma_{zz}}$ being slightly different, with $|\overline{\sigma_{zz}}| > |\overline{\sigma_{xx}}|$, and call $\overline{\sigma'_{zz}} = \overline{\sigma_{zz}} - \overline{\sigma_{xx}}$ (for this simple case, G and ρ are obviously independent of ϕ). It can be checked at once that β-quartz has a larger volume than α-quartz (*6*), hence we must take $\overline{\sigma} = \overline{\sigma_{xx}}$. Then Eq. 3 reduces to

$$2G = \overline{\sigma'_{zz}}^2 [s_{ijkl}\, u_{iz}\, u_{jz}\, u_{kz}\, u_{lz}] \quad (7)$$

which for β-quartz becomes (*6*) (up to a constant which does not affect ρ)

$$2G = [.12 \sin^2\theta - .25 \sin^4\theta]$$
$$\overline{\sigma'_{zz}}^2 10^{-12} \, \text{dyne/cm}^2 \quad (8)$$

We check at once that G is minimum for $\theta = 0$ and $\theta = \pi/2$ (notice that W is independent of ψ as well as ϕ). Taking plausible values for V and $\overline{\sigma'_{zz}}$ completes the determination of ρ. For instance, if $V \sim 10^9$ (angstroms)^3, $\overline{\sigma'_{zz}} \sim 100$ bars, we find standard deviations of a few degrees around the most probable orientations. Reliable results on β-quartz recrystallization have been reported by Green (*7*). Indeed, it

is found that for moderate growth, crystallites are distributed around $\theta = 0$ and $\pi/2$ with standard deviations of a few degrees. As expected for moderate growth, the distribution of crystallites is close to the distribution of nuclei. It is also clear from the experiments (*7*) that growth favors the direction $\theta = 0$. In particular, if the specimen is annealed, the distribution of large crystallites around $\theta = 0$ is extremely sharp. Small crystallites, on the other hand, that are less affected by growth, are not so strongly oriented (*7*).

Preliminary data (*7*) on α-quartz can also be easily interpreted in the light of the theory. It can easily be checked that the distribution of nuclei in orientation for α-quartz happens to be essentially independent of the choice of $\overline{\sigma}$. Hence we need not concern ourselves with the sign of the change in volume during the recrystallization. For α-quartz (again up to an irrelevant constant and taking, for instance, $\overline{\sigma} = \overline{\sigma_{xx}}$), we have (*6*)

$$2G = [.86 \sin^3\theta \cos\theta \cos\psi$$
$$(\cos^2\psi - 3 \sin^2\psi) - .22 \sin^2\theta +$$
$$.56 \sin^4\theta]\, \overline{\sigma'_{zz}}^2 10^{-12} \, \text{dyne/cm}^2 \quad (9)$$

G now depends on ψ as well as θ. Experimentally only the distribution of c-axes is given (*7*). This corresponds to the marginal distribution in θ, obtained by integrating ρ over ψ. It is easier and qualitatively correct to replace ψ by the value that makes G minimum. Then

$$2G \simeq [- .86 \sin^3\theta \,|\cos\theta\,| -$$
$$.22 \sin^2\theta + .56 \sin^4\theta]$$
$$\overline{\sigma'_{zz}}^2 10^{-12} \, \text{dyne/cm}^2 \quad (10)$$

In the present case G, given by Eq. 10, is minimum for only *one* value, $\theta_0 \simeq 47°$ (the direction $\pi - \theta_0$ is, of course, essentially the same solution). The standard deviation is again of a few degrees (taking the same V and $\overline{\sigma'_{zz}}$ used earlier for β-quartz). Growth will make the distribution sharper but the orientation of the crystallites will remain centered around $\theta = \theta_0$ as checked by experiments (*7*).

In conclusion, the distribution of nuclei in orientation computed from the present theory is consistent with experimental results. Once a reliable growth law is known it will be possible to compute the final distribution of crystallites exactly by using the initial distribution of nuclei as determined here. The influence of the initial distribution is more important when growth is allowed to proceed only a short time. The initial distribution is centered around the *minima* of the Gibbs potential and is sharper for big nuclei, large deviatoric stress, and soft materials.

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8. I acknowledge helpful discussions with Profs. N. L. Carter and R. Vaisnys, Yale University.

7 August 1968 ∎

Multiple Forms of Bacterial NADP-Specific Isocitrate Dehydrogenase

Abstract. *Electrophoretically distinct forms of nicotinamide adenine dinucleotide phosphate–specific isocitrate dehydrogenase have been observed in extracts of* Escherichia coli *grown under different culture conditions. In glucose-grown cells, two distinct bands of isocitrate dehydrogenase activity were observed on polyacrylamide gels and have been completely resolved by employing ion-exchange chromatography. These multiple forms of the enzyme have been studied and their possible metabolic role is discussed.*

Recent studies in our laboratory have demonstrated the existence of two electrophoretically distinct NADP-isocitrate dehydrogenases (*1, 2*) in extracts obtained from *Escherichia coli*, strain E-26, grown aerobically in a simple mineral salts medium containing glucose as the sole carbon source (*3*). In this report, we describe the chromatographic separation of these two forms of the enzyme and present further evidence for the existence of multiple forms of bacterial NADP-specific isocitrate dehydrogenase.