[AMERICAN JOURNAL OF SCIENCE, VOL. 253, OCTOBER 1955, PP. 574-579]

INTERFACIAL TENSIONS AND THE MEASUREMENT OF STRESS DIFFERENCES IN METAMORPHIC ROCKS*

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ABSTRACT. Consideration of the thermodynamics of surfaces shows that, under conditions of chemical equilibrium, the interfacial tensions between minerals in metamorphic rocks can be used to measure the differences between the principal compressions.

From measurements on oriented pyrite euhedra in metamorphic rocks of the Chester Dome, Vermont, it appears that the difference between the maximum and minimum compressions could hardly have exceeded 1000 baryes (1 millibar) during the final stages of the main metamorphic crystallization. Kyanite, a so-called "stress" mineral, is apparently capable of survival under such almost hydrostatic conditions. The measurements also suggest that the average interfacial tension between pyrite and the observed adjacent minerals within the plane of schistosity is from ½ to ⅓ that between pyrite and adjacent minerals perpendicular to the schistosity.

"Familiarity is the opiate of the imagination."—Toynbee

INTRODUCTION

In many areas of regionally metamorphosed rocks there is considerable evidence that chemical equilibrium was closely approached under the conditions of metamorphism. This equilibrium can in general be assumed to have applied to systems whose volumes are well represented by the areas of thin sections, although, in some cases, it is evident that the condition of approximate equilibrium probably applies to considerably smaller, less regularly shaped volumes. Although interfaces are commonly ignored in considering such problems of chemical equilibrium, it is of interest explicitly to include them. There is considerable evidence of their importance (Turner and Verhoogen, 1951, p. 511-513). Further, such phenomena as ellipsoidal pebbles, flattened in the plane of bedding schistosity, and boudinage in many areas of regionally metamorphosed rocks suggest that, at least for the competent beds, approximately irrotational pure shear strain has resulted from symmetrically disposed shearing stresses. These shearing stresses can alternatively be considered as three principal compressions oriented at right angles to each other (Furry, Purcell, and Street, 1952, p. 89). It is the purpose of this paper to show that, under the equilibrium assumption, it is possible to use the interfacial tensions of a crystal with the habit of a rectangular prism to measure the *differences* between the principal compressions in a metamorphic rock.

NOTATION

a, b, c	linear dimensions of crystal (fig. 1)
1, 2, 3	subscripts denoting surface perpendicular to a, b, and c respectively
σ	surface phase indicated by subscript
P	external compression normal to face indicated by subscript
γ	interfacial tension (Helmholtz free energy per unit area) for face indicated by subscript[1]

* This paper is derived in large part from a Harvard doctoral dissertation entitled "Geology of the southern part of the Chester Dome, Vermont." It is intended to be the first of several papers dealing with interfacial properties and the fabric of metamorphic rocks.

[1] Actually, as can be seen in plate 1, the interfacial tensions must be somewhat variable on the faces, dependent on the nature and relative orientation of both adjacent minerals and interfaces. The variations on a particular face cannot have been large because the

X	internal compression normal to face indicated by subscript
V	volume
V′	volume of internal phase
V″	volume of external phase(s)
F	Helmholtz free energy
F_V	volume term of Helmholtz free energy
F_σ	surface term of Helmholtz free energy

Use of the Helmholtz free energy seems most convenient for reactions involving surfaces alone because, under the most reasonably assumed geologic conditions (constant temperature, volume, and composition), it leads to interesting conclusions.

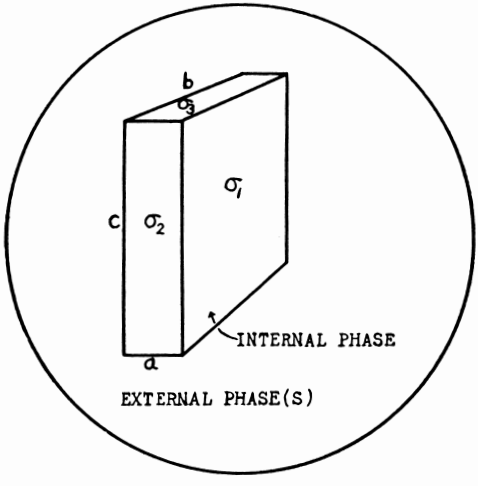


Fig. 1. Schematic diagram for treatment of the interrelationship between the interfacial tensions and the principal compressions.

THEORY

For constant values of temperature, composition, interfacial tensions, and total volume for the system, it follows that

$$dF_V = -XdV' - PdV'' = -(X-P)\,dV' \qquad (1)$$

inasmuch as the total volume is constant (i.e. $dV' = -dV''$).

Also,

$$dF_\sigma = \Sigma(\gamma dA). \qquad (2)$$

Hence,

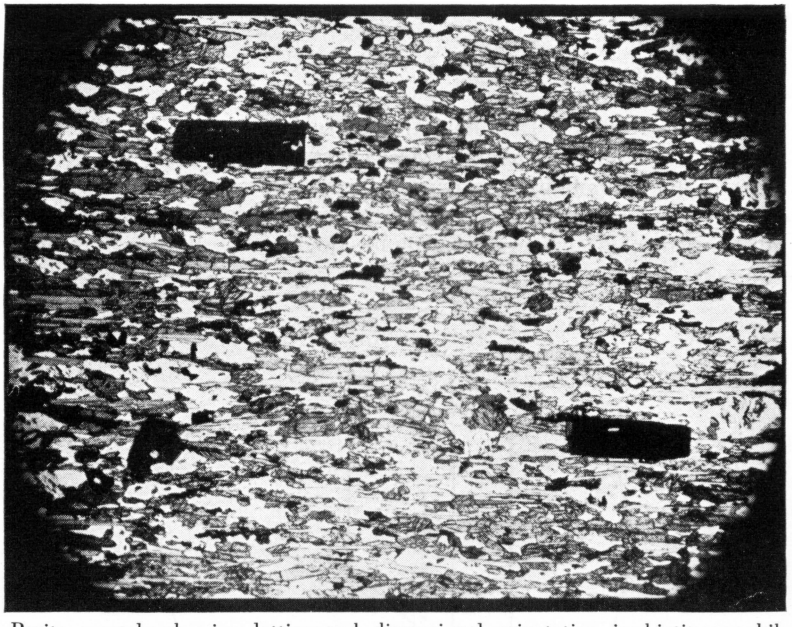
$$dF = -(X-P)\,dV' + \Sigma(\gamma dA). \qquad (3)$$

Since, under equilibrium conditions, the Helmholtz free energy is minimum (i.e. $dF = 0$), it follows that:

$$(X-P)\,dV' = \Sigma(\gamma dA). \qquad (4)$$

faces are relatively plane (see Shuttleworth, 1952, p. 347). It would seem reasonable to assume further that the average values for the interfacial tensions of similarly oriented faces in a rock of relatively constant mineralogical composition should be approximately constant.

PLATE 1



Pyrite crystals showing lattice and dimensional orientation in biotite amphibolite from south end of Rattlesnake Mountain in Townshend, Vermont. Magnification = 16X.

Let us consider the case of σ_1 moving a uniform normal distance da while b and c remain constant. Then,

$$(X\text{–}P)\ dV' = (X_1\text{–}P_1)\ bc\ da$$

and

$$\Sigma(\gamma dA) = 2(\gamma_3 b + \gamma_2 c)\,da.$$

Hence,

$$(X_1\text{–}P_1)\ b\ c\ da = 2(\gamma_3 b + \gamma_2 c)\,da$$

or

$$(X_1\text{–}P_1) = 2(\gamma_3/c + \gamma_2/b). \tag{5a}$$

Similarly,

$$(X_2\text{–}P_2) = 2(\gamma_3/c + \gamma_1/a) \tag{5b}$$

and

$$(X_3\text{–}P_3) = 2(\gamma_2/b + \gamma_1/a). \tag{5c}$$

Since an internally stressed solid is not stable (Gibbs, 1906, p. 197),

$$X_1 = X_2 = X_3. \tag{6}$$

Thus:

$$(P_1\text{–}P_2) = (X_1\text{–}P_2) - (X_1\text{–}P_1) = 2(\gamma_1/a\text{–}\gamma_2/b) \tag{7a}$$

and

$$(P_2\text{–}P_3) = 2(\gamma_2/b - \gamma_3/c) \tag{7b}$$

and

$$(P_1\text{–}P_3) = 2(\gamma_1/a - \gamma_3/c). \tag{7c}$$[2]

[2] Equations 7a, b, and c are basically similar in form to Shuttleworth's equation D.4, which he applied to the equilibrium of a thin loaded polycrystalline wire at elevated

If $(P_1-P_2) = (P_2-P_3) = (P_1-P_3) = 0$ (i.e. the pressure is hydrostatic), then,

$$\gamma_1/a = \gamma_2/b \text{ or } \gamma_1/\gamma_2 = a/b, \tag{8a}$$

and

$$\gamma_2/b = \gamma_3/c \text{ or } \gamma_2/\gamma_3 = b/c, \tag{8b}$$

and

$$\gamma_1/a = \gamma_3/c \text{ or } \gamma_1/\gamma_3 = a/c. \tag{8c}$$

Hence,

$$\gamma_1/a = \gamma_2/b = \gamma_3/c, \tag{9}$$

which represents Wulff's law (Seitz, 1940, p. 97) for the case considered. Wulff's law is derived as a special case of a more general law.

It can be shown by further reasoning that, if the linear dimensions of the crystals of a particular mineral stand in constant ratio regardless of the values of these linear dimensions, then the differences between the principal compressions must have been negligible at the time of crystallization. Thus, from (7a),

$$P_1 - 2\gamma_1/a = P_2 - 2\gamma_2/b$$

or

$$a/b = \frac{(P_1-P_2)\,a - 2\gamma_1.}{-2\gamma_2} \tag{10}$$

It is evident that, for a/b to remain constant, the variable term, (P_1-P_2) a, must reduce to zero. For different finite values of a, this can occur only when $(P_1-P_2) = 0$. Under such circumstances, in accord with (8a), the linear dimensions of the crystal stand in the ratio predicted by Wulff's law. It is likewise clear from equation (7a) that, if $P_1 > P_2$, the ratio a/b will get smaller as the crystals get larger, assuming the interfacial tensions to be constant. Thus the larger crystals would tend to show more distortion than the smaller crystals if there were differences among the principal compressions. This latter effect is somewhat analogous to that in an example familiar to almost everyone, that a large drop of quicksilver shows more departure from a spherical shape than a small one (Bragg, 1925, p. 93-94).

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temperatures (Shuttleworth, 1952, p. 346). Thus his equation D.4 is

$$mg = 2\pi r\,[\gamma_S - (2r/L)\,\gamma_B],$$

where m refers to the suspended mass, g is the gravitational acceleration, r is the radius of the crystal, L is the length of the crystal, and the subscripts S and B refer to the surfaces and intercrystalline boundaries respectively. If both sides of D.4 are divided by the cross-sectional area of the wire, the following expression results:

$$mg/\pi r^2 = P_S - P_B = 2(\gamma_S/r - 2\gamma_B/L),$$

which is analogous to equations 7a, b, and c in the text above.

OBSERVATIONS AND DISCUSSION

If equation (10) and the assumptions underlying it are correct, then the final crystallization in many areas of regionally metamorphosed rocks must have occurred under approximately hydrostatic conditions. Table 1 represents measurements of pyrite crystals having the habits of rectangular prisms from quartz-sericite schist of the Savoy formation (Emerson, 1917, p. 42) about one mile south-southeast of West Townshend, Vermont. All the crystals were flattened in the plane of schistosity, and each had an a axis normal to the schistosity. There was no apparent preferred orientation of a axes within the schistosity. From table 1 it is apparent that the crystals are approximately square in the plane of schistosity. Because of the approximately uniaxial symmetry, the ratio $a(cb)^{-1/2}$ (i.e. the ratio of the shortest dimension to the geometric mean of the two longest dimensions) seems most useful in comparing the normal compression to that in the plane of schistosity. In table 1 it is apparent that there is no striking relationship between size of crystal and the ratio between the linear dimensions. Substitution of maximal values for γ_1 and γ_2 (ca. 1000 ergs cm^{-2} and 2000 ergs cm^{-2}) in equation (10) suggests that variations in the ratios of linear dimensions of pyrite crystals of different observed sizes should be easily observable for values of (P_1-P_2) greater than 1000 baryes (one millibar). Equation (10) suggests further that the interfacial tension of the face perpendicular to the schistosity is approximately twice that of the face within the plane of schistosity in accord with Wulff's law.

TABLE 1

Measurements of Pyrite Crystals in Savoy Formation, Townshend, Vermont

No.	a (cm)	b (cm)	c (cm)	$a(cb))^{-1/2}$	Volume ($cm^3 \times 10^{-3}$)
1	0.171	0.348	0.353	0.485	21.1
2	0.164	0.314	0.323	0.515	16.6
3	0.126	0.271	0.286	0.452	9.8
4	0.129	0.223	0.241	0.554	6.9
5	0.110	0.208	0.259	0.475	5.7
6	0.122	0.195	0.211	0.600	5.0
7	0.093	0.175	0.185	0.516	3.0
8	0.079	0.155	0.169	0.488	2.1
9	0.053	0.131	0.178	0.346	1.2
			Average = 0.492		

Plate 1 shows similarly oriented pyrite crystals in amphibolite from the west limb of the Chester dome near the village of Townshend, Vermont, about 0.2 mile northwest across strike from a locality of conglomeratic gneiss with pebbles approximately discoidal in the plane of schistosity (average ratio = 1.26:1:0.08). Since the ratios between the linear dimensions of the pyrite crystals do not appear to show variation with size, the assumption of approximately hydrostatic conditions during the final stages of recrystallization is apparently valid at this locality also. In this case the ratio between the interfacial tensions was about 1:3 according to equation (10). These pyrite crystals are found in an area where rocks of appropriate composition contain kyanite,

a so-called "stress mineral." The kyanite is apparently capable of survival under almost hydrostatic conditions.

It might be asked why an isometric mineral of cubic habit should, under conditions of hydrostatic equilibrium, depart from equidimensionality. It does so because γ varies greatly with orientation of the surface relative to the crystallographic axes and "in such a manner as to have a large number of sharply defined minima" (Gibbs, 1906, p. 316). Were this not true, crystals would not necessarily show faces under equilibrium conditions, because, for a crystal of constant volume, $d\Sigma(\gamma A)$ must equal zero or the sum, $\Sigma(\gamma A)$, must equal the lowest possible value. Indeed, solution of these equations leads to Wulff's law.[3] In an isotropic medium, such as liquid (e.g. magma) or gas, a crystal of cubic habit should therefore be equidimensional because the qualities of all the cube faces would be identical. Such equidimensionality might also be expected where a crystal grows in a more finely crystalline medium devoid of preferred orientation. When a crystal is growing in a medium in which the fabric is oriented, however, (e.g. most metamorphic rocks), the qualities of the interface should vary both with the *orientation of the crystal* relative to the orientation of the contacting minerals and the *orientation of the interface* relative to the crystallographic axes. That interfaces of relatively low interfacial tension should commonly be oriented normal to the maximum compression will be discussed in a subsequent paper.

ACKNOWLEDGMENTS

The writer would like to acknowledge the benefits received in stimulating discussions with G. J. F. MacDonald, E-an Zen, J. Gilluly, and J. B. Thompson, Jr. Dr. Louis Lund of the Physics Department at Missouri School of Mines and Metallurgy kindly checked the writer's calculations. He is grateful to Professors E. S. Larsen, Jr., M. P. Billings, and H. E. McKinstry for their early supervision and criticism of the general research, of which the material herein is part. Bruce Doe has offered helpful suggestions in regard to exposition. No discredit should accrue to any of the above for any erroneous ideas that might have been expressed; they are the sole responsibility of the writer.

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[3] Wulff's law could be expressed as follows: The perpendicular distance of a face from the center of a crystal is directly proportional to the interfacial tension of that face. It seems clear that Gibbs had this law in mind some years before Wulff (see Gibbs, 1906, p. 322, lines 21-24).