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THE THERMODYNAMICS OF THE EARTH'S CRUST

I

Preliminary Survey of the Principal Forces and Reactions in the solid Crust.

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Introduction.

During field studies and theoretical considerations of metamorphism and metasomatism I have arrived at the opinion that the apparently so multifarious and intricate processes of metasomatism are led by very simple principles. By recognizing these principles, we may get a clear and simple survey of the total metabolism of the Earth's crust.

After the works of V. M. Goldschmidt¹, P. Eskola² and others it has been a matter of course that the paragenetic transitions during metamorphism of a rock are led by chemical forces. But such transitions do not demand any considerable transport of matter. In most cases the minerals are in direct contact with each other. But as soon as the distances over which the substances must have been transported have reached a considerable amount, a mechanical transport of exceptionally mobile compounds has been suggested. For instance: injection of magmas along planes of schistosity, flow of aqueous solutions through smaller or greater fissures in the rocks, transport of gaseous compounds such as: FeCl_3 , SnF_4 etc., and transport of the pore liquid in the so-called intergranular film. But the forces which drive this wandering of compounds have never been fully understood.

¹ Die Kontaktmetamorphose etc. Skr. Vid.-selsk. Kristiania, Mat. Nat. kl. No. 1. 1911.

² Om Sambandet etc. Bull. Comm. Géol. Finland. No. 44, 1914.

The new point of view in this theory is that even the *transport of materials over long distances are governed by chemical forces*; and accordingly that we can apply the thermodynamic laws of the variation of these chemical forces in minerals (vapor tension, activity) with mechanical pressure (P), with temperature (T), with composition (X), size of minerals (Y), and with surrounding phases (Z), during the study of the metabolism of the earth's crust.

An example: the origin of a granite pegmatite several kilometres away from the parent granite is caused by the difference between the chemical activities of the granite minerals in the granite itself, and in the fissure in the country rock in which the pegmatite develops. The high mechanical pressure in the parent granite, and the low mechanical pressure in the fissure (a "mechanical vacuum") create a corresponding difference in the activities of the minerals at the several places.

Every condensed phase: the crystalline minerals, the molten magmas, and the aqueous solutions (for instance the pore liquid) consists, at any one given time, of two essentially different categories of atoms or ions: viz.: (1) Atoms possessing a so small kinetic energy that they become fixed to their environments, unable to jump out of the field of attraction of the nearest neighbours; and (2) atoms possessing sufficient kinetic energy to jump out of the field of attraction of their closest neighbours.

The former category we may name the *consolidated atoms* or the *consolidated phase*. The consolidated phase is in itself chemically inactive; only indirectly *via* the dispersed phase (see below) it can react chemically. To mechanical forces, however, it yields *en bloc* and may move, together with its contents of dispersed atoms, in the direction of the gradient of mechanical force. Examples: flow of liquids, translations in the lattice of crystals, crushing of minerals etc.

The latter category we may name the *dispersed atoms* or the *dispersed phase*. These atoms are the chemically active ones; they are able to migrate inside and outside the lattice in the direction of the gradients of the chemical activity. The dispersed atoms therefore can migrate away from one compound into another and react there, and they can exchange places with foreign atoms.

The principal forces leading the migration of the dispersed phase are differences in the chemical activities at different places in space. (The chemical activity of an element in the dispersed phase is

approximately equal to the partial pressure of this element; the total chemical activity of a compound is equal to the sum of the partial pressures of the dispersed elements with which the compound is in equilibrium.¹⁾ But during the mechanical transport of the consolidated phase *en bloc*, the dispersed atoms are usually also moving with as a whole; this is a mechanical transport of the dispersed phase. The supposed flow of a pore liquid through the interstices between the minerals in a rock is a good example on such a mechanical transport of dispersed atoms.

Indirectly, the dispersed atoms are greatly influenced by mechanical forces; the chemical activity (the pressure of the dispersed phase, or the vapor tension) will always increase with increasing mechanical pressure acting on the condensate. This is a fact of the greatest importance for the study of metamorphism and metasomatism. It is the old Riecke's principle² in a new form which we will apply in the investigation of the thermodynamics of the Earth's crust.³

There is obviously an equilibrium between the consolidated atoms and the dispersed atoms so that dispersed atoms will consolidate if they are led to the condensate, and consolidated atoms will disperse if the dispersed atoms migrate away from the condensate.

The present theory is built up on the laws governing the variations of the mentioned equilibrium with mechanical pressure, with temperature, and with composition and size of the condensates (minerals).

We can combine the laws giving the variation of the partial pressure of dispersion (vapor tension, activity) of minerals, with mechanical pressure and temperature respectively⁴:

$$D = K \cdot e^{\frac{m \cdot (P - D_T) - \Delta F \cdot S}{RTS}} \quad (1)$$

where D is the pressure of dispersion — or the chemical activity — K is a constant if the composition of the mineral is constant; in mixed crystals, K varies continuously with the composition. ΔF is the difference in free energy between the consolidated atoms and the dispersed atoms, S is the specific gravity of the mineral, m is the

¹ Taylor: Treatise on Physical Chemistry, Vol. I, Edit. 2. p. 423. 1931.

² F. Riecke, Nachrichten Königl. Ges. Göttingen, Math.-Phys. Kl. p. 278, 1894.

³ See also H. Ramberg, Vid.-Akad. Avhand. I. No. 3, 1944.

⁴ H. Ramberg, loc. cit.

atomic weight of the considered element, P is the mechanical or the total pressure acting on the mineral, T is the temperature, R is the gas constant, and D_T is the pressure of dispersion at the temperature T when the mineral is exposed to a total pressure equal to its own vapor tension.

We shall not discuss this equation here; we shall only keep in mind that D usually increases with T if P is constant, and increases with P at constant T . The lower the specific gravity of the mineral, and the higher the atomic weight of the considered element, the more rapid the increase of D with pressure P .

Within confined parts of a rock a state of mutual thermodynamic equilibrium is approached during the metamorphism.

Ideally, all the solid rocks, the magmas, and the aqueous solutions in the crust should be in chemical interreaction *via* the dispersed phase which is able to migrate through the rocks in all directions, each element individually obeying the command of the chemical activities.

These ideal conditions are only developed when the system has a sufficiently long time at its disposal, and when and where the rate of chemical transport of matter in the dispersed phase is greater than the rate of mechanical transport by the consolidated phase. The mechanically flowing magmas and solutions, in which the resistance against the mechanical movement — the viscosity — is low, have therefore never reached equilibrium with the solid neighbouring rocks. But after a certain time stationary magmas and solutions must be in equilibrium with the solid surroundings *via* the dispersed phase (contact metamorphism and metasomatism).

The above mentioned ideal conditions are most completely developed in the solid rocks in the deepest parts of the crust. Because of the increase of chemical activity with pressure (and with temperature), the rate of the chemical reactions is greater than the rate of mechanical movement in sufficiently great depths. At higher levels, however, the rate of the chemical reactions decreases; in the clastosphere therefore the mechanical movements even of the rigid solid rocks will play a more important rôle than the chemical migrating processes.

At the deepest levels of the crust the volumes within which all the condensed phases (the solid rocks, the melts and solutions) are in a mutual chemical interreaction *via* the dispersed phase, are of regional dimensions (perhaps the total crust at these levels is able to

interreact chemically). The volumes within which the thermodynamical equilibrium is attained, gradually narrow as successively higher levels are reached. Only the mineral units lying within a distance of a few cm apart, are in chemical equilibrium; at the top of the crust, however, even the minerals lying in direct contact with each other may represent an unstable assemblage.

Due to differences in mechanical pressure, P , temperature, T , chemical composition, X , and sizes of mineral units, Y , at different places in the earth's crust, the chemical activities — or the partial pressure of the various elements in the dispersed phase — must also vary. The locality at which the chemical activities are lowest must therefore imbibe from the dispersed phase the atoms necessary to establish the equilibrium. And these atoms must be drawn from places where the activity of the same atoms is higher. *Dispersion of minerals at places where the activities are great, Migration of the dispersed atoms towards places where the activities are less, and Consolidation there constitute the fundamental causes for the metamorphic and metasomatic processes in the Earth's crust.*

In that way the Earth's crust may be regarded as a complex precipitate in equilibrium with its solution; the precipitate corresponds to the rocks and minerals, the "solution" to the dispersed phase which is made up of those mineral-atoms that have sufficiently high kinetic energy to be able to migrate in the directions of the activity gradients.

The difference in the chemical activities at different places in the Earth can only be caused by the five variables: the mechanical pressure (P), the temperature (T), the chemical composition (X), and the size of the mineral units (Y), and the surrounding phases (Z).

The Influence of Primary Differences in Pressure.

The variation of the chemical activity with pressure is given by the equation:

$$D_P = D_T \cdot e^{\frac{m \cdot P}{RTS}} \quad (\text{see p. 100}) \quad (2)$$

The fact that minerals have different specific gravities in combination with the effect of mechanical pressure on the activity causes an undifferentiated solid crust to try to split up by dispersion, migration and consolidation and mechanical plastic flow into monomineralic concentric layers, the heaviest below, the lighter above.¹

¹ H. Ramberg, loc. cit.

Even at low temperatures high mechanical pressures are able to transform solid matter into a super-dispersed phase which has a behaviour analogous to that of a highly compressed gas. In this super-dispersed state of matter all substances seem to be able to form homogeneous mixtures; i. e. when different minerals or rocks are sufficiently compressed, they will transform into *one* single homogeneous phase — the super-dispersed phase.

According to my view, thus is the state of matter encountered in the Earth's core. (This hypothesis will be discussed in a later paper.)

In an ideally differentiated Earth the partial as well as the total pressures of dispersion are at a minimum — the free energy, F , is a minimum. At any one definite level in the Earth the composition of the consolidated phase as well as the composition of the dispersed phase are constant all over the level. The composition of the consolidates (the minerals), however, varies discontinuously in the vertical direction since the minerals are arranged in concentric homogeneous layers. The composition as well as the concentration of the dispersed phase exhibit a gradual variation in the vertical direction. The concentration of all the dispersed elements increases exponentially with the depth, but the concentration of the heaviest atoms increases more rapidly than does the concentration of the light atoms.

If and when there exists a gradient in the mechanical pressure along a surface of constant temperature in the crust, then there must exist an activity gradient in the same direction. This activity gradient will cause the dispersed atoms to migrate along the gradient: the *minerals must disperse at high mechanical pressure and consolidate at low mechanical pressure.*

This is a general principle.

Now, the activities of different minerals are different under the same P , T -conditions. The elements of those minerals which have the greatest activities therefore are most concentrated — or have the greatest partial pressure — in the dispersed phase. Further, the variation with mechanical pressure of the partial activities of minerals depend on the specific gravity of the minerals and on the atomic weight of the elements. The forces which drive the dispersed atoms along a given gradient of mechanical pressure are therefore different for the various elements, and the resistance against the migration of different atoms through the rocks varies. *The different rocks in the crust must*

be regarded as semi-permeable "membranes" which to a various degree are permeable for the various atoms or ions

In that way the elements that migrate along a mechanical pressure gradient are selected, and consequently the minerals which consolidate at low mechanical pressure are also selected.

This process I propose to call *chemical squeezing*.

In an open fissure in a solid rock at a definite level the mechanical pressure is approximately zero, in the surrounding rocks the pressure equals the weight of the superincumbent load. *Into such a mechanical "vacuum" the selected atoms in the dispersed phase must migrate and consolidate to special minerals.*

In that way I explain the origin of quartz veins, of mineral veins, of alpine veins, and of the granite pegmatites which occur within the migmatite frontier.

In the crust under an ocean depression or under a geosyncline, the pressure is less than the pressure in the same level under the surrounding continents. Consequently there exist chemical activity gradients in the directions towards such a depression in the Earth's surface; the materials from the surroundings must disperse, migrate and consolidate again at the low pressure under the depression. This process in connection with plastic mechanical flow of the solid sial, is, in my opinion, the cause of the granitisation and of the orogenesis.

Thus great bodies of granite and granodiorites are formed at low temperature in the solid state. Perhaps the problem of the origin of anorthosites can be solved in an analogous way.

During the consolidation of minerals at low mechanical pressures, the heat of dispersion (ΔF), is liberated: Around the pegmatites and the petroblastically (see definition p. 109) formed granites the liberated heat will cause an increase in the temperature of the neighbourhood, and accordingly a contact metamorphism.

The regional metamorphism can be explained by the liberation of heat during the consolidation of the granitic dispersed phase in connection with the regional granitisation.

In the same way local magma masses will form when the increasing temperature reaches the melting interval of the rocks. The maximum temperature which can occur during the consolidation of dispersed atoms is given by the difference between the mechanical pressure in the surroundings and in the place of consolidation; the greater the pressure difference, the greater the increase in temperature.

The differences between the mechanical pressures in an open fissure and in the surrounding solid rocks increases with the depth in the Earth. Perhaps this pressure difference is insufficient to cause a refusion at higher levels than at some depths in the basic substratum; this will be an interesting explanation of the great excess of basalts in relation to acid lavas.

During orogeneses however, great heat quantities are liberated during the granitisation, and refusion of acid magmas is possible.

I have explained the granitisation phenomena during an orogenesis as a migration of granitic ions from the surroundings, where the activities of the minerals are high, into the geosynclinal depression where the activities are low.

But, as a consequence of the increase of activities with the pressure, and of the low specific gravities of the granitic minerals, there ought to take place a regional granitisation all over the crust provided that the interior of the earth is not yet fully differentiated. In this case the activities of the light granitic minerals: quartz, potash feldspar and albitic plagioclase, are greater at low levels than those corresponding to the level concerned. The outer shell must therefore imbibe the ions of the granite, the ions gradually migrate outward through the crust until all the consolidated granitic materials in the Earth's interior have dispersed.

This upward migration is caused by the low density of the solid granitic material, not by the low density of the dispersed phase.

Ideally, all the light granitic solid (condensed) material of the Earth will be assembled in an outer layer; unsaturated dispersed granitic atoms (K, Si, Al, Na), however, will exist in great concentration in the rock layers farther down.

The Influence of Primary Differences in Temperature.

The relation between temperature and activity of a mineral is:

$$D = K \cdot e^{\frac{-\Delta F}{RT}} \quad (3)$$

where K is a constant, D is the partial activity of an element in the mineral, and ΔF is the difference in free energy between the dispersed atoms and the consolidated atoms of the considered element.

Accordingly there must exist activity gradients along a temperature gradient in the crust. But such an activity gradient caused only by

a temperature gradient does not necessarily cause a migration of dispersed atoms through the rocks.

The migration of dispersed atoms along an activity gradient caused by a difference in mechanical pressures in solid rocks, takes place because of the very high viscosity of solids so that P-differences cannot rapidly enough be neutralized by mechanical flow.

Analogously, whether or not a migration of dispersed matter shall take place along an activity gradient caused by a temperature difference, is determined by the relation between the rate of heat conduction, and the rate of migration of dispersed atoms through rocks.

The most important primary *T*-differences in the crust are perhaps that occurring around a hot magma which is injected into cold solid rocks, and that represented by the vertical temperature gradient of the crust. The contact metasomatism is perhaps therefore partly caused by the difference in the activities of the hot magma and of the cold minerals in the surroundings. (The most important processes of contact metasomatism are probably caused by the difference in composition of the surrounding rocks and of the gases and solutions from the magma masses; the active solutions are mechanically transported into the wall rocks where they react chemically with the solid minerals.)

The vertical temperature gradient of the crust creates activity differences which may cause the dispersed atoms to migrate to the surface and solidify at higher levels. (In the undifferentiated crust the variation of activity with pressure will cause a migration of the dispersed atoms of the light minerals towards the top, and a downward migration of the heavy mineral atoms. At the same time the *T*-gradient will *accelerate* the upward diffusion of granitic substance, and *retard* the downward diffusion of basic matter. The net result being that diffusion moves more substance upward than downward. Naturally this must be compensated for by a mechanical downward flow of basic matter.)

As the dispersion, migration and consolidation, caused by differences in mechanical pressure at different places, result in an increase of the temperature where the pressure is low (p. 104), thus differences in the temperatures may, because of the consolidation of dispersed atoms at low temperature, result in a high mechanical pressure where the temperature is low (analogous to the osmotic phenomena).

The Influence of Primary Differences in Chemical Composition.

The third variable which can cause variations of the chemical activities, is the chemical composition of the system.

The activity of minerals unable to form isomorphous solutions, is constant at constant T and P (K in equations 1, 2, and 3 is a constant). The partial activity of isomorphous elements in mixed crystals increases gradually with the concentration of the considered element in the crystal.

We shall treat systems where T and P are homogeneous, i. e. do not vary within the system, but where the chemical composition is heterogeneous, i. e. the chemical composition varies from place to place within the system.

Differences in chemical activities, and consequently migrations and reactions of the dispersed atoms along the activity gradients will occur only if the phases (rocks and minerals) are paragenetically incompatible. Such a paragenetical incompatibility can be caused in different ways, viz.: (1) Mechanical transport of substances into the system, and (2) increasing or decreasing of P and/or T all over the system.

As a result of mechanical transport of condensed phases (rocks, magmas, solutions, and sediments) under conditions at which the rate of chemical reactions is low in relation to the rate of mechanical movements, associations of materials may occur in which activity differences exist. As time goes on, however, and especially if the pressure and the temperature increase, the dispersed atoms will migrate towards the places of lowest activity, and new minerals or rocks will appear.

The liberation and absorption of heat of reaction at the different places in the system (crust) will result in more or less local T -variations. Analogous to osmotic phenomena the above mentioned processes will cause minerals as well as rocks to grow against high mechanical pressure (the force of crystallization, crystalblastesis, petroblastesis). (The free energy liberated during dispersion of matter at high activities, migration towards low activities, and consolidation there, can be transformed both to mechanical work and to heat.)

The most conspicuous metasomatic rock which is formed by diffusion of dispersed materials along activity gradients caused by differences in chemical composition, is perhaps the so-called reaction skarn between limestone and silicate minerals.

The contact metasomatism and the injection metamorphism are mostly caused by activity differences occurring when solutions are mechanically transported into the surroundings.

The paragenetic transitions which take place in a single rock exposed to varying P and T are exactly of the above mentioned type of reaction. P and T are homogeneous all over the system (rock); dispersion, migration, and consolidation take place because the chemical composition has become unstable.

Mixed crystals lying at the same level in the crust will theoretically react by dispersion, migration, and consolidation until they have attained a homogeneous composition (problem of the origin of anorthosites). That component of the mixed crystals which has the greatest rate of migration (the highest chemical activity) will migrate towards the components that have lower rate of diffusion (lower chemical activities). In that way the mixed crystal will not be distributed all over the level in dilute concentration in all the rocks, but it may be assembled in greater homogeneous masses.

Minerals which are paragenetically unstable, are even unstable when lying at different places in the same level in the crust. There exist activity gradients which may cause the dispersed atoms to migrate between the paragenetically unstable minerals, to react and to form new minerals (rocks).

In other words: All minerals all over the crust must, if chemical equilibrium exists, be paragenetically compatible. This conclusion is one of the weakest points of my theory. But we must remember: (1) Chemical equilibrium is not generally attained in the upper parts of the crust. (2) Only the minerals with the highest chemical activities are able to migrate over longer distances.

It is therefore reasonable that the minerals having the highest activities are mutually chemically compatible, and also that they are able to exist together with the minerals with the lowest activities without reaction. The minerals in the crust which have the lowest activities are not able to react with each other *via* the dispersed phase over longer distances; therefore it is probable that those minerals are not mutually compatible.

According to my opinion the granitic minerals: potash feldspar, quartz, albite, and perhaps some minerals rich in Fe in relation to Mg, have the greatest chemical activities (under the P , T -conditions

existing in the geologically known levels of the crust). These minerals are those which are able to migrate long ways.

The basic minerals: pyroxene, hornblende, anorthite, epidote etc. seem to be less active chemically. They are usually not able to migrate over longer distances. Exposed to mechanical forces they often react by being crushed; the granitic minerals, on the contrary, usually react by dispersion and migration.

The Influence of the Size of Mineral Units.

The activity of a mineral increases with decreasing size of the mineral units in an analogous manner as does the vapor pressure of small drops.

Large crystals will therefore grow against great mechanical pressure if lying together with smaller grains of the same mineral. There exist relations between the differences in size, and the mechanical pressure against which the greatest crystal can grow (force of crystallization).

The Origin of Petroblastic Rocks.

According to the view maintained in this paper apparently "magmatic" rocks (rocks with hypidiomorphic or granitic textures) can be formed far below their melting intervals. They appear by consolidation of the dispersed phase (the atoms possessing so great kinetic energy that they are able to migrate inside and outside the lattices) at places where the activities of the minerals of the rocks are lowest.

The general requirement for the origination of rocks of "magmatic" aspect, is not that they are formed by crystallization of a liquid or a melt, but only that they are formed within the stable P, T -field of their minerals.

At the proposal of professor Tom. F. W. Barth, I will name the rocks which are formed in sub-solidus state by consolidation of the dispersed atoms without reaction with older minerals, *petroblastic rocks*. (Crystaloblasts are minerals formed in the same way.) The most typical example of petroblastic rocks is a granite pegmatite which, according to my opinion, is formed by consolidation of the dispersed atoms in

a fissure (or at a place of exceptionally low mechanical pressure) in the crust.

If the dispersed phase reacts with old minerals at the place of consolidation, the newly formed rock is to be named metasomatic. (Examples: reaction skarn, some granitized rocks in which the old minerals have reacted with the dispersed phase forming granitic minerals.)

The petroblastic rocks originate by consolidation of the dispersed atoms of the solid minerals at places of low activities caused by low mechanical pressure or low temperature (pp. 103—106). (If the dispersed atoms of a melt or an aqueous solution consolidate to solid minerals, the ordinary magmatic or hydrothermal rocks occur.)

Where the activities are low due to the chemical environments, the dispersed atoms must react with the older minerals; the rocks which form are metasomatic (pp. 107—108).

In this theory I assume that the transport of matter during the metasomatic and metamorphic processes in the crust takes place without the help of the so-called volatile substances or other "carriers" which commonly are assumed to be the active agents during the transport of the mineral atoms.¹ (CO_2 , H_2O , Cl, F, S etc.)

An example: If a quartz dike is formed by precipitation from an aqueous solution, very great quantities of water must have been transported through the fissure. Silica has, as we know, a low solubility in water. At 336° the concentration of SiO_2 in a saturated aqueous solution is 0.22 per cent,² i. e. 1220 kg water must be transported through the fissure to form 1 kg quartz assuming that all the silica is precipitated from the solution. But only a smaller part of the solute (quartz) will precipitate, and then much greater quantities of water are necessary.

Further we must assume that the temperature during the whole time of precipitation must have been lower in the quartz dike than in the surroundings. The cause of the crystallization of SiO_2 from the solution must in that case be due to a cooling of the solution.

If, on the other hand, the quartz vein is formed in accordance with this theory, only those atoms which are consolidated in the quartz crystals need have been transported to the place of consolidation.

¹ Tyrrel, G. W. *The Principles of Petrology*, London p. 252 and 324, 1938; and Eskola, P. in: *Die Entstehung der Gesteine*, Berlin p. 373, 1939.

² Morey, G. W. and Ingerson, E. *Economic Geol.* Vol. XXXII No. 5, p. 732, 1937.

And the cause of the supersaturation of the dispersed phase in the fissure is not a lower temperature in the fissure than in the surroundings, but the low mechanical pressure in the fissure in relation to the adjacent rocks. (The activity or vapor tension of every compound must always increase with the pressure; the solubility will in most cases decrease with pressure; the solubility in water of but a few compounds increase with pressure¹ if both precipitate and solution are exposed to equal pressures.) Further: the rising temperature in the quartz dike caused by the liberation of heat of dispersion will not hinder the consolidation until the temperature has reached a certain definite value higher than that in the neighbourhood.

We have seen how the reactions in the Earth can be classified in: (1) Mechanical reactions during which the condensed phases react more or less *en bloc*; the forces governing the movements are mechanical pressure gradients. (2) Chemical processes which take place in the dispersed phases; the forces driving both the dispersion and consolidation as well as the movements in the dispersed phase are chemical activity differences. The differences in chemical activities are caused by five factors, viz.: Differences in the mechanical pressure at a certain level in the crust, differences in the temperature in the crust, differences in the chemical composition of the phases (minerals) differences in the size of the mineral units, and finally, by different surrounding phases.²

During the development of the crust the slow chemical processes: dispersion, migration, and consolidation aim at the attainment of complete thermodynamic equilibrium. The rapid mechanical processes often disturb the equilibrium.

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¹ Gibson, R. E. *Scient. Monthly Washington* 46, 1938.

² See notice p. 115.

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