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A physico-chemical model of element separation in the differentiation of mantle material

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[Plate 3]

Available experimental data on the phase equilibria of silicate systems at high pressure under 'dry' and 'wet' conditions as well as the results obtained by the authors on the separation of elements during zone melting of the silicate phase of chondrites have thrown light on geochemical regularities in the process of differentiation in the Earth's mantle. The basis of the work is the idea of incongruent melting of metasilicates and the concentration of silica and most of the lithophilic elements in the liquid phase. These elements form compounds with SiO_2 or are dissolved in it, causing a lowering of the liquidus temperature. Regularities in the dynamics of the process of element separation during zone melting of the mantle are established and an explanation is given of the chief physical ideas on which the physico-chemical model of this process is based.

Data on the present geochemical structure of the Earth lead to ideas about the chemical differentiation of the planet. A synthesis of these data has shown that the chief peculiarities in the differentiation of the Earth into crust (with hydrosphere and atmosphere) and mantle may be understood on the basis of ideas about differentiation during crystallization of the primary homogeneous matter (the silicate fraction of chondrites) which is accompanied by separation of the gaseous phase (Goldschmidt 1930; Vinogradov 1955, 1959a, b, c, 1962). The abandonment of the idea of a wholly fused Earth and the related ideas about the mechanism of differentiation in the liquid state and subsequent solidification of the silicate shell from the depths to the surface, leads to the necessity of considering the problem of the appearance of fused regions in the solid mantle and their further evolution as a mechanism of planetary evolution. The investigation of the geochemical aspects of this problem leads to the hypothesis of an analogy between the mechanism of mantle differentiation and the process of zone melting (Vinogradov 1955). Experiments showed the possibility of fractionation of the silicate phase of chondrites in the process of zone melting (Vinogradov 1959b, c). The resultant notions about the physical conditions for the realization of such a mechanism in the Earth's mantle (Harris 1957; Shimazu 1961; Magnitsky 1964; Yaroshevsky 1964; Vinogradov & Yaroshevsky 1965) allow us to consider the physico-chemical model of the process and to trace its chief peculiarities.

SEPARATION INTO PHASES

Olivines, pyroxenes and plagioclases, being stable under ordinary pressures, are the chief phases which determine the separation of elements during crystallization and melting of ultrabasic and basic rocks. The liquidus relations of the corresponding systems at normal pressure have been sufficiently well studied; however, at high pressures these mineral associations undergo transformations which substantially affect the trend of the differentiation of the magma during crystallization. Of special importance is the appearance of garnet on the liquidus of systems with compositions corresponding to basalts at pressures above 2–2.5 MN m⁻² (20–25 kbar) (Yoder & Tilley 1962; Davis & Schairer 1965; Green, Ringwood, Green & Major



1966); and change of liquidus relations of olivine and pyroxene (Yoder 1964, Tilley & Yoder 1964 and Kushiro 1965). The peculiarities of phase equilibria at high pressures in systems of basaltic composition allowed the consideration in detail, in a number of papers, of the factors that influence the composition of the 'primary' basaltic magma and its further differentiation (Yoder & Tilley 1962; Yoder 1964; Green *et al.* 1966).

In systems corresponding in composition to the material of the mantle (i.e. the silicate phase of chondrites) and approaching ultrabasic rocks in the ratios of their main components, the phase relations differ somewhat from the 'basaltic' ones. For an understanding of the processes of differentiation in the mantle, the regularities of melting and crystallization of systems of ultrabasic composition are of importance; let us briefly enumerate the main results necessary for the purpose:

(1) Experimental data show that in systems corresponding in composition to peridotites (garnet peridotites, 'pyrolite') the chief phases on the liquidus surface are olivines, orthopyroxenes and, more rarely, clinopyroxenes and spinel. It is these phases which determine the fractionation of the elements (O'Hara 1963*a*, *b*; Ringwood, MacGregor & Boyd 1964; Mac-Gregor 1964, 1965; Boyd & England 1964; Davis & Schairer 1965; Green *et al.* 1966; Ito & Kennedy 1967).

(2) For the determination of the tendency to separation of elements, especially during the generation of magma saturated with silica, an important role is played by the melting ratios of ortho- and meta-silicates, olivines and orthopyroxenes. Experiments at high pressure have indicated a congruent melting of enstatite (Boyd & England 1963; Kushiro 1964) and an increase of the field of crystallization of pyroxenes in the corresponding systems (Yoder 1964; Tilley & Yoder 1964; Davis & Schairer 1965; Green *et al.* 1966). These data have led to the conclusion that the region of most easily fusible compositions during the melting of peridotites (garnet peridotites) at high pressures approaches olivine bearing tholeiites, not saturated with silica (O'Hara 1963*a*; Davis & Schairer 1965; Green *et al.* 1966; Kushiro 1968). This has impeded the comprehension of the basic tendency of mantle differentiation, the fused melts being rich in silica (Vinogradov & Yaroshevsky 1967). An assumption has appeared about the possible role of incongruent melting of garnet in the formation of melts enriched in silica during the melting of garnet peridotite (O'Hara 1963*a*).

(3) Recent data on phase equilibria of the system forsterite-diopside-silica at high-water pressure (Kushiro & Yoder 1969; Kushiro 1969*a*) are of great interest in connexion with this problem. It was found that, in this case, the incongruent melting of enstatite (with decomposition into forsterite crystals and a liquid richer in silica) is preserved up to 3 MN m⁻² (30 kbar) of water pressure, both in the binary system forsterite-silica and in the ternary system forsterite-diopside-silica. Owing to these relations, the most easily fusible compositions in the system forsterite-diopside-silica at high pressures of water proved to be oversaturated with silicic acid.[†]

These results allow us to return to the fundamental chemical idea underlying the notions about the separations of the primary chondritic mantle matter, the idea of incongruent decomposition of meta-silicates and the extraction by melting of silica and all elements which lower the liquidus temperature. These elements go into the easily fusible phase and rise to the surface of the Earth (Vinogradov 1959 b, c). But it must be stated that water (and probably also the other volatile components) play a very important role in these processes, determining to a substantial

 \uparrow It is of importance that in this system, which does not contain calcium, amphibole does not appear as a stable phase on the surface of the liquidus, even at water pressures of up to 3 MN m⁻².

degree the composition of the liquid formed. In this connexion it is interesting to note that in most of the systems studied [forsterite-silica-water, diopside-silica-water (Kushiro 1969*a*), anorthite-silica-water (Stewart 1957)], as well as during the melting of eclogite in the presence of water (Green *et al.* 1966) the addition of water displaces the compositions of the most easily fusible liquids (eutectics) towards a greater enrichment in silica. Obviously from these data a general tendency of water to influence the relations of silica fusibility may be traced, which is of great significance.

Thus, on the basis of an analysis of available data on phase equilibria at high (up to 3-5 MN m⁻²; 30 to 50 kbar) pressures, the conclusion may be drawn that the principal phases controlling the separation of the elements in the process of zone melting of the mantle are ortho- and meta-silicates, olivines, orthopyroxenes and monoclinic (calcic) pyroxenes. The crystallization diagram of these phases at different pressures is shown in figure 1. As this system does not contain iron it can only be regarded as a simplified model of the mantle.

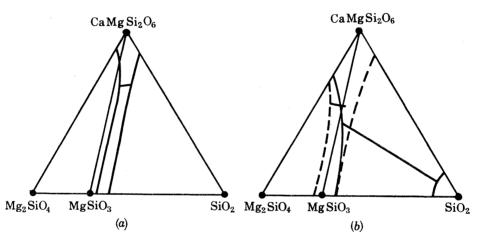


FIGURE 1. Diagram of crystallization of the system Mg_2SiO_4 -Ca $MgSi_2O_6$ -SiO₂: (a) under atmospheric pressure (from Kushiro & Shairer 1963); (b) under a pressure of 20 kbar (2 MN m⁻²) (dotted line) (from Kushiro 1964) and under water pressure of 20 kbar (solid line) (from Kushiro 1969*a*).

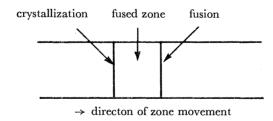


FIGURE 2. Principle of zone melting.

For the modelling of the distribution of elements between phases in the melting process in such systems, we again carried out experiments on zone melting of the silicate phase of chondrites. Zone melting consists in moving a narrow fused zone along a cylinder of the material in such a way that at the front of the zone complete fusion occurs followed by crystallization as the material leaves the heated zone (figure 2). Passage through the zone of melting is accompanied by chemical differentiation with the accumulation in the liquid of more easily fusible components which lower the liquidus temperature (Pfann 1958).

The experiments consisted (Vinogradov 1959b, c) in the multiple passage (5 to 8 times) of a

narrow fused zone through a cylinder of the silicate phase of chondritic material which had been separated magnetically from the metallic phase. The silicate phase, in the form of a powder which had been sintered at 1200 to 1300 °C, was placed in a molybdenum boat which was slowly (5 mm h⁻¹) drawn through the coil of the heat. The experiments were carried out in an argon atmosphere at 1650 ± 50 °C. The silicate phase of the chondrite Saratov and of the brecciated chondrite Kunashak were used. After the experiment the cylinder usually has the following structure:

The first part of the cylinder is composed of large crystals of olivine and ortho-pyroxene with a variable amount of glass often crystallized with the formation of 'quench' pyroxene. The latter shows spicular shaped and sliced aggregates and differs from the large pyroxene crystals which form from the melt during slow crystallization. Typical forms of olivine in this part of the cylinder are shown in figure 3, plate 3.

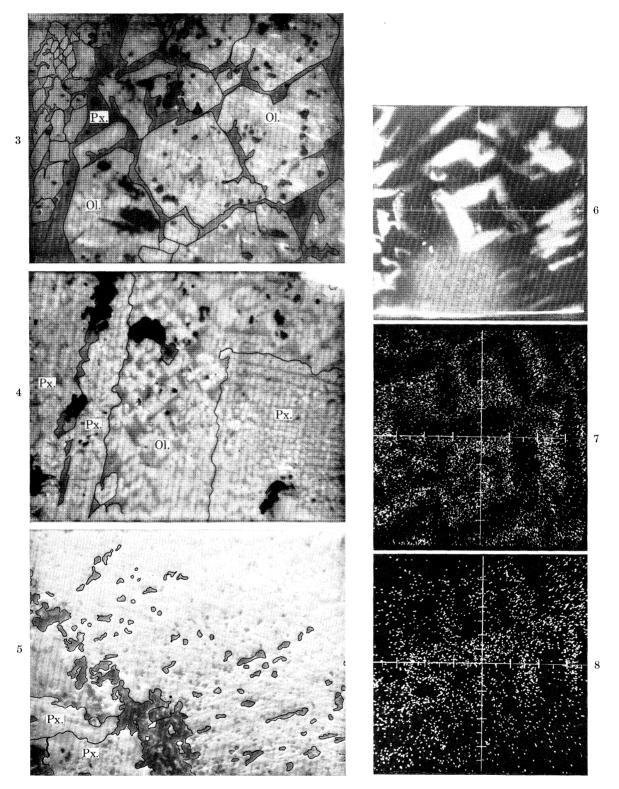
The central part of the cylinder, which is the largest part by volume, is composed of a fine grained aggregate of olivine and pyroxene grains, in which large pyroxene crystals are sometimes found (figure 4, plate 3).

The end part of the cylinder, where the most easily fusible material accumulates, is wholly or in part composed of glass or of a very fine-grained aggregate of birefringent crystals which are scattered among large pyroxene crystals (figure 5, plate 3).

The structure of the cylinder indicates the general tendency of the separation occurring in the silicate phase of chondrites during zone melting. This consists in the enrichment of the first part of the cylinder in a refractory ('residual') phase, olivine, and in the accumulation of the liquid as a glass in the end part. These changes in the proportions of the phases along the cylinder are the cause of the changes in chemical composition in the direction of zone movement. To find the characteristics of element separation in this process the distribution of some components along the cylinder was investigated after the experiments were completed. The results show noticeable variations in the content of some elements in different parts of the cylinder from experiment to experiment. However, the relative change of element content in the direction of movement of the fused zone proved to be recurrent and obviously characteristic of the process. The results obtained are given in table 1.

It was found that, during zone melting of the silicate phase of chondrites, silica is the most mobile material and that in some experiments it is noticeably enriched in the end part of the cylinder. Chromium, manganese and magnesium behave in a contrary manner. Aluminium accumulates to some extent towards the end of the cylinder, but its content invariably decreases in the final zone. In some experiments calcium behaves in a similar way, but usually its distribution is highly uneven and sometimes even a drop in its concentration is observed towards the end of the cylinder (table 1).

The variations of element content along the cylinder may be connected with the uneven distribution of different phases formed during zone melting of a complicated multicomponent system, such as the silicate phase of chondrites. This unevenness is in its turn conditioned by the rhythmic crystallization of different phases which is a characteristic of the zone melting of systems in which eutectic mixtures are formed. For a more strict interpretation of the melting process, it is necessary to investigate the role of individual phases when elements are separated by zone melting of the silicate phase of chondrites. The distribution of some elements among crystals of olivine and glass (the 'quench' phase) was studied by the method of electron-probe microanalysis in the part of the sample where olivine is the prevailing phase. Vinogradov et al.



- FIGURE 3. First part of the cylinder. Large (lighter) olivine crystals among the 'quench' phase (dark parts between the crystals). (Reflected light, magn. ×270.)
- FIGURE 4. Middle part of the cylinder. Large skeletal pyroxene crystals (in the right lower corner of the photo) and a fine-grained aggregate of olivine and 'quench' phase. (Reflected light, magn. × 270.)
- FIGURE 5. Fine-grained aggregate of slightly birefringent crystals in the end part of the cylinder. (Reflected light, magn. $\times 270$.)
- FIGURE 6. Two-phase structure of the sample obtained by recording the absorbed electron current. Light: olivine crystals; dark: the 'quench' phase.
- FIGURE 7. Scanning picture of magnesium distribution.

FIGURE 8. Scanning picture of calcium distribution.

Polished sections of samples covered by a thin carbon layer (about 30 nm) were investigated with a 'Hitachi' X-ray microanalyser. First the samples were studied on the scanning attachment of the analyser: in the picture produced by recording the absorbed electron current a distinct two-phase structure was seen (figure 6, plate 3). The most typical scanning pictures of element distribution are given in figures 7 and 8, plate 3. Scanning pictures of the distribution of magnesium, calcium, iron, aluminium and silicon, as well as background pictures, were photographed. All pictures show differentiation of elements by phases, a very great enrichment of olivine crystals in magnesium and their depletion (compared to the phase filling the interstices between crystals) in calcium, aluminium, silicon and iron being observed.

TABLE 1. RELATIVE DISTRIBUTION OF COMPONENTS AFTER ZONE MELTING OF THE SILICATE PHASE OF THE CHONDRITES SARATOV AND KUNASHAK

Distance from the apical end of cylinder mm	SiO2	TiO2	Al_2O_3	MgO	CaO	Cr	Ni	Mn
Saratov (sample 1)								
160	1			1	1			
122	1		1	1	0.8			-
85-37	0.9		0.9	1	0.9			
6-4	1.1		2.2	1	1.5			
4–1	1.3		1.6	1.2	1.3			
1–0	1.4		0.5	0.6	0.8			
Saratov (sample 3)								
17 - 15	1	1	1	1	1			
14 - 13	1	1	0.8	0.9	0.9			
10-8	0.9	1	0.7	1	1.4			
3-2	0.9	1	1	1	0.9			
2-1	1.1	1.1	1.3	1	1			
1-0	1.2	1.3	1		0.9			
Kunashak								
35	1	1	1	1	1	1	1	1
30	î	1.3	1.1	1	0.7	0.7	1.1	0.9
20	î	1.0	1.1	î	0.2	0.6		0.9
2 0 5 -0	1.1	0.7	0.9	0.9	0.2	0.4		0.9

The content of components in the first part of the cylinder is accepted as equal to 1.

These qualitative results were made more precise by setting the electron beam on to a definite part of the sample which could be visually observed on the electron scanning picture. For the estimation of the degree of differentiation of elements between the phases, a semiquantitative microanalysis of the relative element content in crystals of olivine and in the 'quench' phase surrounding it was carried out. The concentration ratio in the two phases was taken to be the ratio of the intensities of the characteristic line of the element being determined in those phases (this is a first approximation to a quantitative X-ray analysis). For each element the analysis was carried out at several points taken in pairs and close to one another on grains of the two phases. The results are shown in table 2.

These results, together with other data characterizing the equilibrium ratios for olivines and pyroxenes and the distribution of elements during their crystallization, allow us to consider

the role of the main phases in the process of element separation during zone melting of the silicate phase of chondrites and thus the matter of the mantle.

Olivine is the most refractory phase; it crystallizes first and constitutes (together with some orthopyroxene) the larger part of the 'residual' matter. The crystallization of olivine is attended by an increase in the Fe/Mg ratio in the liquid (which is preserved also at high pressures to judge by the relations of melting temperatures of forsterite and fayalite with pressure (Davis & England 1963; Hsu 1967)) and an increase in the content of silica and practically all other (lithophilic) elements, the distribution factors of which during olivine crystallization are less than 1. Nickel, cobalt and magnesium appear to be exceptions; they form stable ortho-silicates which give solid solutions with olivine, they are therefore concentrated in this phase. Their behaviour is determined by the relations of the melting temperatures of these molecules. Ringwood (1956) and Bradley (1962) have shown that the Ni/Mg and Mn/Mg ratios must increase in the process of olivine crystallization but the decrease in the concentration of magnesium and iron during differentiation of the whole system must obviously lead to a decrease of their content in the liquid formed by fusion.

TABLE 2. DISTRIBUTION COEFFICIENTS (CONCENTRATION RATIO IN THE CRYSTAL AND THE 'QUENCH' PHASE) OF ELEMENTS FOR OLIVINE OF THE SILICATE PHASE OF CHONDRITE KUNASHAK

distribution coefficient
0.78 ± 0.02
10 ± 1
0.5 ± 0.05
< 0.03
$< 0.01^{+}$
1 ± 0.1

† Calcium is practically absent in olivine crystals.

Orthopyroxenes represent the second most important phase. If the process follows an ideal, theoretical course they will appear during the middle stages of crystallization and, together with olivine, compose the chief mass of the 'residual' matter. Crystallization of this phase also leads to an increase in the Fe/Mg ratio in smelting liquids. The possibilities of isomorphic replacement in orthopyroxenes are wider than those in olivines. The data bear witness to a substantial dissolution of calcium silicate, alumina and compounds of other elements in these minerals. However, it is important for the characterization of the melting process that the distribution factors of calcium and aluminium during crystallization of orthopyroxenes, for which there are data, are less than 1; these relations are preserved at high pressures (Boyd & Schairer 1957; Kushiro 1969b; Davis 1963; MacGregor 1964; Boyd & England 1964) although the elevation of pressure lowers the solubility of alumina in orthopyroxenes (MacGregor 1964; Boyd & England 1964). There are no experimental data for most of the lithophilic elements; however, the ideas about the conditions of their isomorphism in this phase, taking into account the small size of the magnesium ion (compared with those of sodium, potassium, rubidium, caesium, strontium, barium, the rare earths, uranium, thorium, zirconium, etc.) force us to believe that low values of the distribution factors (less than 1) are quite probable for these elements and that they must accumulate in residual liquids during crystallization of orthopyroxenes.

Clinopyroxenes (calcium-bearing) appear in the final stages of evolution of the melt. All data indicate considerably greater possibilities of isomorphous replacement of elements in them.

Large amounts of alumina[†] (Tsvetkov 1951; O'Hara & Schairer 1963; O'Hara 1963*b*), titanium (Tsvetkov 1951; Huckenholz 1969), chromium and vanadium (Tsvetkov 1951) may be dissolved in them. Also diopside forms series of continuous solid solutions with hedenbergite, aegirine (Yagi 1966) and, at high pressures, with jadeite (Bell & Davis 1965). From the available experimental data it follows that, during the crystallization of clinopyroxenes (and also of jadeite at high pressures) the distribution factors of iron, sodium, aluminium and titanium are less than 1; that is, these elements must accumulate in the melt. Crystal chemical considerations (Kirkinsky 1964; Kirkinsky & Yaroshevsky 1967) suggest that most lithophilic elements will behave in a similar way. The increase in the Na/Ca ratio is characteristic of the process of clinopyroxene crystallization. It corresponds to regularities during crystallization in the plagioclase series.

TABLE 3. Assumed behaviour of elements and change of some element ratios

IN	THE	PROCESS	OF	ZONE	MELTING	IN	THE	MANTLE

elements lowering the liquidus					
temperature of the melt and	elements accumulating in the				
accumulating in the liquid	'refractory' residue; the ratio				
formed; the ratio in the liquid	in the 'refractory' residue				
formed increases	increases				
Si, Na, K, Ca, Al, Ti, Li, Rb, Cs, Be, Sr, Ba, Y, r.e., Th, U, Zr, Hf, V, Nb, Ta, K/Na, Sr/Ca	Mg, Fe, Ni, Mn, Cr, Mg/Fe, Mn/Fe, Ni/Fe				

It is interesting to compare the behaviour of sodium and potassium during crystallization of calcium minerals and first of all of clinopyroxene, as it is the basic phase in which these elements can locate themselves in the mantle. There are no experimental data for potassium. Crystal chemical considerations and data on the sodium and potassium content of natural pyroxenes indicate that it is substantially more difficult for potassium to enter these minerals than it is for sodium. This difference is displayed to a still greater degree at high pressures. In contrast to sodium alumosilicates which undergo transformation to jadeite, which is isostructural and isomorphous with diopside, potassium alumosilicates do not experience analogous transformations (Ryabinin, Markov, Petrov & Delitsin 1966). This impedes the inclusion of potassium in phases crystallizing in the mantle and augments its concentration in residual liquids. The distribution factor of potassium must be substantially lower than the distribution factor of sodium.

Thus the crystallization of olivine and pyroxenes from melts having the composition of the silicate phase of chondrites, must lead to an accumulation of the most lithophilic elements in the liquid phase. In combination with silica these form an 'easily fusible' phase which is carried out through the mantle to the surface of the Earth.

Table 3 has been constructed on the basis of these considerations. It may be considered as independent of the empirical geochemical results on the distribution of chemical elements in the shells of the Earth and as predicting the behaviour of elements during mantle differentiation in the process of zone melting. The practically complete coincidence of the expected distribution with the observed one (figure 9), to which attention has already been drawn (Vinogradov 1961, 1964) is remarkable.

[†] Apparently clinopyroxenes and, to some extent, orthopyroxenes, are the fundamental phases in which aluminium is dispersed during the fusion processes in the mantle. As was mentioned above, garnet, which is the mineral most enriched in aluminium is of minor importance at liquidus temperatures in a system of ultrabasic composition.

Dynamics of the separation process

The way in which elements are redistributed in the process of zone melting with a constant width of the fused zone is shown in figure 10. This distribution corresponds to the equation (Pfann 1958)

$$c_{i}(x)/c^{0} = 1 - (1 - k_{i}) \exp((-k_{i}x/l)),$$

where c_i^0 is the initial concentration of the element in the matter being subjected to separation, $c_1(x)$ the concentration after one passage, k_1 the distribution factor, x the distance, l the width of

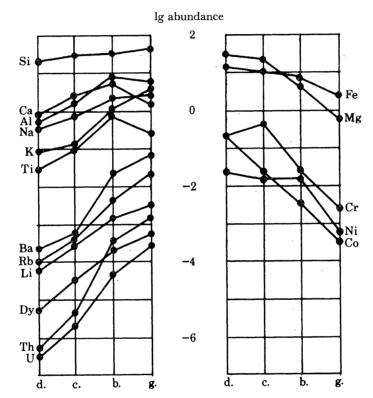


FIGURE 9. Element distribution in the system: silicate phase of chondrites (c.), dunites (d.), basalts (b.) and granites (g.) of the crust.

the fused zone. Three sections may be singled out: the first being depleted (or enriched, depending on the distribution factor) in an element, the middle, steady section which practically does not participate in the differentiation and the final section, liquid being formed which is enriched in the 'easily fusible' components. The behaviour of the eutectic system does not differ in principle from that described (Yaroshevsky 1968). For the quantitative characterization of the efficiency of the differentiation process two values may be used: c_i^{liq}/c_i^0 the concentration coefficient in the liquid being formed (c_i^{liq} is the concentration in the liquid being formed) and m_i^{liq}/m_i^0 , the differentiation coefficient (m_i^{liq} is the mass of the element in the liquid being formed, m_i^0 the mass of it in the whole system being subjected to separation). When the steady régime is reached the concentration coefficient is $1/k_1$.

Estimates of the concentration coefficient of chemical elements in the rocks of the Earth's crust are given in table 4; these are based on the theory of the process, and calculated from geochemical data. The elements are grouped according to the values of the concentration

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coefficients which correlate sufficiently well with the expected distribution factors of elements in the process of zone melting of mantle material. The condition of the geochemical balance in the differentiation of the mantle (regarded as the system: silicate phase of chondrites-basaltresidual dunite) allow us to calculate the depth at which differentiation of the mantle takes

TABLE 4. CONCENTRATION COEFFICIENTS OF ELEMENTS IN BASALTS AND GRANITES OF THE EARTH'S CRUST AND DEPTH OF MANTLE DIFFERENTIATION DURING BASALTIC MAGMA GENERATION

	concentratio	n coefficient†	depth of mantle differentiation‡/km	
Element	in basalts	in granites		
Si	1.1	1.5	9	
Mg	0.25	0.031	22	
Ca	3.4	0.8	34	
Na	2.5	3.3	52	
Al	5.0	4.4	73	
Ga	3.6	4	58	
Ti	9	2.3	150	
\mathbf{Li}	5	13	65	
K	10	39	180	
Rb	8.2	36	150	
Sr	44	30	580	
Ba	50	140	1870	
\mathbf{Eu}	10	15	135	
\mathbf{Th}	75	450	1100	
U	35	230	550	

† Abundance of elements in the silicate phase of chondrites, dunites, basalts and granites is taken according to Vinogradov (1961, 1962).

[‡] When calculating the depth of mantle differentiation the summary thickness of basalts in the crust is accepted to be 20 km; the average crust material density is 2.8, the average mantle material density is 4.

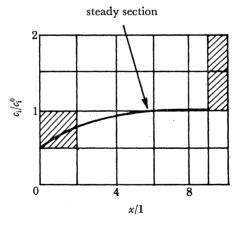


FIGURE 10. The single-pass distribution of component during zone melting. Hatched areas illustrate the principle by which the depth of mantle differentiation is estimated.

place during the generation of basaltic magma for various elements (Vinogradov 1959c). The principle of the calculation is shown in figure 10 and the results in table 4. The calculated depths indicate the different intensity of reworking the mantle for different elements in the same differentiation process. According to the theory this may be explained by the unequal role of steady zones for different elements depending on their distribution factors. Three groups of

elements differing in the calculated values of the depth in the mantle at which they are affected by the differentiation process may be singled out:

- Si, Mg, Ca, Na;
 Al, Ga, Ti, Li;
- (3) K, Rb, Sr, Ba, Eu, Th, U.

These groups correspond to the different mobility of elements during the melting process in the mantle and must correlate with values of their bulk distribution factors[†] (i.e. with their concentration coefficients in the crust which are a direct function of distribution factors). A proper interpretation of the character of the element distribution in the mantle is shown in figure 11.

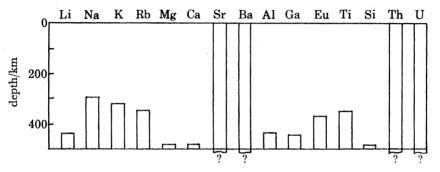


FIGURE 11. Depth of mantle differentiation for different elements in the process of basalt melting.

The calculation of the depth of mantle differentiation during generation of crustal material by melting is hampered first of all by the uncertainty of our estimates of crustal composition. On the basis of the given figures one can obviously speak about only two characteristics of the process of mantle differentiation: the different depths of mantle differentiation for different elements and the generally substantial (not less than 500 km) depth of mantle reworking in the process of generation of crustal basalts, which is obtained from calculations concerning the most mobile elements.

The law of element distribution in the mantle produced by differentiation according to the zone melting mechanism leads to a number of interesting consequences.

(1) Refractory differentiation products are not confined solely to the parts of the upper mantle immediately below the crust, but are also present at considerably greater depths. In connexion with this let us note that the massifs and belts of ultrabasic rocks (dunites, peridotites, serpentinites) observed in the Earth's crust cannot be regarded as direct products of zone melting of the mantle. The mechanism of their rise and intrusion into the crust, including the question of the state of aggregation of the ultrabasic material during intrusion, is an independent problem. Zone melting must be considered as the fundamental mechanism leading to the formation of ultrabasic matter in these rocks as a definite geochemical system during the differentiation of the primary mantle (silicate phase of chondrites). From a geochemical point of view the matter of ultrabasic rocks is considered as a residual one after melting, being depleted in 'easily-fusible' components.

(2) The essentially steady character of the zone melting process in the mantle leads to a constancy in the composition of the liquid which is a very important characteristic of the process

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[†] By the bulk distribution factor is meant the ratio of the average concentration of a component in all solid phases being crystallized at a given stage to its equilibrium concentration in the liquid.

of magma generation in the mantle. The process of zone melting, which is an aspect of fractional crystallization, being controlled by an extensive parameter, the heat content of the melt may be opposed to the process of selective fusion during which the melt composition is determined by the temperature of the system and the fraction of the liquid being generated and must vary strongly depending on the geological position and the age of the magma (Yaroshevsky 1968).

(3) It is of great importance that, in this process of thermal differentiation of the mantle, the Fe/Mg ratio in the differentiation product must increase upwards, in the direction of the motion of the fused zone (cf. the Fe/Mg ratio in the silicate phase of chondrites and basalts). This distribution is contrary to that which is expected in the case of gravitational separation and may prove to be critical for the choice between these two mechanisms (Yaroshevsky 1965).

THE PHYSICAL BASIS OF THE MODEL

The chief physical ideas about zone melting of the mantle may be summarized as follows:

(1) The fusion occurs at a great depth in the mantle as a result of the general heating of the planet chiefly due to the decay of radioactive elements (Vinogradov 1959c).

(2) This heating proceeds irregularly and leads to the appearance of large fused regions within the mantle; the cause of local fusion may be any inhomogeneity of the material of the mantle. Since the melting point is reached against a background of a general rising of temperature, these inhomogeneities may be quantitatively of small magnitude (Vinogradov & Yaroshevsky 1965).

(3) The relation between the melting temperature gradient and the adiabatic temperature gradient in the mantle is such that the fused regions which have arisen in the mantle prove to be unstable in relation to convective intermixing (Magnitsky 1964; Vinogradov & Yaroshevsky 1965). This fundamental peculiarity of the conditions for the existence of a fused region in the mantle leads to an intermixing of the melt. It also leads to a transfer of heat in the melted zone from the lower boundary to the upper which must be accompanied by crystallization on the bottom of the region of melting and by fusion of the roof; consequently the whole fused zone moves upwards by a mechanism which is completely analogous to zone melting (Shimazu 1961; Magnitsky 1964; Vinogradov & Yaroshevsky 1965). In fact the problem of the instability of a fused region in the mantle is identical to the classic problem of the solidification of the primarily fused planet which was solved by Adams (1924).

Thus, for the realization of this mechanism and the rise of the fused zone it is necessary that the heat transfer within it must be convective and considerably higher than in the surrounding solid mantle. As has been mentioned already (Vinogradov & Yaroshevsky 1965) the process must have a periodic, pulsating character; this follows from the relations between the heat accumulation rates and the convective heat removal from the melting region in the mantle. These peculiarities of zone melting in the mantle follow also from calculations on the thermal history of the Earth in which the effect of melting and the transfer of melts upwards to the surface of the Earth by the mechanism of zone melting is taken into account (Tikhonov, Lubimova & Vlasov 1969).

The conditions for convective mixing within the fused region depend on the fraction of the material which has become melted. The greater the amount, the less its viscositv and the more intensive is this process. Obviously there must be some minimum fraction of liquid in the mixture of crystals and liquid in the region of the mantle where heating and fusion is taking

place so that the process can become effective. When this state is reached mixing of the whole 'porridge' with attendant processes of crystallization and fusion and the moving upwards of the zone will begin.

The general heat balance of the process and the interval of depth at which it is developing is determined by the heat content which the melt receives at the moment of its birth in the interior parts of the planet. As soon as the zone is fused, conditions are reached at which mixing begins; the zone of fusion will rise upwards 'tearing itself away' from the region where it was supplied with heat. As was noted above the rise upwards is driven wholly at the expense of energy liberated on the bottom of the magma chamber during crystallization; this energy is spent in heating and fusing the rocks of the roof. The process will cease when all the heat stored during fusion has been spent in heating and remelting the colder rocks through which the fused mass is rising, by the mechanism of zone melting. According to the calculations of geophysicists (Tikhonov *et al.* 1969) the process of zone melting embraces mantle depths from 400 to 100 km.

Thus the model of zone melting in the mantle allows us to elaborate sufficiently harmonious notions which easily explain the chief peculiarities of the transfer of heat and mass in the process of smelting of the material of the Earth's crust from the mantle.

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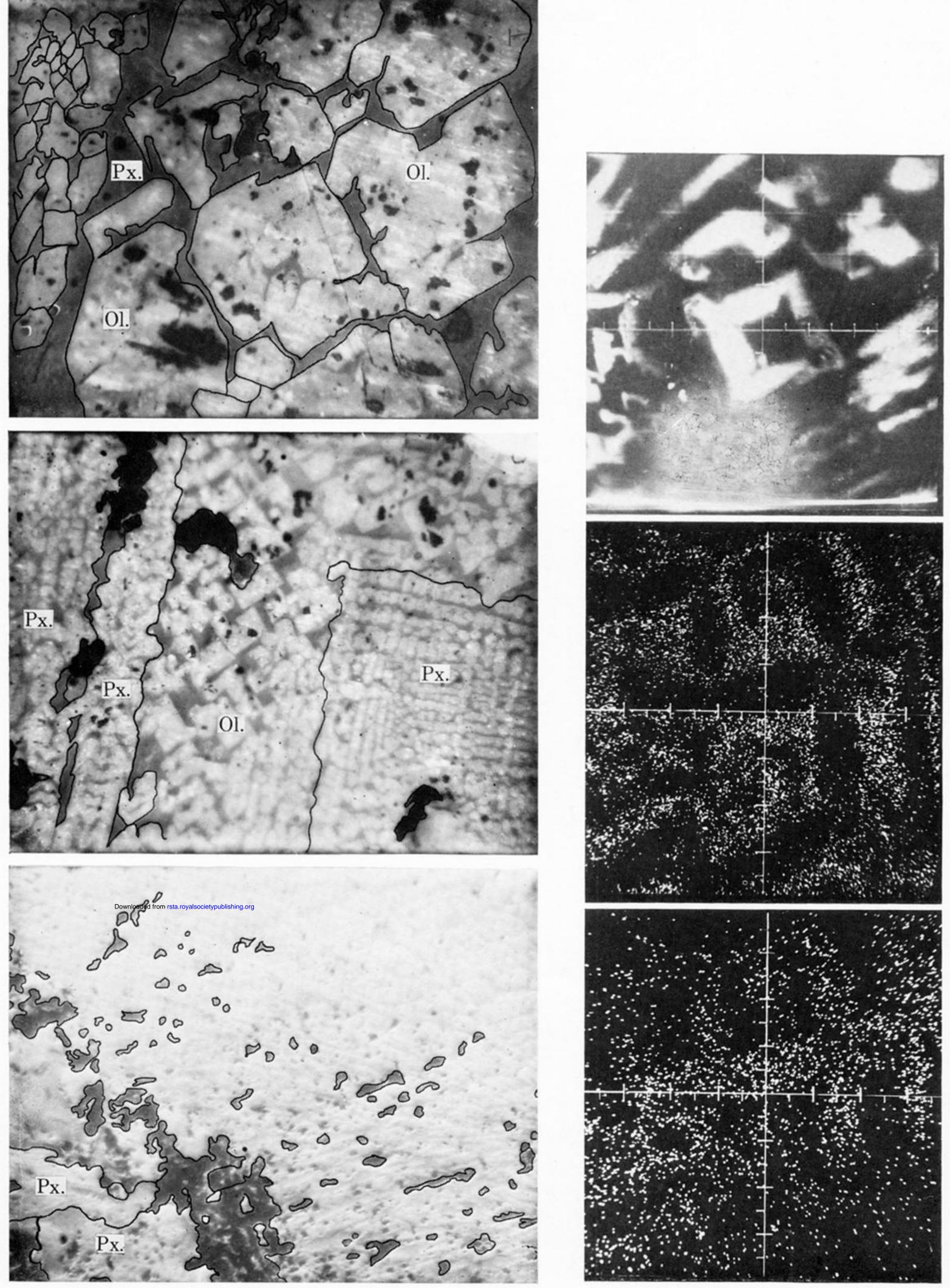
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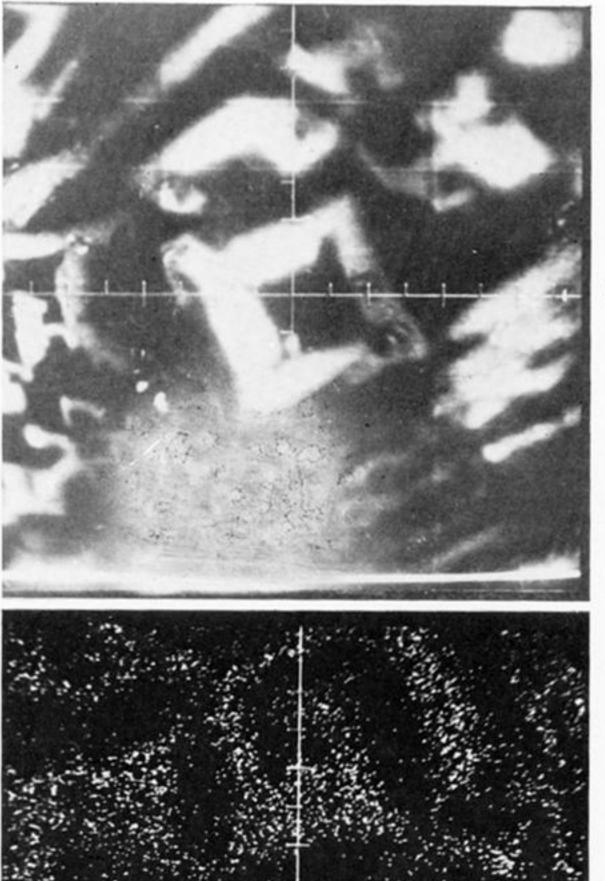
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PHILOSOPH TRANSACTI



IGURE 3. First part of the cylinder. Large (lighter) olivine crystals among the 'quench' phase (dark parts between the crystals). (Reflected light, magn. $\times 270.$)

GURE 4. Middle part of the cylinder. Large skeletal pyroxene crystals (in the right lower corner of the photo) and a fine-grained aggregate of olivine and 'quench' phase. (Reflected light, magn. ×270.)

GURE 5. Fine-grained aggregate of slightly birefringent crystals in the end part of the cylinder. (Reflected light, magn. $\times 270.$)

