The Effect of Temperature and Pressure on the Distribution of Iron Group Elements Between Metal and Olivine Phases in the Process of Differentiation of Protoplanetary Material

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The distribution patterns of Ni, Co, Mn, and Cr were studied in olivines of various origins: from meteorites (chondrites, achondrites, pallasites), which are likely analogs of the protoplanetary material, to peridotite inclusions in kimberlite pipes, which are analogs of mantle material.

According to X-ray microanalysis data, each genetic group of olivines is characterized by a specific concentration of these elements. Nickel is concentrated (up to 0.34 percent) in peridotite olivines, while manganese is concentrated in meteoritic olivines. The maximum chromium content (0.2 percent) was found in ureilites, which were formed under reducing conditions.

Experiments at pressures of 20 to 70 kbar and temperatures of 1100 to 2000°C have shown that in a mixture of olivine and Ni metal or NiO nickel enters the silicate phase (up to 4 percent), displacing Fe into the metallic phase.

Equilibrium temperatures were estimated from the Fe, Ni distribution coefficients between the metal and olivine: 1500 K for pallasites, 1600 K for olivine-bronzite H6 chondrites, 1200 K for olivine-hypersthene L6, 900 K for LL6, and 1900 K for ureilites (at $P = 1$ atm). The equilibrium conditions of peridotites are close to $T = 1800$ K and P over 100 kbar.

The distribution patterns of the transition elements are explained on the basis of physical-chemical properties. It is concluded that there is a sharp difference between the conditions of differentiation of the protoplanetary material at the time meteorites were formed and the conditions of differentiation of the planets into concentric layers.

It is important to study the reactions of metallic and silicate phases under conditions of varying P and T in order to analyze the process of differentiation of the protoplanetary material during the early stages of formation of the planets and asteroids after accretion. The most significant aspect of this interaction is the exchange of the transition metals, iron, nickel, cobalt, and chromium, that enter into the composition of the silicate and metallic phases in meteorites, as well as in silicate minerals of deep terrestrial and lunar rocks.

The transition metals of the iron group are characterized by variable valence states, due to structural features of their electron shells. Changes in valence and, consequently, the appearance of lithophilic, siderophilic,

Table 1.—*Transition Metal Content in Olivines From Meteorites, Lunar Rocks, and Ultrabasic Terrestrial Rocks*

Samples	Number of Samples	Fe wt.%	Mn wt %	Ni ppm	Cr ppm	Co ppm
Pallasites	8	8.4–9.8	0.16–0.28	50	160–200	40
H6 Olivine-Bronzite	3	13.6–15.0	0.33–0.35	90	110	30
Olivine-Hypersthene						
L 6	4	17.1–18.0	0.36–0.38	70	210–290	30
LL 6	2	20.9–21.8	0.40–0.42	70	380–410	40
Ureilites	1	17.5	0.35	70	2000	40
Chassignites	1	24.2	0.43	300	250	60
Nakhlites	1	37.4	0.49	80	150	80
Lunar Regolith	3					
Peridotites Inclusions			0.19–0.26	40	280–470	40
in Kimberlite Pipes	15	5.2–6.2	0.06–0.08	2800–3400	40	40–90
Alpine-Type Ultrabasites	4	5.5–6.5	0.08–0.09	2600–3000	30	70–90

and chalcophilic properties in these elements are in conformance with the conditions of mineral formation. The equilibrium constants for the distribution of transition metals between the silicate and metallic phases depend on the temperature of the process, as well as on the pressure, as is indicated by significant volumetric effects when cations in the olivine structure are replaced by transition metals.

Attempts to calculate the conditions of equilibrium in meteorites using the distribution of iron and nickel between the silicate and metal phases in meteorites have been previously attempted (refs. 1 and 2). However, the authors did the calculations using excessive nickel contents for the silicate phase of the meteorites and, in addition, they used experimental equilibrium constants determined for the metal-pyroxene reaction. Therefore, they obtained equilibrium conditions in meteorites corresponding to a temperature of 2000 K and a pressure on the order of 100 kbar. Such parameters cannot be acknowledged to be real for the parent bodies of meteorites. In this work the task is to define more precisely the content of transition metal trace elements in olivine meteorites, to compare olivines of different origins, to conduct an experimental study of the distribution of these elements between the metal and olivine phases, and to model the processes of differentiation at various pressures and temperatures. Based on the chondrite model of the mantle of the Earth proposed by Vinogradov (ref. 3), the main comparison has been drawn between meteorites, which are most likely similar to the primary matter of the protoplanetary nebula, and peridotites from kimberlite pipes, which are assumed to be analogs of mantle material. For a comparison of the processes taking place under the conditions of the Earth and bodies of smaller sizes such as the Moon and asteroids, samples of lunar rocks and achondrites also were studied. All samples were analyzed in an X-ray microanalyzer under identical conditions and using single standards.

Samples Studied and the Analytical Procedure

In order to perform the tasks set forth, 42 samples were analyzed: eight pallasites; nine olivine-hypersthene and olivine-bronzite chondrites; three achondrites; 15 garnet and spinel peridotites from the Mir, Udachnaya vostochnaya, Dama, Novinka, and Obnazhyennaya kimberlite pipes; and four terrestrial harzburgites and three olivines from the lunar regolith (Luna 16).

Sample preparation for the majority of samples, excluding the chondrites and achondrites, consisted of selecting a monomineralic fraction mounted in epoxy resin, with subsequent sectioning and polishing of the minerals. Polishing was done only with diamond powder. The usual crystal dimensions were from 30 to 40 μ for lunar and chondrite olivines and up to 2 to 3 mm for ultrabasic rocks.

Olivines from the Pavlodar and Mar'yalakhti pallasites, as well as olivines from peridotites, were used as standards.

The standard samples were prepared particularly carefully. A portion of the crystals analyzed for uniformity was then used for chemical analysis of the content of trace elements. Analysis of the standard samples was carried out by several methods. Initially, iron, manganese, nickel, chromium, and cobalt were determined by the method of total silicate analysis of homogenized samples. Subsequently, the same elements were determined on 20- to 30-mg samples by atomic absorption spectrophotometry. In addition, the nickel and cobalt concentrations were precisely determined, by highly sensitive methods, using special methods of organic solvent extraction (ref. 4) of nickel with α-furyl-dioxime and cobalt with β-nitroso-α-naphthol.

Determination of the concentrations of Ni, Cr, Mn, and Co, as well as iron, in the olivines was carried out by X-ray spectral microanalysis using an XMA–5V microanalyzer. A previously developed method of trace element analysis, with increased sensitivity of determination of these elements,

was used. The limits of detection for Ni and Mn were 10 ppm and, for Cr and Co, 20 ppm at the 3-sigma level.

Counting times for one measurement of line intensity and background was 1 to 2 min. At least five points in each microregion, 200 to 300 μm in size, were analyzed: for chondrites and lunar olivines the microregion was 30 to 50 μm. In this manner a statistically significant number of measured counts (3 000 to 10 000 counts) was collected in one olivine grain. For each sample the number of olivine grains was usually 3 to 5; it was 10 in some cases, such as in analyses of cobalt and nickel in pallasites and chondrites. The values presented in the tables are averages of 30 to 50 determinations of a given element in each sample. Analysis for uniformity showed that for the majority of samples the deviation from the mean was within the limits of statistical error, 2 to 3 percent for terrestrial samples and pallasites, 5 to 6 percent for lunar olivines and achondrites, 3 to 5 percent for the chondrites, and up to 5 percent for synthetic samples.

Results for Natural Olivines

The concentrations of the transition elements, iron, nickel, cobalt, manganese, and chromium in olivines of different origins are presented in table 1.

Within each of the groups studied there are no sharp differences in trace elements contents. All groups, with the exception of the achondrites and lunar regolith, are quite uniform in trace element contents. Small differences in concentrations are practically within the maximum permissible error of measurement. The variations observed in manganese contents are regular, as is nickel within the peridotite group.

The observed similarities in content of transition trace elements is evidence of the genetic similarities of the samples within each of the groups analyzed.

A completely different picture emerges on comparison of olivines from different genetic groups. As seen from table 1, the quantity

Table 2.—*Scheme for the Two-Stage Olivine Synthesis*

Apparatus	Initial Charge	Synthesis Conditions			Processes	Mineral	Natural Analog
		P(kbar)	T(°C)	(min)			
High-frequency heating unit	Oxide mixture	10^{-3}	1600– 1900	10	Melting and crystal- lization	Olivine [1]	Olivines of pallasites
Modified Bridgman anvil-type high- pressure unit	Olivine [1] + Ni or NiO	20–70	1100 1500 2000	30–50	Recrystal- lization	Olivine [2]	Olivines of the Earth's mantle

NOTES: (1) Synthetic olivine not containing Ni (<0.004 percent).
(2) Olivine synthesized from olivine [1] plus nickel.

of trace elements changes regularly when go-ing from one group of samples to another. Thus, the greatest concentrations of man-ganese are in olivines from achondrites and chondrites (up to 0.42 percent) in olivine-hypesthene chondrites and up to 0.49 per-cent in achondrite-nakhlites). The lowest Mn content is observed in ultrabasic terres-trial rocks, especially in peridotite inclusions in kimberlite pipes (up to 0.06 percent).
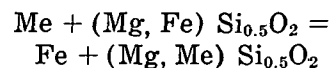
In contrast to manganese, nickel is concen-trated in deep terrestrial rocks—up to 0.34 percent in olivines from peridotites—and its content is almost two orders of magnitude less in pallasite olivine (40 ppm). Low nickel concentrations are found in olivines of the lunar rocks (30 to 50 ppm).

The behavior of chromium is quite con-vincing: its maximum concentrations were measured in carbon- and diamond-containing achondrites (up to 0.2 percent in ureilites). The chromium content is considerable in olivines from lunar mare rocks and chon-drites.

Samples of different origin differ little from one another in cobalt content. Some in-crease in cobalt concentrations is noted in ultrabasic terrestrial rocks and in achondrite-nakhlites. Iron is one of the principal major elements in olivines, but it does not have typi-cal concentrations for each group. There is only a general increase of this element in go-ing from ultrabasic terrestrial rocks · to chondrites and achondrites.

Experimental Investigation of the Distribution of Elements Between Metal and Olivine Phases at High Pressures and Temperatures

To confirm the regularities found in analy-sis of natural samples, experiments were per-formed to model the interaction of metal and olivine phases under conditions of changing P and T. Olivines were synthesized by a two-stage method (table 2). Initially, impurity-free ferromagnesian olivine were synthesized in a high-frequency heating unit. Mixtures of oxides were placed in a container, and the heater was a graphite ring in a high-frequency field. The experiments were carried out in a nitrogen atmosphere. Subsequently, the metal and olivine phases were reacted at pressures from 20 to 70 kbar and tempera-tures of 1100 to 2000° C in a modified "Bridg-man anvil" type of unit. Mixtures used for the experiment consisted of the previously prepared, impurity-free olivine and metallic nickel or nickel monoxide. Nickel was used as the reagent for carrying out the exchange re-action.

$$Me + (Mg, Fe) \ Si_{0.5}O_2 = Fe + (Mg, Me) \ Si_{0.5}O_2$$

Nickel was chosen because, of all the transi-tion metals, it especially produces appreciable concentrations in the metallic phase of mete-

Table 3.—*Dependance of the Composition of the Products of the Exchange Reaction of the Conditions of the Synthesis*

Synthesis P (kbar)	Conditions T (°C)	Initial charge	Composition of the Products Olivine		Ni-Fe alloy Fe wt %	Ni wt %
			Fe wt %	Ni wt %		
20		Olivine with 5.5-wt %	5.4	0.016	2.1	97.8
50	1100	iron	5.2	0.018	3.6	96.1
70		Metallic nickel constitutes	3.8	0.021	4.0	95.9
		5.5-wt % of weight of				
20		entire charge	3.5	0.041	5.0	94.8
50	1500		3.1	0.072	5.9	94.1
70			2.8	0.110	6.2	93.4
20		Oilvine with 11-wt %	7.6	0.410	3.0	96.1
50	2000	metallic nickel (5.5 per-	6.7	0.542	4.0	94.6
70		cent of charge weight)	5.1	0.621	10.6	88.1
20		Olivine with 11-wt % iron	6.9	2.211	2.3	97.1
50	2000	Nickel monoxide consti-	5.5	2.902	3.2	95.6
70		tutes 7.0 percent of weight of entire charge	4.2	3.846	Finely dispersed phase not analyzed	

orites and in meteorite and terrestrial silicates. In addition, the calculated volumetric effect for the substitution of iron in the olivine structure by other transition metals is at a maximum, in absolute value for nickel: $- 1.4$ $cm^3/mole$, compared with $- 0.39$ for cobalt and $+ 0.85$ for manganese.

The ratios of the metallic and silicate portions were selected based on the composition of pallasite. Thus, metallic nickel was 5.5 wt %, which corresponds to the second group of pallasites in the classification of Yavnel' (ref. 5). When nickel was incorporated in the mixture in the oxide form, the amount of nickel monoxide was 7 wt %. Evaluation of the experimental conditions showed that the error in determination of pressure in the reaction chamber is not over 10 percent of the nominal value at temperatures from 1100 to 1500° C. The temperatures were measured with a tungsten-rhenium thermocouple, and the accuracy of determination of sample temperature was $\pm 20°$ C, with allowance

for thermal gradients in the chamber. The oxidation-reduction conditions in the chamber were estimated indirectly from the reaction minerals present at the boundary with the graphite container (iron carbides and pyroxenes), which were determined by X-ray diffraction and X-ray spectral microanalysis. This is evidence that oxygen was removed from the system and, consequently, that the conditions in the synthesis were reducing.

Microanalysis of the synthesized olivines demonstrated their uniformity (coefficient of variation is not over 5 percent), indicating achievement of equilibrium in the system.

Study of the distribution of iron and nickel in the olivine-metal system in synthetic samples at temperatures from 1100 to 2000° C and pressures up to 70 kbar has shown that the nickel content in olivine increases with increasing pressure. Thus, with increasing pressure (from 20 to 70 kbar at 1500° C), the content of nickel in olivine increases from 0.04 to 0.11 wt % (see table

3). With increasing temperature to 2000° C, the nickel concentration in olivine increases from 0.41 to 0.62 wt % at a similar increase in pressure. At low temperatures (1100° C) diffusion processes are hampered, and the trace element content in olivine increases negligibly (from 0.016 to 0.021 wt %).

The content of oxygen in the system strongly affects the course of the exchange reaction. In experiments where nickel was incorporated into the reaction mixture in the form of the monoxide, the olivines obtained were strongly enriched in nickel (up to 3.85 wt %), which is never encountered in nature. The highest concentration of iron in the melt has been found in samples subjected to pressures of 70 kbar (up to 10.6 percent at $T = 2000°$ C).

In scanning photos of samples synthesized at $T = 2000°$ C and pressures of 20 kbar (fig. 1) and 70 kbar (fig. 2), it is evident that in the exchange reaction between metallic and olivine phases, iron in the olivine is replaced by nickel. In this case, the iron forms an alloy with unreacted nickel.

In scanning photos using reflected electrons (figs. 1a and 2a), white drops of metal of different sizes stand out from the light gray background of the silicate portion. In photos using the characteristic X-rays of nickel and iron (figs. 1 and 2), it is seen that the metal drops are a nickel-iron alloy.

Photos in the characteristic X-rays of silicon (fig. 1c) and magnesium (fig. 2c) confirm the absence of silicate inclusions in the metallic phase. The scanning photos (figs. 1b and 2b) show that nickel is distributed through the entire silicate portion of the samples, which is evidence of the completeness of the nickel-ferromagnesian olivine exchange reaction, both in the case where the reagent was nickel monoxide and in the case where metallic nickel was used. This is evidence of the possibility that the exchange reaction occurs without additional amounts of oxygen.
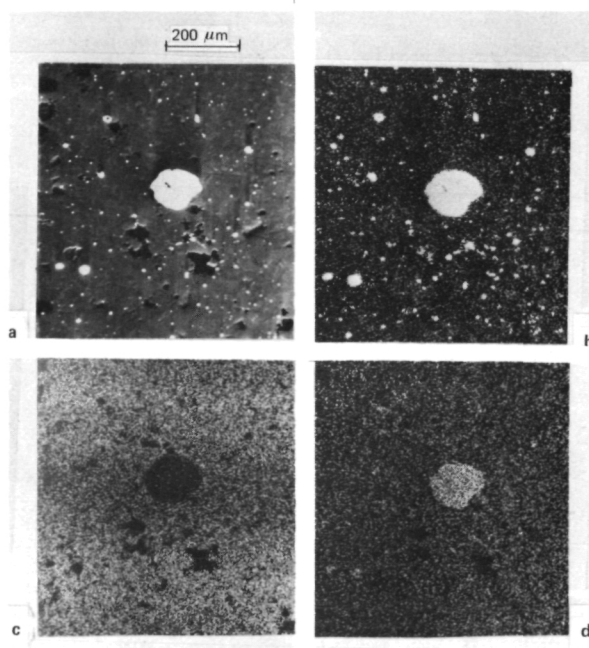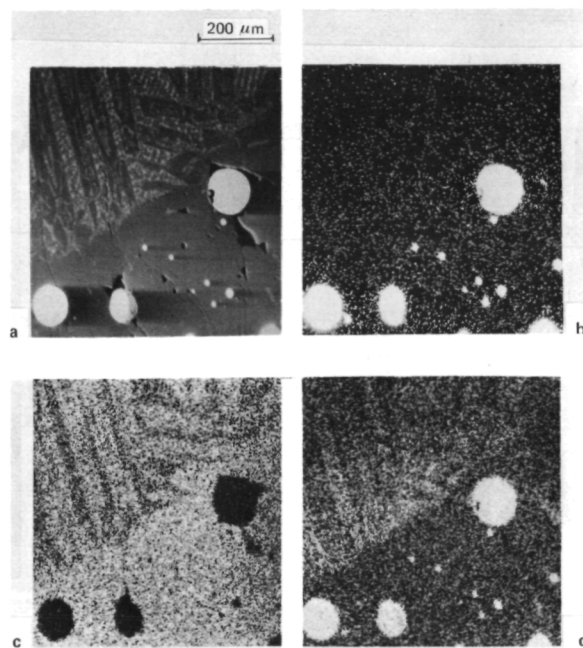

Figure 1.—*Scanning photographs of synthetic sample, produced at* T = 2000° C *and* P = 20 kbar *(starting materials were olivine + NiO): (a) in reflected electrons; (b) in characteristic* Ni_{K_a} *X-radiation; (c) in characteristic* Si_{K_a} *X-radiation; and (d) in characteristic* Fe_{K_a} *X-radiation.*

Figure 2.—*Scanning photographs of synthetic samples, produced at* T = 2000° C *and* P = 70 kbar *(starting materials were olivine + Ni): (a) in reflected electrons; (b) in characteristic* Ni_{K_a} *X-radiation; (c) in characteristic* Mg_{K_a} *X-radiation; and (d) in characteristic* Fe_{K_a} *X-radiation.*
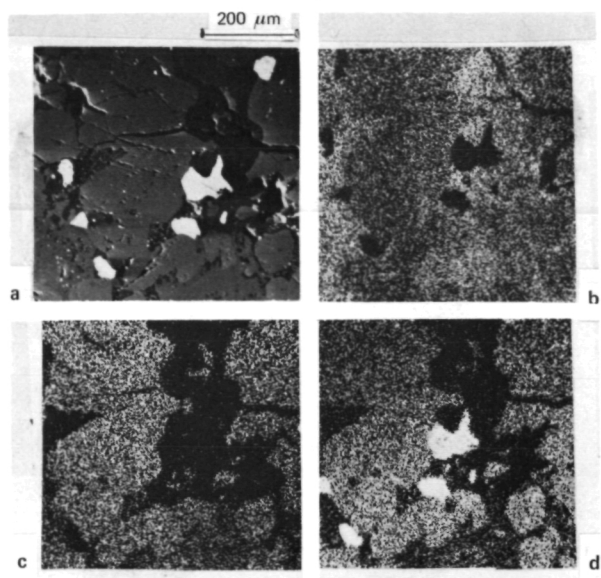
Figure 3.—*Image of Nikol'skoye chondrite structure before the experiment: (a) in reflected electrons; (b) in characteristic Si_{K_a} X-radiation; (c) in characteristic Mg_{K_a} X-radiation; and (d) in characteristic Fe_{K_a} X-radiation.*

Figure 4.—*Image of Nikol'skoye chondrite structure after the experiment (T = 1500°C and P = 70 kbar): (a) in reflected electrons; (b) in characteristic Fe_{K_a} X-radiation; (c) in characteristic Ni_{K_a} X-radiation; and (d) in characteristic Si_{K_a} X-radiation.*

Figure 5.—*Image of Kaande chondrite structure after the experiment (T = 1100°C and P = 150 kbar): (a) in reflected electrons; (b) in characteristic Si_{K_a} X-radiation; (c) in characteristic Fe_{K_a} X-radiation; and (d) in characteristic Ni_{K_a} X-radiation.*

Besides the tests with synthetic mixtures, chondrite material was used to model the differentiation processes in the mantle of the Earth. Olivine-hypersthene (Kaande) and olivine-bronzite (Nikol'skoye) chondrites were held at pressures from 60 to 150 kbar and temperatures of 1000 to 1500° C. Comparison of the scanning images of the microstructure of the chondrites before and after the experiment (fig. 3) shows that a great change took place in the meteorite structure. In the scanning photos, traces of metal flowage are seen (fig. 4), and emulsion structures of sulfides and nickel iron are frequently observed on rapid cooling (fig. 5).

Interesting results were obtained by holding the Kaande chondrite at a pressure of 150 kbar and $T = 1000°$ C for a period of 10 min. Diamond was formed from the graphite that diffused into the chondrite material from the reaction chamber, with the metallic phase of the chondrite serving as a catalyst for the process. Changes occurred in the olivine composition: the amount of nickel increased and the manganese content
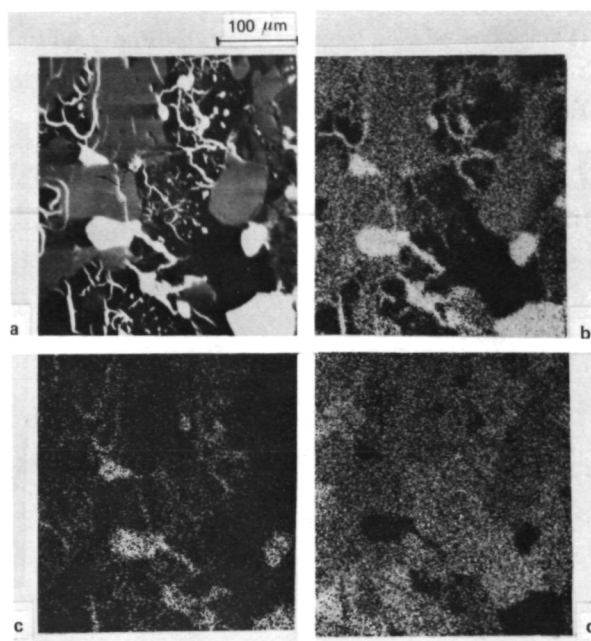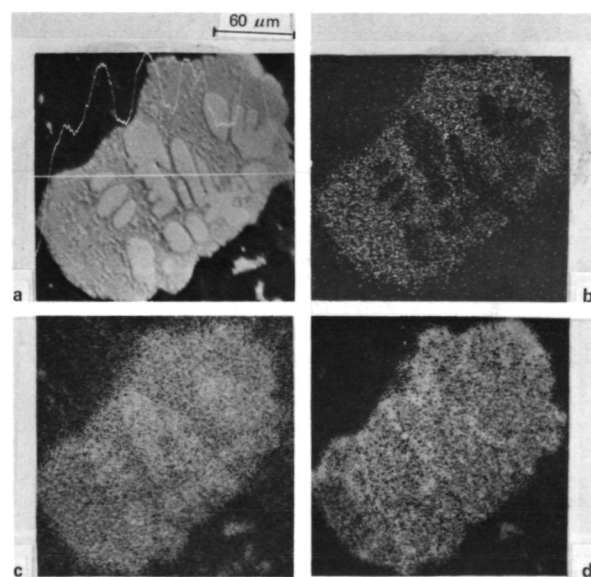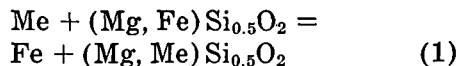
decreased somewhat, but all these processes are negligible, most likely because the low temperature restricted diffusion.

The experimentally confirmed tendency of nickel to enter into the olivine structure at high pressures allows calculation of the metal-olivine phase equilibrium conditions, not only for pallasites, chondrites, and achondrites, but also for rocks of the Earth's mantle.

Calculation of Equilibrium Conditions for the Metal-Olivine System in Natural Materials

On the basis of data on the content of trace elements in olivines as well as data on the composition of the metallic phase, one can calculate the equilibrium constant for exchange reactions of the type

$$Me + (Mg, Fe) Si_{0.5}O_2 = Fe + (Mg, Me) Si_{0.5}O_2 \qquad (1)$$

where iron group elements are the metal which is isomorphically replacing iron in olivine and forming solid solutions with iron in the metallic phase of meteorites. The equilibrium constant is shown below

where γ_{Fe}^{alloy} and $\gamma_{FeSi_{0.5}O_2}^{olivine}$ are the activity coefficients of a given component in the metallic and olivine phases, respectively, and

X_{Fe}^{alloy} and $X_{FeSi_{0.5}O_2}^{olivine}$ are the mole fractions of the components.

It is known that iron-magnesium, iron-nickel, and magnesium-nickel olivines, as well as iron-nickel binary solid solutions, differ little from ideal solid solutions at temperatures of about 1000° C and above. There-

$$K = \frac{(\gamma_{Fe}^{alloy})(X_{Fe}^{alloy})(\gamma_{MeSi_{0.5}O_2}^{olivine})(X_{MeSi_{0.5}O_2}^{olivine})}{(\gamma_{Me}^{alloy})(X_{Me}^{alloy})(\gamma_{FeSi_{0.5}O_2}^{olivine})(X_{FeSi_{0.5}O_2}^{olivine})}$$

Figure 6.—*Equilibrium constants versus temperature for reaction $Ni + FeSi_{0.5}O_2 = Fe + NiSi_{0.5}O_2$ (at P = 1 atm).*

fore, using methods of calculation for ideal solutions, the equilibrium constant can be calculated for the reaction

$$Ni + (Mg, Fe) Si_{0.5}O_2 =$$
$$Fe + (Mg, Ni) Si_{0.5}O_2 \qquad (2)$$

knowing only the ratio of the mole fractions of the components and taking the activity coefficients of the components in nearly ideal solid solution to be unity. Thus,

$$K = \frac{X^{alloy}_{Fe} \times X^{olivine}_{FeSi_{0.5}O_2}}{X^{alloy}_{Ni} \times X^{olivine}_{NiSi_{0.5}O_2}}$$

Using the thermochemical data presented in references 6 and 7, we calculated the values of the free energy of the exchange reaction at temperatures from 1100 to 1500 K, as well as the equilibrium constants of this reaction. On the basis of the calculations, a graph was plotted of the logarithm of the equilibrium constant versus temperature (fig. 6). The distribution coefficients for iron and nickel between the metallic and olivine phases were plotted on this graph for pallasites, ureilites, and chondrites of groups H6, L6, and LL6, as calculated from the analytical data in this paper. As is seen, the distribution factors for pallasites and chondrites of groups H6 and L6 fit well in this temperature range.

For all the pallasites studied, the equilibrium temperatures are close together and correspond to a temperature of 1500 K (at a pressure of 1 atm). In group H6 chondrites the equilibrium between the metal and olivine phases corresponds to a temperature of 1600 K; in group L6 chondrites, the equilibrium corresponds to a temperature of 1200 K. Lower temperatures characterize the equilibrium in group LL6 chondrites (900 K), and higher temperatures, up to 1900 K, are characteristic in achondrites.

An approximate calculation of the distribution factor between olivines from ultrabasic terrestrial rocks and metal, containing 8 percent Ni on the average, gives values that differ sharply from the equilibrium constants of the reactions, as calculated for atmospheric pressure. This suggests that other factors affect the interactions of the metallic

and silicate phases during early stages of formation of the Earth's mantle from chondrite material.

Shift of the metal-olivine equilibrium in the direction of formation of olivines with a high nickel content may be due to two factors besides temperature, i.e., total pressure and the oxygen fugacity in the system. However, there is not sufficiently reliable information at the present time on the fugacity of oxygen at various depths.

The effect of pressure on the distribution constant can be expressed in the following manner:

$$P'' - P' = -\frac{2.3\,RT}{\Delta V} \log \frac{K''}{K'}$$

where P'' and P' express the change in pressure and K'' and K' the change in distribution constants. In the $\sim$ 100-kbar pressure region, $P'' >> P'$, and the formula is simplified to the form:

$$P'' = -\frac{2.3\,RT}{\Delta V} \log \frac{K''}{K'}$$

Using data on the nickel and iron concentrations in olivines from peridotite inclusions in kimberlite pipes and considering the inadequacy of the oxidation-reduction conditions in different parts of the mantle, the pressure for garnet peridotites can be estimated (at a temperature of 1800° C) to be approximately 100 kbar.

Conclusions and Discussion of Results

The data obtained allow determination of the relationship between the trace element content in olivines and the conditions of formation of rocks containing these minerals.

The highest concentrations of nickel and lowest concentrations of manganese are observed in the deepest rocks, garnet peridotites, which are characterized by maximum pressures and high temperatures of formation. In proportion to decreasing pressure in the series of mantle inclusions—achondrites, lunar rocks, chondrites—there occurs a de-

crease in the amount of nickel and an increase in the amount of manganese.

Chromium does not follow the regularities noted for nickel and manganese. Its maximum concentration is found in olivines from carbon- and diamond-containing achondrites and lunar soil.

High chromium content in lunar olivines also has been noted in work (ref. 8). The Cr_2O_3 concentration (up to 0.4 percent) of lunar olivines exceeds even that of olivines included in diamonds from kimberlite pipes (up to 0.06 to 0.09 percent) (refs. 9 and 10).

A sharp increase in chromium concentration, under conditions known to be reducing, is evidence that this element can be used as an indicator of the oxidation-reduction conditions of mineral formation.

Variations in the measured cobalt concentrations in meteorite and mantle olivines are negligible and cannot be considered as reliable indicators of the formation conditions.

The behavior of iron is also very nonunique in conformance with the diversity of factors which can change the concentrations of this macrocomponent. According to a large amount of experimental data, there is a strong dependence of the iron content in olivine on oxidation-reduction conditions, pressure, and temperature of the process.

Earlier, Vinogradov (ref. 11) examined the question of the cause of differentiation of trace elements between the metal and oxide phases in the protoplanetary cloud. It was shown that elements whose oxygen partial pressure of the reversible equilibrium of metal with the oxide is lower than in the Fe-FeO system at the melting temperature of iron (1803 K) can be oxidized to an oxide and do not dissolve in the metallic Fe-Ni phase. Manganese and chromium are among these elements. Chemical elements requiring higher oxygen partial pressures (P_{O_2}) for their oxidation will remain predominantly in the metallic phase. Nickel and cobalt are among these elements. Thus, at an early stage of differentiation of the protoplanetary material, oxidation-reduction conditions played a decisive part, and maximum concentrations of Mn and Cr, with minimum Ni

and Co contents, were actually observed in the olivines of chondrites which are analogs of the primary material.

Subsequent differentiation in solid bodies is caused by a set of physical-chemical factors whose roles are still difficult to distinguish. Attention should be given first to the specific physical-chemical properties of the transition elements of the iron group. The main feature of these elements is variable valence. Change in valence of the transition metals depends on the ratio of the values of the successive ionization potentials. For chemical elements with comparatively low ionization potentials such as the transition elements, a small increase in temperature leads to a transition to a more highly ionized state, i.e., to an increase in valence. This concerns Fe and Cr first of all, because the low values of the first, second, and third ionization potentials, as well as the differences between them, are characteristic (the difference between the second and third ionization potentials for iron and chromium are minimal, 14.66 and 14.51 eV, respectively).

With change in oxidation-reduction conditions or temperature fluctuations, Fe and Cr will first change valence and move from one phase (mineral) to another, as shown for example by the increase in valence of these elements in the series metal-silicate-chromium spinel. Therefore, Cr and Fe can serve as indicators of the temperature and oxidation-reduction conditions.

For transitions of Ni and Mn to higher valence states, considerably more additional energy of ionization is required, 18.01 and 18.05 eV, respectively, and for Co, 16.44 eV. It can be assumed that their differentiation among phases is determined by other factors. In addition to the effect of the oxygen partial pressure (P_{O_2}) already noted, one such factor is the volumetric effect of the substitution reaction.

It is evident from table 4 that the greatest volume gain occurs for the substitution of manganese for iron in the olivine structure; that the least effect is observed for substitution by Ni; and that there is very little effect for Co. The substitution of Mn for Fe is posi-

Table 4.—*Volumetric Effects of Substitution Reaction*

Reaction	$Me + MgSi_{0.5}O_2 = Mg + MeSi_{0.5}O_2$	$Me + FeSi_{0.5}O_2 = Fe + MeSi_{0.5}O_2$
Metal	$\Delta V \dfrac{cm^3}{mole}$	$\Delta V \dfrac{cm^3}{mole}$
Mn	+ 9.06	+ 0.85
Fe	+ 8.21	—
Co	+ 7.82	− 0.39
Ni	+ 7.77	− 1.44
Mg	—	− 8.21

tive, i.e., it leads to an increase in volume of the olivine unit cell by expanding of the crystal structure.

In this manner one may use the physical-chemical factors considered to qualitatively explain the regularities of distribution of the transition elements Fe, Ni, Co, Cr, and Mn between metal and silicate phases established in this work; that is, increasing Ni and decreasing Mn contents in olivines from rock formed at high pressures and the concentration of Cr in rocks formed under reducing conditions.

Comparison of the analytical data of iron group transition element content in olivines of various origins, with the experimental results of modeling the interactions of the "metal-olivine" phases under conditions of high pressure and temperature as well as with thermodynamic calculations, permits the very specific conclusion that there is a sharp difference between the conditions of differentiation of the protoplanetary material during the formation of meteorites and asteroids and the conditions of differentiation of the planets and the Moon into concentric layers.

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