The Chemical Composition of the Cores of the Terrestrial Planets and the Moon

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Using models of the quasi-chemical theory of solutions, the activity coefficients of silicon are calculated in the melts Fe-Si, Ni-Si, and Fe-Ni-Si. The calculated free energies of solution of liquid nickel and silicon in liquid iron in the interval 0 to 1400 kbar and 1500 to 4000 K, shows that Fe-Ni-Si alloy is stable under the conditions of the outer core of the Earth and the cores of the terrestrial planets. The oxidation-reduction conditions are studied, and the fugacity of oxygen in the mantles of the planets and at the core-mantle boundary are calculated. The mechanism of reduction of silicon is analyzed over a broad interval of P and T. The interaction between the matter of the core and mantle is studied, resulting in the extraction of silicon from the mantle and its solution in the material of the core. It is concluded that silicon can enter into the composition of the outer core of the Earth and Venus, but probably does not enter into the composition of the cores of Mercury, Mars, and the Moon, if in fact the latter possesses one.

The question of the composition and mechanism of formation of the cores of the Earth and the terrestrial planets is still open. Among the various approaches to the solution of this problem, one of the most significant is analysis of a number of processes from the physical-chemical standpoint. In the first approximation they can be reduced to the following questions: (1) what were the redox conditions in the protoplanetary cloud; (2) what are the redox conditions in the mantle and at the core-mantle boundary; (3) what is the possibility of formation of alloys of iron with other chemical elements upon condensation from the protoplanetary cloud; (4) what is the possibility of solution of chemical elements in the liquid iron core; and (5) what is the possibility that equilibrium exists between the core and mantle.

The experimental data currently available allow sufficiently accurate calculation of processes occurring under the P–T conditions corresponding to the interior of the Earth.

After experimental studies (refs. 1 and 2) on the dynamic compressibility of iron-nickel alloy confirmed the hypothesis of Birch (ref. 3) about the inconsistency of the concepts of formation of a core of this composition, it became conclusively clear that in addition to the basic iron-nickel components the core contains other, lighter substances which reduce its density by 10 to 20 percent in comparison to the density of nickel-containing iron under the same conditions.

MacDonald and Knopoff (ref. 4) and Ringwood (ref. 5) suggested that such substance might be silicon.

It is the purpose of the present work to analyze the following problems: (1) the possibility of solution of silicon and nickel in liquid iron over a broad interval of P and T; (2) the mechanism for inclusion of silicon in the cores of the planets due to its reduction in the mantle; and (3) the mechanism for inclusion of silicon in the cores of the planets due to interaction between the material of the core and mantle.

Solubility of Silicon and Nickel in Liquid Iron

Information on the inclusion of impurities in the core can be produced by calculating the free energy of solution of a chemical element or compound in liquid iron, which consists of the free energy of the process at a constant temperature and the contribution of high pressure:

$$\Delta G_T^P = G_T^\circ + \int_0^P \Delta V dP$$

The first term in the right-hand portion of the equation can be obtained experimentally or found theoretically using well-founded models of the theory of solutions. The second term is the difference between the partial molar volume of a component in a solution and the volume of the pure component at the same pressure.

THERMODYNAMIC PROPERTIES OF MELTS IN THE FE-NI-SI SYSTEM AT 1 ATM.

Metals similar in their properties to iron form nearly ideal solutions (quasi-ideal solutions) with iron.

Consider a dilute solution

$$Ni_{(l)} = [Ni] \text{ in } Fe_{(l)}$$

For one mole of dissolved material, the change in partial free energy between its initial state in the form of a pure component and its final state in the form of an ideal solution is

$$\Delta G_T^\circ \text{ soln.} = G_i - G_i^\circ = RT\ln a_i = RT\ln X_i \qquad (3)$$

where X_i is the molar fraction of the dissolved material.

The calculated values of ΔG_T° (soln.) with a content of 10 wt. % Ni in the solution are presented in table 1.

Liquid alloys of iron and silicon do not follow the regularities of ideal solutions, but are described in terms of stricter theories in which the close order, as well as the temperature and concentration dependence of the energies of the interatomic interaction, must be considered in melts (refs. 6 and 7).

The activity of silicon in melts at various temperatures has been calculated by an asymmetrical version of the quasi-chemical theory of solutions (ref. 7). The method of calculation and initial thermodynamic characteristics were described in detail in reference 8.

The activity of silicon in Fe-Si and Ni-Si melts at $X_{Si} = 0.2$, which corresponds to 11.2 wt. % Si, was calculated by two methods. In

$$\begin{aligned}\ln a_2 = {} & \ln X_2 + 1/RTX_1^2\,(X_1\Delta\bar{G}_2^{o(E)} + X_2\Delta\bar{G}_1^{o(E)})\,(1 + \eta + X_2\frac{\partial\eta}{\partial X_2}) \\ & + X_1^2X_2(1 + \eta)1/RT\,(\Delta\bar{G}_1^{o(E)} - \Delta\bar{G}_2^{o(E)}) + \tfrac{1}{2}Z\Big\{\Big[X_2 - X_1\eta + X_1X_2(1 + \eta \\ & - X_1\frac{\partial\eta}{\partial X_2})\Big]\ln\frac{X_2 - X_1\eta}{X_2} - X_1^2(1 + \eta + X_2\frac{\partial\eta}{\partial X_2})\ln\frac{X_1 - X_2\eta}{X_1} \\ & + 2X_1^2(1 + \eta)\ln(1 + \eta) + 2X_1^2X_2\frac{\partial\eta}{\partial X_2}\ln(1 + \eta)\Big\}\quad ;\end{aligned} \qquad (5)$$

$$\begin{aligned}\frac{\partial\eta}{\partial X_1} = {} & -\frac{\partial\eta}{\partial X_2} = \frac{1+\eta}{1-\eta}\Big\{\frac{\eta\ (X_2 - X_1)}{X_1X_2} + \frac{2(\Delta\bar{G}_2^{o\,(E)} - \Delta\bar{G}_1^{o\,(E)})}{ZRT} \\ & \times\Big[\eta - X_1X_2(1+\eta)^2\Big]\Big\}.\end{aligned} \qquad (6)$$

the first case, calculations were made using the equation

$$\ln a_2 = \frac{X_1 Q_{12}(1+\eta)}{RT(1-\eta)}$$

$$(X_1 - X_{2\eta}) + \ln X_2 + \tfrac{1}{2} Z \ln\left[\frac{X_2 - X_1\eta}{X_2}\right] +$$

$$+ \tfrac{1}{2} Z X_1 (X_1 - X_{2\eta}) \left(\frac{1+\eta}{1-\eta}\right)$$

$$\ln \frac{X_1 X_2 (1+\eta)^2}{(X_1 - X_{2\eta})(X_2 - X_1\eta)}, \qquad (4)$$

where η is the close order parameter; $Q'_{12} = Q_{12} + (ZRT\ln 2)/2$ takes into account the dependence of mixing energy on temperature, where

$$-Q_{12} = \Delta\overline{H}^{\circ}{}_1 + qX_1 = -\Delta\overline{H}^{\circ}{}_2 - qX_2,$$
$$q = \Delta\overline{H}^{\circ}_2 - \Delta\overline{H}^{\circ}_1\,;\ X_1 \text{ and } X_2$$

are the molar fractions of the first and second components. In the second case, equations 5 and 6, found on the preceding page, were used.

The value of the close order parameter η, considering the deviation in distribution of atoms in a binary solution from random distribution, can be determined from the equation

$$(B-1)(1+\eta_{12})^2 X_1 X_2 - B\eta_{12} = 0 \qquad (7)$$

The probability parameter B was calculated by two methods:

$$B = \exp\left(-\frac{2Q_{12}}{ZRT}\right) \qquad (8)$$

and

$$B = exp\left[\frac{2(X_1 \Delta\overline{G}_2^{o(E)} + X_2 \Delta\overline{G}_1^{o(E)})}{ZRT}\right] \qquad (9)$$

where $\Delta G^{(E)} = \Delta G - \Delta G^{(\text{ideal})}$,

and Z is the mean coordination number.

Calculation of the averaged values of log γ_{Si} using equations (4) and (5) by the method of least squares in the interval 1500 to 4000 K leads to the following equations.

In the Fe-Si system

$$\log \gamma_{Si} = -\frac{4588}{T} + 0.656 \qquad (10)$$

In the Ni-Si system

$$\log \gamma_{Si} = -\frac{7268}{T} + 0.71 \qquad (11)$$

Let us now estimate the influence of 10 percent Ni on γ_{Si}, a_{Si}, and the free energy of solution of silicon in the ternary system Fe-Ni-Si. In the first approximation, this calculation can be expressed by the equation

$$\log \gamma_{Si_{(\text{Fe-Ni-Si})}} = X_{Fe} \log \gamma_{Si_{(\text{Si-Fe})}} + X_{Ni} \log \gamma_{Si_{(\text{Si-Ni})}} \qquad (12)$$

Combining the earlier calculated data on γ_{Si} in liquid binary systems, we produce:

$$\log \gamma_{Si_{(\text{Si-Fe-Ni})}} = -\frac{4856}{T} + 0.661 \qquad (13)$$

When 10 percent Ni is added to a melt, the values of γ_{Si} and a_{Si} decrease. However, this reduction is slight and the differences in free energies of solution of liquid silicon in liquid iron and in liquid nickel-iron are also not great, amounting to approximately 1.2 kcal through the entire temperature interval.

Calculation of the errors of thermodynamic parameters of Fe-Si, Ni-Si, and Fe-Ni-Si melts was described in an earlier work (ref. 8).

INFLUENCE OF HIGH PRESSURE ON SOLUBILITY OF NICKEL AND SILICON IN LIQUID IRON

In order to calculate the free energy of the process of solution at high pressures, information is required on the volumes of the pure liquid metals and the partial molar volumes of the metals dissolved in liquid iron.

In earlier works (refs. 1, 2, and 9 through 12), results are presented from studies of the dynamic compressibility of pure metals, iron-nickel, and iron-silicon alloys up to megabar pressures. From these data, the partial molar volumes of Ni and Si were calculated at pressures of 300, 500, 1000, and 1400 kbar (ref. 8).

The values of free energy of solution of liquid nickel (10 wt. %) and silicon (~ 10 wt. %) in liquid iron as functions of P and T are presented in table 1.

Table 1.—*Free Energies of Dissolution of Liquid Nickel (10 wt. %) and Liquid Silicon (10 wt. %) in Liquid Iron*

	$Ni_{(l)}$ = [Ni] (in $Fe_{(l)}$)					$Si_{(l)}$ = [Si] (in $FeNi_{(l)}$)				
T,K P,bar	1	3.10^5	5.10^5	10^6	$1.4.10^6$	1	3.10^5	5.10^5	10^6	$1.4.10^6$
1500	−7 000	−5 070	−5 450	1 130	3 370	−22 480	−44 060	−52 350	−76 970	−106 800
2000	−9 330	−7 400	−7 780	−1 200	1 040	−22 570	−44 150	−52 440	−77 060	−106 890
2500	−11 660	−9 730	−10 110	−3 530	−1 290	−22 660	−44 240	−52 530	−77 150	−106 980
3000	−14 000	−12 070	−12 450	−5 870	−3 630	−22 750	−44 330	−52 620	−77 240	−107 070
3500	−16 330	−14 400	−14 780	−8 200	−5 960	−22 840	−44 420	−52 710	−77 330	−107 160
4000	−18 660	−16 730	−17 110	−10 530	−8 290	−22 930	−44 510	−52 800	−77 420	−107 250

The free energy of solution of nickel decreases with increasing temperature (this follows from equation (1)), since the partial molar volume of nickel is greater than the volume of the pure element, i.e., $\Delta V > 0$. As composition changes, ΔG_T^P changes in a rather complex manner.

Figure 1 shows the change in free energy of solution of liquid nickel in liquid iron as a function of concentration of Ni at various temperatures at a constant pressure of 1400 kbar. The extremes on the curves result from the dependence of the partial molar volume of nickel in the melt on concentration of nickel. At parameters characteristic for the core-mantle boundary (~ 1400 kbar), the free energy has a minimum, indicating the stability of the Fe-Ni melt with nickel concentration ≃ 10–18%.

The data produced indicate that up to pressures on the order of 500 kbar, nickel is dissolved in liquid iron at all of the temperatures studied. At pressures of 1000 to 1400 kbar, its solution is possible if the temperature is over 2000 K (table 1).

Table 2 presents certain data that allow us to judge the distribution of temperatures and pressures in the terrestrial planets and the Moon. At the core-mantle boundary of Mercury, Mars, and the Moon[1], the pressures do not exceed 300 kbar. The positive value of the contribution $\int \Delta V dP$ to the value of ΔG_T^P is not great; the free energy of solution is a negative value and nickel may therefore be included in the composition of the cores of

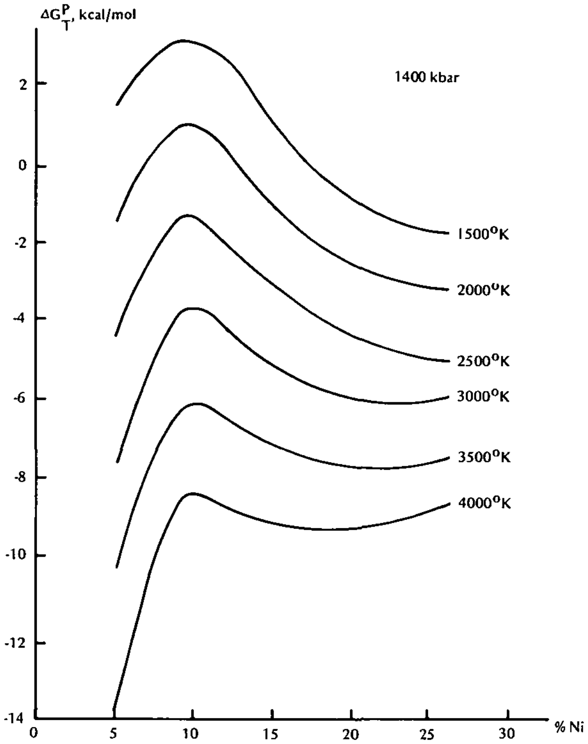

Figure 1.—*Change in free energy of solution of liquid nickel in liquid iron as a function of concentration of nickel in Fe-Ni system at 1400 kbar and various Temperatures.*

Table 2.—*Assumed P–T Conditions at the Core-Mantle Boundary for Earth-Type Planets*

Planet	Mean Radius of Planet (km)	Mean Radius of Core (km)	Pressure at Core-Mantle Boundary (kbar)	Temperature at Core-Mantle Boundary (K)
Mercury	2437	1700–2000	~ 100	1400–2000
Venus	6054	~ 3000	~ 1400	~ 4000
Earth	6371	3471	~ 1400	~ 4000
Mars	3386	500–1000	250–300	1000–1500
Moon	1737	200–300	~ 50	1000–1500

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[1] It is not clear if the Moon has a core. The latest data presented at the Soviet-American Conference on the Cosmochemistry of the Moon and Planets did not clear up the question. Our calculations show that iron-nickel alloy is stable under the P-T conditions of the interior of the Moon, but they neither study nor answer the question of the existence of a core.

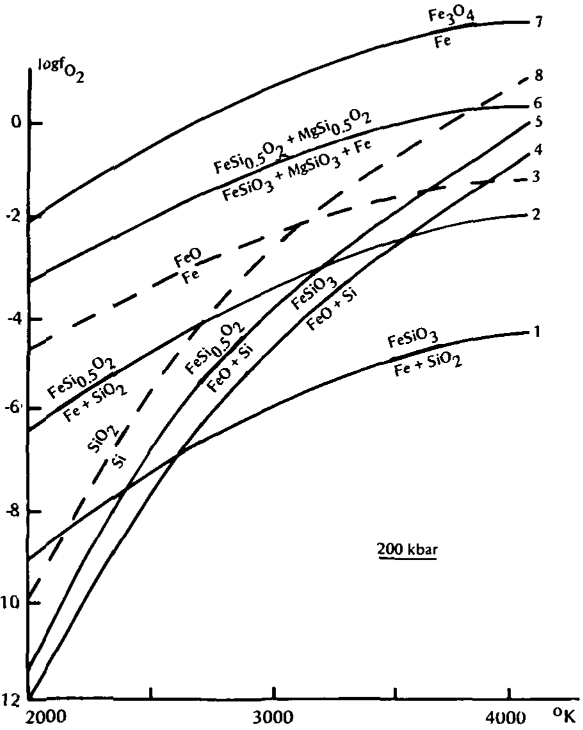

Figure 2a.—*Dependence of oxygen fugacity on temperature in the mantle of the Earth.* P = *200 kbars. Reactions:*

1. $FeSiO_3(s) = SiO_2(st.s) + Fe(l) + \frac{1}{2}O_2$
2. $FeSi_{0.5}O_2(sp.s.) = \frac{1}{2}SiO_2(st.s) + Fe(l) + \frac{1}{2}O_2$
3. $FeO(s) = Fe(l) + \frac{1}{2}O_2$
4. $FeSiO_3(s) = FeO(s) + Si(l) + O_2$
5. $FeSi_{0.5}O_2(sp.s) = FeO(s) + \frac{1}{2}Si(l) + \frac{1}{2}O_2$

6a. $FeSi_{0.5}O_2(sp.s) + MgSi_{0.5}O_2(sp.s) = MgSiO_3(s) + Fe(l) + \frac{1}{2}O_2$
6b. $2FeSi_{0.5}O_2(sp.s) = FeSiO_3(s) + Fe(l) + \frac{1}{2}O_2$
6c. $FeSi_{0.5}O_2(sp.s) + MgO(s) = MgSi_{0.5}O_2(sp.s) + Fe(l) + \frac{1}{2}O_2$
6d. $FeSiO_3(s) + MgO(s) = MgSiO_3(s) + Fe(l) + \frac{1}{2}O_2$
7. $\frac{1}{4}Fe_3O_4(s) = \frac{3}{4}Fe(l) + \frac{1}{2}O_2$
8. $SiO_2(st.s) = Si(l) + O_2$

these celestial bodies. At the core-mantle boundary of the Earth and Venus, the pressure is approximately 1400 kbar, but insofar as the temperature at the boundary is greater than 2000 K, the total change of the value $\Delta G_T^p < 0$ and Fe-Ni cores are not stable.

Thus, calculations show that Fe-Ni melts are stable in the ranges of temperatures and pressures characteristic for the terrestrial planets and the Moon.

The free energy of solution of liquid silicon and liquid iron is practically independent of temperature (due to the increase in activity), but decreases quite sharply with increasing pressure (due to high negative volume change), i.e., an increase in pressure facilitates the process of dissolution, table 1.

Calculations show that throughout the entire interval of *P*, *T*, and concentrations, the ΔG_T^p for the solution of silicon in liquid iron or nickel-iron has a large negative value. This indicates the stability of Fe-Si and Fe-Ni-Si melts under the conditions of the outer core of the Earth and the *P–T* conditions of the cores of terrestrial planets.

The stability of Fe-Si melts at the temperatures and pressures of the core of the Earth and the other planets is a necessary but not sufficient condition since we do not know even the principal means and mechanism of inclusion of silicon in the core. In order to understand this, we must study the redox reactions in the mantle of the Earth and the other planets.

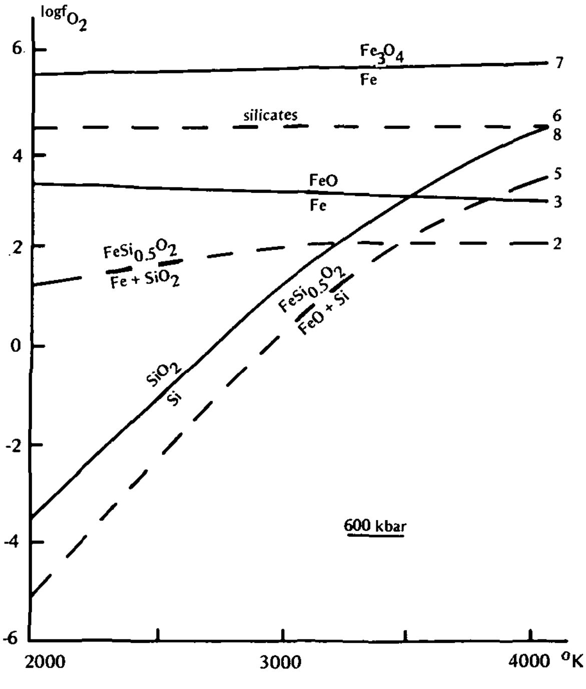

Figure 2b.—*Dependence of oxygen fugacity on temperature in the mantle of the Earth.* P = *600 kbars.*

Redox Reactions in the Interiors of Terrestrial Planets

The fugacity of gases in the mantle in the early stage of evolution of a planet (after its formation from the protoplanetary cloud, but before the descent of iron into the core) can be calculated on the basis of equilibria of metallic iron with ferromagnesium silicates and oxides. We will consider the fugacity of oxygen (f_{O_2}) as an indicator of the redox situation (refs. 13, 14, and 15).

For the reaction $aA + bB = cC + dD + O_2$, the nature of the change of fugacity as a function of phase composition, P, and T and is determined by the expression:

$$\log f_{O_2} = \log f^0_{O_2} + a\log a_A + b\log a_B - c\log a_C - d\log a_D - \frac{1}{2.303RT}\int_0^P \Delta V_s dP$$

where $f^0_{O_2}$ is the equilibrium fugacity of oxygen for a reaction in which all components are in the standard state; ΔV_s is the change in volume of the condensed phases; and a_i is the activity of the iron-containing component in the solid solution. In the calculations we assume $a_i = 0.1$. All calculations were performed with consideration of compressibility data.

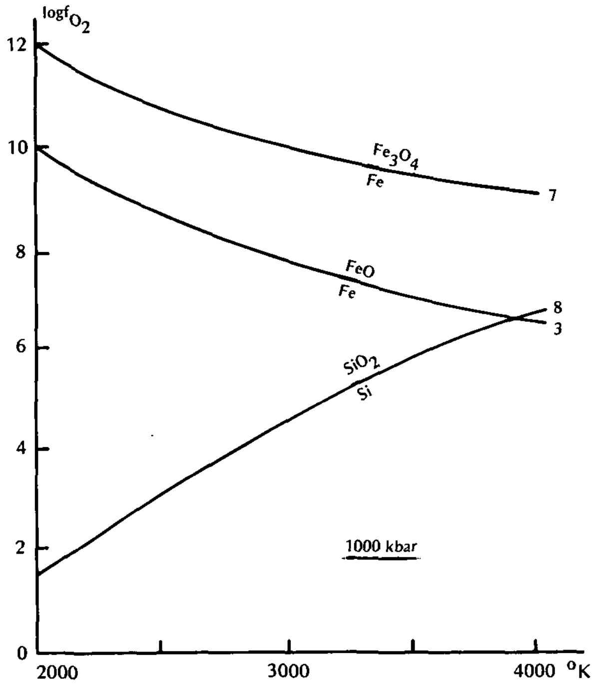

Figure 2c.—*Dependence of oxygen fugacity on temperature in the mantle of the Earth.* P = *1000 kbars.*

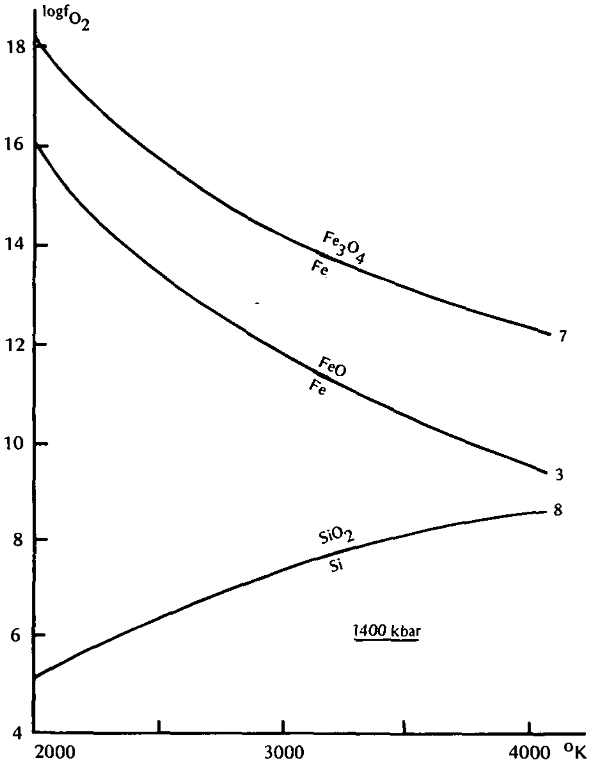

Figure 2d.—*Dependence of oxygen fugacity on temperature in the mantle of the Earth.* P = *1400 kbars.*

The results of calculating the fugacity of oxygen for a number of limiting buffer reactions in the interval 200 to 1400 kbar and 2000 to 4000 K are presented in figures 2a, 2b, 2c, and 2d.

EARTH, VENUS

Interpretation of the results of calculations is based on available information on the composition and structure of the concentric layers of the Earth, obtained from experimental laboratory data at high pressures and seismology. Information on the structure of the other planets is quite sparse. Therefore, analogy is assumed between the chemical composition of the Earth and the terrestrial planets; it is also assumed that all planets have iron cores.

Let us study the limiting buffer reactions which controlled the fugacity of oxygen at various depths in the Earth during the early stages of its development.

At 200 kbar (~ 600 km), the lower limit of f_{O_2} was controlled by reaction (2) for reduction of spinel to Fe and stishovite (fig. 2a). At lower values of f_{O_2}, ferromagnesium silicates are reduced to Fe + SiO_2 or FeO + Si, contradictory to the seismic data which indicate that the transition layer of the mantle consists of Fe and Mg silicates.

The upper limit of f_{O_2} is probably controlled by the equilibrium of iron and magnetite, while the optimal value of f_{O_2} is that which changes according to curve (6) which reflects the Fe-Mg, silicate-Fe equilibrium and essentially combines four reactions (6a, b, c, d).

We can see from figure 2a that the reduction of liquid silicon and its formation of a melt with iron can occur under conditions corresponding to the intersection of reactions (2) and (5), i.e., at $\log f_{O_2} \geq -2.8$ and $T \geq 3200$ K.

However, these temperatures are significantly higher than the melting point of iron and of silicate matter (refs. 16, 17, and 18) and, judging from known thermal models, planetary interiors probably never reached such values. Consequently, the reduction of silicates to silicon at these depths could not have occurred.

Calculations show that the process of reduction becomes possible at pressures of over 400 kbar (~ 1000 km).

The Birch-Magnitsky hypothesis presumes that the lower mantle basically consists of the oxides FeO and MgO (NaCl-type structure) and SiO_2 (stishovite). Recently, this has been experimentally confirmed in experiments on the decomposition of Mg_2SiO_4 to periclase and stishovite at 330 kbar (ref. 19).

We can therefore accept the buffer equilibrium between stishovite and silicon as the lower limit of f_{O_2} in the lower mantle of the Earth, although we cannot exclude the possibility of conversion of the rutile-like modification of SiO_2 into the fluorite-like modification and we can accept the Fe-Fe_3O_4 equilibrium (7) as the upper limit (figs. 2b, 2c, and 2d).

The mass of the current terrestrial core is about one-third of the mass of the planet; consequently, it is obvious that the system Fe-FeO should have controlled f_{O_2} in the lower mantle of the Earth and of any other planet until the iron sank into the core. In other words, this system was responsible for the distribution of oxygen in the mantle, and all other systems were of secondary significance.

At a pressure of 600 kbar (~ 1400 km), T_m (Fe) = 3100 K (ref. 16). The reduction of stishovite becomes possible at $T \geq 3500$ K and $\log f_{O_2} \geq 3.1$ (fig. 2b). Under these conditions, liquid silicon is dissolved in the iron core forming an Fe-Si melt, which later forms the outer core. At 1000 kbar (~ 2200 km) and 1400 kbar (~ 2900 km), T_m (Fe) $\simeq$ 3600 K and 4100 K, and the reduction of silicon could have occurred at $T \geq 3900$ K and 400 K (fig. 2c, 2d). Calculations of the thermal history of the Earth show that such temperatures were reached during the first hundreds of millions of years of its evolution.

Calculations of the thermal history of Venus (refs. 20, 21, and 22) show that the distribution of temperatures in the interior of Venus differs little from the terrestrial values and allows us to assume the presence of an iron core (ref. 23). We will probably not be far off if we assume that the reduction of silicon in the core of Venus occurs at the same *P–T* parameters as on Earth.

As was pointed out in the first section, the free energy of solution of silicon in iron or nickel-containing iron is negative (table 1), which indicates the formation of Fe-Ni-Si melts in the lower mantle of the Earth and Venus. If we accept the scheme of Elsasser (ref. 24), this melt has an unstable equilibrium and descends, forming the outer core.

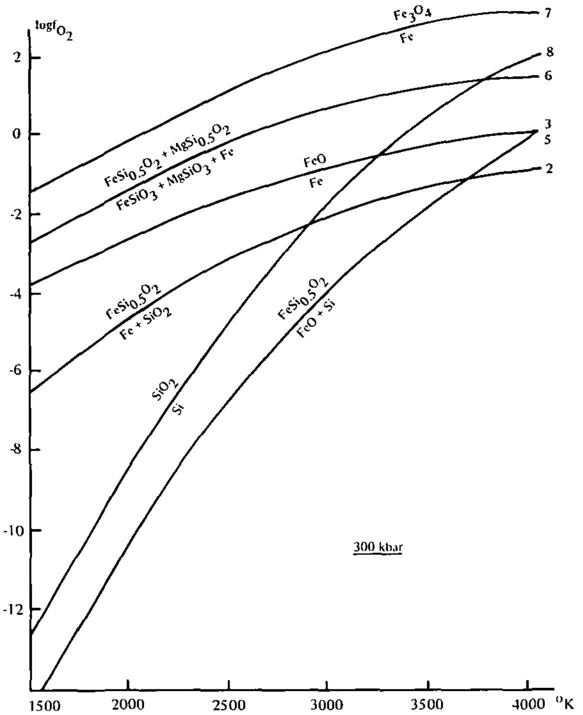

Figure 3.—*Oxygen fugacity as a function of temperature at the presumed core-mantle boundary of Mars.*

MARS

Calculations of models of Mars with an iron core show that the core amounts to not over 4 percent (ref. 25) or 9 to 10 percent (ref. 26) of the mass of the planet. Calculations of the thermal history of Mars, as a function of the concentration of radioactive elements, show that either the interior of the planet below 300 km is at the present time partially or fully molten or 50 percent of the volume of Mars is in the molten state, while the central parts remain solid (ref. 27). In the opinion of Sharma (ref. 28), modern Mars should have lower temperatures than the Earth at the same depths and should contain no liquid core. On the other hand, calculations of the thermal history performed by Toksoz (ref. 23) indicate a solid mantle and molten core.

The pressure at the core-mantle boundary of Mars is approximately 300 kbar (refs. 29 and 30).

Figures 2a and 3 show the results of calculation of the fugacity of oxygen for a number of reactions at 200 and 300 kbar.

At 200 kbar, the mantle of Mars consists of solid solutions of silicates and, as was noted earlier, the lower limit of reduction of silicon corresponds to a temperature of ≥ 3200 K.

At a pressure of 300 kbar, two versions are possible: either a silicate or an oxide mantle. In the former case, the reduction of silicates and formation of Fe-Si melt is possible at $\log f_{O_2} \geq -1.2$ and $T \geq 3650$ K (at the intersection of reactions 2 and 5), the second case is possible where $\log f_{O_2} \geq -0.5$ and $T \geq 3200$ K (at the intersection of reactions 3 and 8).

Study of the thermal history of Mars does not allow us to judge whether such temperatures were reached in the early stages of its development. Processing of data produced by Mariner 6 and 7 allowed Anderson (ref. 31) to propose that the entire core of the planet was not separated from the mantle. This means that the heating of Mars was insufficient to melt all of the available iron, of which the core is made. Analogy with the Earth also gives us reason to believe that temperatures of 3200 to 3600 K have not been reached in the interior of Mars.

Thus, using the currently available information on the thermal history and models of Mars, we can conclude that the reduction of silicates and stishovite to silicon has not occurred in the interior of the planet and, consequently, silicon should not enter into the composition of the core.

MERCURY, MOON

The high mean density of Mercury indicates that it has an iron core amounting to some 60 to 70 percent of the mass of the planet (refs. 25 and 32). According to the calculations of Plagemann (ref. 33), the core of Mercury has a radius of 2112 km. Processing of the data from Mariner 10 has indicated that Mercury has a magnetic field and that the presumed diameter of the core is rather large, approximately equal to that of the Moon (ref. 34).

Iron is practically free of radioactive elements, and, therefore, their concentration in the material of Mercury should be significantly less than in the material of other planets. Calculations of the thermal history with an initial temperature at the center of 1000 K show that the temperature in the interior never rose above 2300 K, which is insufficient for melting and the formation of a core (ref. 20). On the other hand, with a higher initial temperature, say 1100 K, we find that the core might be either liquid or solid (ref. 23).

In spite of the many studies of specimens of lunar soil, measurements of heat flux, and interpretation of seismic data, the existence of a lunar core is still problematical. If a core exists, its radius does not exceed 200 to 300 km, with a temperature in the core of about 1500° C (ref. 35).

The characteristics of the material composition of the Moon and Mercury are not clear. We can assume, by analogy with Earth, that their interiors consist of ferromagnesium silicates. The pressure at the center of the Moon is about 46 kbar; at the core-mantle boundary of Mercury about 100 kbar (ref. 25). As the available calculations show, the reduction of silicates to silicon can occur at such pressures at temperatures of over 2500 to 3000 K.

Since these temperatures are apparently unrealistic for these celestial bodies, we can conclude that silicon should not enter in the composition of their cores.

Anderson (ref. 31), based on thermodynamic calculations of the condensation of the protoplanetary cloud, states his opinion that the Moon accumulated from Al, Ca, and Ti compounds such as gehlenite ($CaAl_2SiO_7$), spinel ($MgAl_2O_4$), and perovskite ($CaTiO_3$), which formed the primary condensate; it also cannot be excluded that Mercury is rich in refractory compounds, in addition to iron, and poor in the silicates of iron and magnesium. However, in this case silicon also should not be included in the composition of the core.

In summary, as a result of processes of reduction and high temperatures in the lower mantles of Earth and Venus in the early stage of their evolution, silicon might have dissolved in the liquid iron or nickel-iron, and this alloy might form the outer cores of the planets. In the interior of Mars, Mercury, and the Moon, the temperatures were insufficient for reduction of silicon, and it should not be included in the cores of these celestial bodies.

In preceding sections, we have studied the possibility of formation of an iron-silicon melt, which forms the cores of planets in the initial period of their evolution.

However, these processes do not limit the possible entry of silicon into the composition of the core. There is also another possibility; namely, the entry of silicon into the composition of the core as a result of interaction of the matter of the core and mantle, which exists at the present time.

Interaction Between Core and Mantle

Seismic data show that at the present time the mantle of the Earth is in the solid state and its outer core is in the liquid state. The interaction between the matter of the mantle and core can be represented in the form of the interaction between stishovite and liquid iron or nickel-iron:

$$SiO_2\ (st.\ 5) + 2Fe(1) = 2FeO(5) + [Si]$$

where [Si] represents a silicon solution (11.2 wt. %) in liquid iron or nickel-iron.

The values of free energies of solution of silicon are presented in table 1; the free energies of reaction are calculated according to the data of Tret'yakov (ref. 36), Robie and Waldbaum (ref. 37), and Kubashewski et al., (ref. 38).

The results of calculating the free energy of the reaction (ΔG_P^T) in the interval 2000 to 4000 K and 300 to 1400 kbar are presented in figure 4.

Free energy is a negative quantity in the pressure interval in question if the tempera-

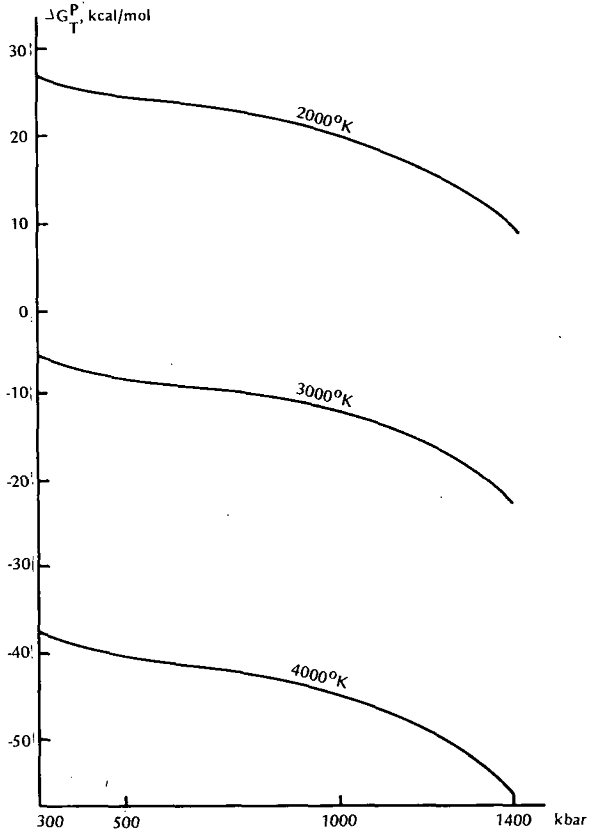

Figure 4.—*Change in free energy of the reaction* $SiO_2(st.s) + 2Fe(l) = 2FeO(s) + [Si](in\ Fe(l)$ *as a function of pressure at 2000, 3000, and 4000 K.*

ture is over ~ 3000 K, i.e., in this case the reaction will be shifted to the right. The pressure at the core-mantle boundary of the Earth and Venus is ~ 1400 kbar, the temperature ~ 4000 K, and the free energy of the reaction − 55.3 kcal/mol. Under these conditions, the core extracts silicon from the mantle; this may explain its growth.

The temperature in the interior of Mars is probably not over 1500 to 2000° C (ref. 26), while the pressure at the core-mantle boundary is approximately 250 to 300 kbar. Therefore, if its mantle consists of oxides, the temperatures are insufficient for the occurrence of this reaction.

The pressure in the interior of the Moon and Mercury is insufficient for the formation of stishovite (but it is possible that coesite is formed), and the mechanism of interaction between the core and the mantle just studied is unsuitable for these bodies.

Conclusions

There are therefore two possible versions of inclusion of silicon in the composition of the iron-nickel cores of the planets. The first proposes the reduction of stishovite, with subsequent formation of an iron-silicon melt which, due to the unstable equilibrium in the gravity field of the planet, sinks to the center. The second possibility is found in the current interaction of the core and mantle, as a result of which silicon is extracted from the mantle and dissolved in the material of the core. Both versions are realized only for the Earth and Venus. The temperatures and pressures in the interior of Mars, Mercury, and the Moon are insufficient for inclusion of silicon in their cores. It is possible that the inclusion of other elements must be studied in this case, for example sulfur or carbon. Only strict quantitative calculations can serve as proof.

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