

Volatile Element Chemistry in the Solar Nebula: Na, K, F, Cl, Br, and P

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The results of the most extensive set to date of thermodynamic calculations on the equilibrium chemistry of several hundred compounds of the elements Na, K, F, Cl, Br, and P in a solar composition system are reported. The calculations are carried out over a wide range of temperatures and pressures and along an adiabat in the primitive solar nebula. Two extreme models of accretion are investigated. In one extreme complete chemical equilibrium between condensates and gases is maintained because the time scale for accretion is long compared to the time scale for cooling or dissipation of the nebula. Condensates formed in this homogeneous accretion model include several phases such as whitlockite, alkali feldspars, and apatite minerals which are found in chondrites. In the other extreme complete isolation of newly formed condensates from prior condensates and gases occurs due to a time scale for accretion that is short relative to the time required for nebular cooling or dissipation. The condensates produced in this heterogeneous accretion model include alkali sulfides, ammonium halides, and ammonium phosphates. None of these phases are found in chondrites. Available observations of the Na, K, F, Cl, Br, and P elemental abundances in the terrestrial planets are found to be compatible with the predictions of the homogeneous accretion model.

INTRODUCTION

One of the most intriguing and perplexing problems in planetary science is the method of retention of volatile elements by the terrestrial planets. The retention of volatiles bears upon the origin of the atmospheres of the terrestrial planets, the origin of the Earth's oceans, and the volatile content of the mantles of the terrestrial planets, a factor which influences local melting and volcanism.

Previous work on the thermodynamics of volatile element retention by the terrestrial planets includes that of Lewis (1972) who briefly addressed water retention and that of Lewis *et al.* (1979) who calculated carbon inventories for the terrestrial planets. In the present study we present the results of an extensive set of equilibrium calculations for the elements Na, K, F, Cl, Br, and P over a wide range of temperatures and pressures.

The objectives of this paper are three-

fold. First, we want to describe the equilibrium chemistry of the elements Na, K, F, Cl, Br, and P in a solar composition system over a wide range of temperatures and pressures. The results of the calculations are presented in some detail because the equilibrium chemistry of the elements studied has been either totally neglected or only cursorily examined by previous workers. No results are presented for Li, Rb, Cs, and I because there are insufficient thermodynamic data for many potentially important gases and condensates of these elements. Some limited information on the equilibrium chemistry of lithium in a solar composition system may however be found in Wai and Wasson (1977).

Second, we want to use the results of the equilibrium calculations to discuss volatile element retention by the terrestrial planets. To this end we compare the results of two extreme models of accretion—the strict homogeneous and strict heterogeneous accretion models—with observational data on

abundances of the elements studied. Our discussion of the two endmember accretion models is based on the concept of a turbulent, chemically homogeneous solar nebula. However, recent work by Cameron (1978) suggests that the nebula may have broken up into a collection of giant gaseous protoplanets, especially at great distances from the Sun. Although the chemical consequences of terrestrial planet formation inside giant gaseous protoplanets may be very different from the consequences of either endmember accretion model we are considering, the complex evolutionary histories proposed for the giant gaseous protoplanets make the chemical consequences of protoplanet formation highly model dependent, and thus difficult to quantify. We will therefore restrict our discussion to a comparison of the two extreme accretion models for terrestrial planet formation in the solar nebula.

Third, we want to provide a firm basis for further discussion of the chemistry of the volatile elements studied. The present results can be used to discuss chondrite mineralogy (Fegley, 1979), and can be integrated into a more quantitative condensation-accretion model in preparation (Barshay and Lewis, 1979).

METHOD OF CALCULATION

An adiabatic temperature-pressure profile for the primitive solar nebula was constructed stepwise using the relationship

$$(P/P_0) = (T/T_0)^{C_p/R}, \quad (1)$$

where P is the total pressure, T the temperature, C_p the bulk heat capacity at temperature T , and R the ideal gas constant. The starting point for the adiabat (P_0 , T_0) was chosen as 10^{-4} bar, 600°K , consistent with available compositional data on planets and satellites and Cameron's nebular models (Lewis, 1974, and references therein).

The heat capacity data for hydrogen and helium at various temperatures were obtained from the *Handbook of Chemistry and Physics* (1961), and a solar abundance

ratio (Cameron, 1973) of H_2 to He (0.122 He + 0.878 H_2) was assumed. The heat capacities of the other gases, which account for less than 1 mole%, were ignored.

The calculated nebular adiabat is shown in Fig. 1. The horizontal scales in Figs. 3 and 4 display numerically the relationships between temperature and pressure and temperature and heliocentric distance along the adiabat. The distance scale was calculated using the relationship

$$(T/T_0) = (R/R_0)^{-1.1}, \quad (2)$$

where T is the temperature and R is the heliocentric distance in astronomical units (AU). The starting point for the distance scale (T_0 , R_0) was chosen as 600°K , 1 AU. Both the chosen functional relationship between temperature and distance in the nebula, and the (T_0 , R_0) point are consistent with the arguments of Lewis (1974).

The assumed solar elemental abundances used in the calculations, which are listed in Table I, were taken from Cameron (1973). The equilibrium stability fields and abundances of some silicate minerals and iron metal along the nebular adiabat were taken

TABLE I
ABUNDANCES OF THE ELEMENTS^a

Element	Normalized abundance (Si = 10^6)
H	31.8×10^9
He	2.21×10^9
O	21.5×10^6
C	11.8×10^6
N	3.74×10^6
Mg	1.06×10^6
Si	1.00×10^6
Fe	0.83×10^6
S	0.50×10^6
Al	85×10^3
Ca	72×10^3
Na	60×10^3
P	9600
Cl	5700
K	4200
F	2450
Br	13.5

^a From Cameron (1973).

from Barshay and Lewis (1979), with some recalculations to adjust for changes in the thermodynamic data for iron oxides, iron-bearing silicates, and alkali aluminosilicates. Thermodynamic data were taken from the JANAF Tables and subsequent supplements (Stull and Prophet, 1971; Chase *et al.* 1974, 1975, 1978), the Geological Survey thermodynamic tables (Robie *et al.* 1978; Robie and Waldbaum, 1968), the National Bureau of Standards compilations (Parker *et al.*, 1971; Wagman *et al.*, 1968, 1969, 1976), and a variety of other sources (Duff, 1972a,b; Gottschal, 1958; Jacques, 1963; Komarek, 1963; Letoffe *et al.*, 1974, 1976; Mills, 1974; Oetting and McDonald, 1963; Orville, 1972; Richardson and Jeffes, 1949; Saxena, 1973; Seck, 1971; Weibke and Schrag, 1941; Wellman, 1969). In several cases the tabulated equilibrium constants were incorrect and had to be recalculated. For example, the tabulated $\log K_f$ data for many phosphorus compounds in Robie and Waldbaum (1968) and Robie *et al.* (1978) are in error because the $\Delta H_{f,298}^\circ$ values are based upon a white phosphorus reference state while the $\log K_f$ values are calculated using thermodynamic functions for red phosphorus. When the $\log K_f$ values are recalculated using a consistent red phosphorus reference state the differences in $\log K_f$ are found to be on the order of 3 to 4 (differences in K_f of a factor of 10^3 to 10^4).

It was also necessary in several cases to calculate from the literature data the equilibrium constant for formation of an element or compound from the constituent elements in their designated reference states. If at all possible this calculation was done by a third-law method and double checked using data from a separate source. In some cases a second-law method, which is less accurate, was used. Details of the second- and third-law treatment of equilibrium data are available in the JANAF tables or any standard thermodynamic text.

A special discussion of the thermodynamic data used to calculate $\log K_f$ values for chlorapatite and bromapatite is also

necessary. Both $\Delta H_{f,298}^\circ$ (Gottschal, 1958) and $\Delta G_{f,298}^\circ$ (Duff, 1972b) values for chlorapatite are available. However, the combination of the data yields a S_{298}° value for chlorapatite which is too low relative to the S_{298}° values for fluor- and hydroxyapatite. Since the $\Delta H_{f,298}^\circ$ values measured by Gottschal (1958) for fluorapatite and hydroxyapatite agree within 1% with other experimental and tabulated values (Jacques, 1963; Parker *et al.*, 1971), we have combined his $\Delta H_{f,298}^\circ$ value for chlorapatite with an estimated S_{298}° value to calculate $\log K_f$ values by the second-law method. Only a $\Delta G_{f,298}^\circ$ value (Duff, 1972a) for bromapatite is available and it was again necessary to estimate a S_{298}° value in order to calculate $\log K_f$ values. In both cases the entropy estimates were made by three separate methods which yielded results that agree within 1%. The subsequent uncertainty in the $\log K_f$ values is probably less than that due to the experimental error in the $\Delta H_{f,298}^\circ$ and $\Delta G_{f,298}^\circ$ determinations. Discussion of entropy estimation methods can be found in Stull and Prophet (1967) and Kubaschewski *et al.* (1967).

The basic computational method used has been described in detail by Barshay and Lewis (1978) and Grossman (1972), and will only be briefly summarized here. The thermodynamic calculations along the nebular adiabat involve the simultaneous determination of the equilibrium abundances of all compounds (gases and condensed phases) included in the data set. Pure condensed phases, e.g., Fe_3P , are stable when their thermodynamic activities equal 1 and are unstable at activities less than 1. Condensed phases which form solid solutions such as the alkali feldspars are stable at activities less than 1.

More than 200 gases and condensates were included in the calculations for this paper. Gases were included in Figs. 2–5 if their equilibrium mole fraction along the nebular adiabat was greater than 10^{-15} at any temperature within the range covered by the figure. The abundances and stability

fields of condensates stable at equilibrium are also indicated in the figures. Condensates which were found to be either unstable or unimportant within the temperature range of a figure and gases which did not satisfy the above stated criterion are listed in the Appendix.

THE HOMOGENEOUS ACCRETION MODEL

The homogeneous accretion model assumes intimate contact between the condensed and gaseous phases, thereby allowing complete chemical equilibrium between all gases and condensates. The chemical composition of the system is a thermodynamic state function and is path independent. Assuming that chemical equilibrium is attained and that the system has solar composition, the results presented in Figs. 1–5 and Table II therefore apply to condensation from a hot totally vaporized mixture, volatilization of a homogeneous cold gas and dust mixture, or any intermediate case.

Figure 1 shows the condensation and formation curves for condensates of the elements Na, K, F, Cl, Br, and P, the condensation and reaction curves from Barshay and Lewis (1976) for some compounds of the major elements, the adiabatic pressure–temperature profile for the primitive solar nebula, and a qualitative repre-

sentation of the formation zones for the terrestrial planets.

Several important points are demonstrated by Fig. 1. First, the sequence of reactions and the composition of condensed phases present at equilibrium are generally pressure independent. Second, the volatile contents (Na, K, F, Cl, Br, and P) of the terrestrial planets and asteroids are in principle predictable by use of this simplified chemical equilibrium model. Third, the correspondence between the phases present at equilibrium and the observed mineralogy of ordinary chondrites reinforces the plausibility of a close approach to chemical equilibrium in the primitive solar nebula.

Table II and Figs. 2–5 provide information on the equilibrium chemistry of Na, K, F, Cl, Br, and P along the nebular adiabat. The results of the calculations are discussed element by element in order of decreasing abundance. Compounds which do not appear in the figures due to extremely low abundances or activities less than 1 are listed in the Appendix.

Sodium

Figure 2 illustrates the equilibrium abundances and stability fields of sodium-bearing compounds along the nebular adiabat. The abundances at equilibrium of both gaseous and condensed sodium-bearing compounds are shown in the figure. Half of all sodium is condensed in plagioclase feldspar ($\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$) by 948°K, and condensation is quantitative at about 858°K. Thermodynamic data for analbite (Robie *et al.*, 1978) and activity coefficient data for plagioclase feldspar (Orville, 1972; Saxena, 1973) were used in the calculations. The 50% condensation curve for $\text{NaAlSi}_3\text{O}_8$ in plagioclase feldspar is shown in Fig. 1. Sodium silicate (Na_2SiO_3) dissolved in enstatite (MgSiO_3) as an ideal solution never exceeds 1% of total sodium. The albite abundance is reduced by the formation of sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$) at

TABLE II

HOMOGENEOUS ACCRETION MODEL: CHEMICAL REACTIONS ALONG THE NEBULAR ADIABAT

T(°K)	Reaction
1520	Condensation of Fe–Ni alloy
1455	Condensation of MgSiO_3 (enstatite)
1225	Condensation of Fe_3P (schreibersite)
950–1050	50% Condensation of $(\text{Na},\text{K})\text{AlSi}_3\text{O}_8$ in plagioclase feldspar
895	Formation of $\text{Na}_4(\text{AlSiO}_4)_3\text{Cl}$ (sodalite)
766	Formation of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (fluorapatite)
714	Formation of $\text{Ca}_9(\text{PO}_4)_6$ (whitlockite)
687	$\text{Fe–Ni alloy} + \text{H}_2\text{S (g)} = (\text{Fe},\text{Ni})\text{S}$
480	Calcium silicates + $\text{H}_2\text{O(g)} = \text{tremolite}$
~460	Whitlockite reacts to form $\text{Ca}_9(\text{PO}_4)_6\text{OH}$
~350	Formation of $\text{Ca}_5(\text{PO}_4)_3\text{Br}$ (bromapatite)

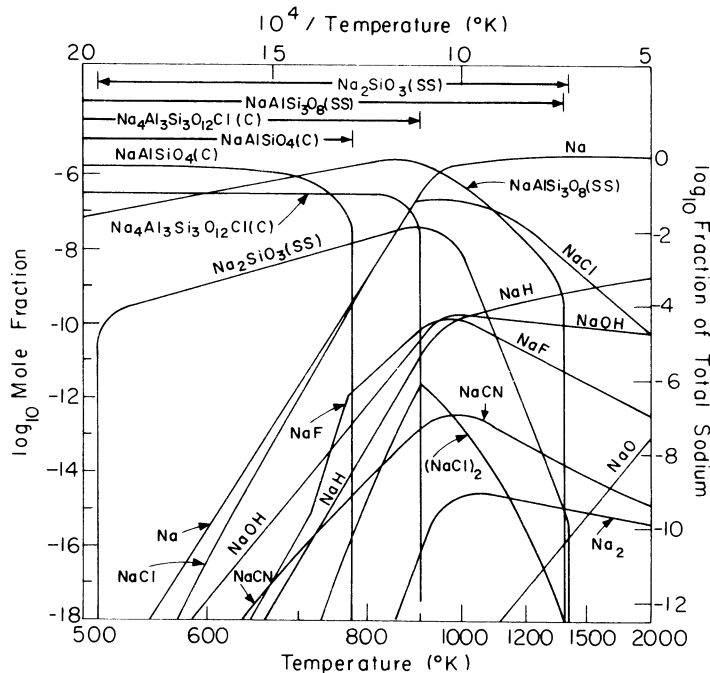


FIG. 2. Equilibrium abundances and stability fields of sodium-bearing gases and condensates along the nebular adiabat. The temperature scale is linear in $1/T$. The mole fraction X_i of a species i is defined as its partial pressure p_i divided by the total pressure P . The heavy lines indicate the stability fields of the four condensates whose abundances are also shown graphically. The abbreviations (c) and (ss) following the condensate formulas indicate a pure crystalline solid and a solid solution, respectively. The fraction of total sodium in each compound is also shown.

ite at about 460°K, while in the latter case all whitlockite is converted to hydroxyapatite at about 507°K.

Figure 1 illustrates the schreibersite, fluorapatite, whitlockite, and hydroxyapatite condensation curves from 10^{-7} to 10 bars pressure. The whitlockite condensation curve is pressure independent in the regions of P-T space where CO and CH₄ are the dominant carbon-bearing gases, and has an inflection at the CO/CH₄ watershed where the abundances of these two gases are equal. The hydroxyapatite condensation curve in Fig. 1 is for condensation of pure hydroxyapatite.

Several other authors (Grossman and Olsen, 1974; Wai and Wasson, 1977; Sears; 1978) have calculated schreibersite condensation temperatures, and we can compare our results with theirs. The Fe₃P condensation temperatures from Fig. 1 are 100–300°

lower than the literature values, and the largest discrepancies are with the values of Sears (1978). For example, at 10^{-3} bar pressure the Fe₃P condensation temperatures calculated by Sears (1978), Grossman and Olsen (1974), and Wai and Wasson (1977) are 1479, 1416, and 1416°K, respectively, while the value from the present work is 1210°K.

Although Grossman and Olsen (1974), Wai and Wasson (1977), and Sears (1978) cite different sources for their Fe₃P thermodynamic data, all the sources cited ultimately derived the same (estimated) data from an evaluation by Richardson and Jeffes (1949) of the Fe₃P enthalpy determinations of Weibke and Schrag (1941). However, the data used by Richardson and Jeffes to calculate ΔG_f° values for Fe₃P are out of date and disagree with currently recommended values. For example, for the

duce the phosphide condensation temperatures of the previous investigators by using the appropriate $\log K_f$ values and phosphorus fugacities. For example, we can duplicate the results of Grossman and Olsen (1974) and Wai and Wasson (1977) by using Richardson and Jeffes' $\log K_f$ data for Fe_3P and our calculated phosphorus fugacities. We can also reproduce the results of Sears (1978) by assuming $\text{P}_2(\text{g})$ to be the dominant phosphorus gas and using Richardson and Jeffes' $\log K_f$ values without considering Ni_3P solid solution.

Although we have assumed an ideal solution of phosphorus in iron in the results in Fig. 2, we have also considered the effect of nonideality in the P-Fe alloy upon the Fe_3P condensation temperature. Assuming that all phosphorus is originally dissolved in the iron metal, and taking an activity coefficient of 10^{-5} for the P-Fe alloy, then Fe_3P condensation along the nebular adiabat is lowered by only 70° . We therefore feel justified in ignoring the effects of nonideality in the P-Fe alloy which are probably less than the effects of uncertainty in the Fe_3P thermodynamic data.

Finally, the present whitlockite condensation temperatures have been compared with some literature values (Wai and Wasson, 1977; Sears, 1978). Wai and Wasson (1977) state that whitlockite is a stable phase below 900°K at 10^{-4} atm and Sears (1978) reports a whitlockite condensation temperature of 770°K . The present value is 714°K . The minor discrepancies appear to be due to differences in the thermodynamic data. Wai and Wasson (1977) and Sears (1978) used the whitlockite thermodynamic data from Robie and Waldbaum (1968) which are incorrect due to inconsistent phosphorus reference states used in compiling the tables. Data for several phosphorus-bearing compounds in the recent compilation of Robie *et al.* (1978) are also incorrect for the same reason. Where necessary we have recalculated by $\log K_f$ values for phosphorus-bearing compounds which are included in our calculations.

Halogens

The equilibrium behavior of chlorine-, fluorine-, and bromine-bearing compounds along the nebular adiabat is shown in Fig. 4 and the stability fields for the pure phases sodalite, fluorapatite, and bromapatite are illustrated in Fig. 1. Sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$) condensation starts at about 895°K and fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] condensation begins at 766°K . Chlorine is 50% condensed at 873°K and completely condensed at 823°K . Fluorine condensation is complete by 741°K . No bromine-bearing condensate is stable above 500°K . Bromapatite [$\text{Ca}_5(\text{PO}_4)_3\text{Br}$] condensation as a pure phase occurs around 350°K , and condensation as an ideal solid solution in fluorapatite is complete at about 434°K . However, the bromapatite condensation calculations are based on low-quality thermodynamic data and may involve a considerable uncertainty. Thermodynamic data are lacking for the fluorine and bromine analogs of sodalite and it is conceivable that these phases could condense at higher temperatures than fluorapatite and bromapatite. The thermodynamic activity of chlorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$] does not exceed 10^{-6} over the temperature range considered and chlorapatite solid solution in fluorapatite is of negligible importance for chlorine retention. For example, at 700°K ideal solid solution of chlorapatite in fluorapatite accounts for only $10^{-5}\%$ of all chlorine.

Potassium

Figure 5 illustrates the chemical equilibrium behavior of potassium-bearing compounds along the nebular adiabat. The results in Fig. 5 model high sanidine (KAlSi_3O_8) condensation as an ideal solution in feldspar. Potassium is 50% condensed at about 1020°K and completely condensed at 952°K . Condensation of high sanidine as a pure phase starts at 943°K and is essentially complete within 100° . Data from Seck (1971) and Saxena (1973) show

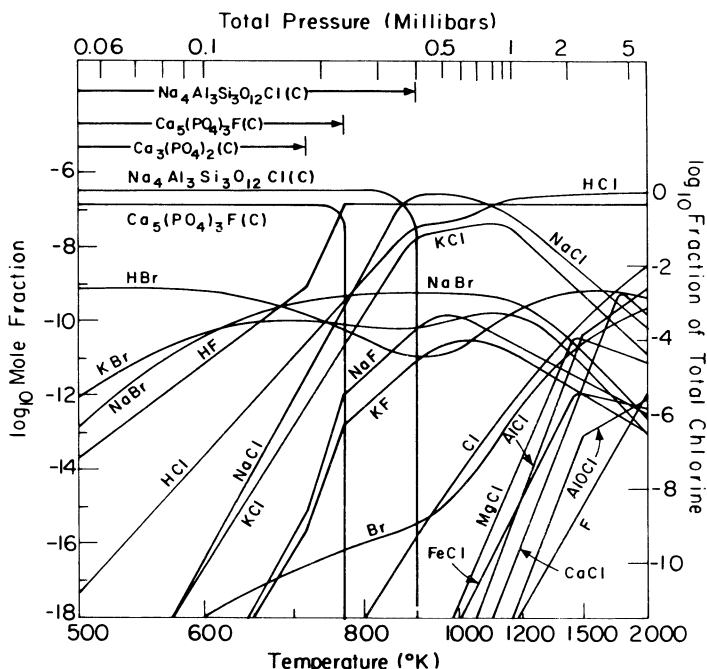


FIG. 4. Abundances and stability fields of chlorine-, fluorine-, and bromine-bearing compounds along the nebular adiabat under equilibrium conditions. The scale across the top shows the approximate total pressure in millibars along the adiabat. The heavy lines indicate the stability fields of the condensates. Chlorine is 50% condensed at about 873°K and is completely condensed at 823°K. Fluorine is completely condensed at about 741°K. Bromine condensation as $\text{Ca}_3(\text{PO}_4)_3\text{Br}$ does not begin until approximately 350°K.

that KAlSi_3O_8 in $\text{NaAlSi}_3\text{O}_8$ – KAlSi_3O_8 – $\text{CaAl}_2\text{Si}_2\text{O}_8$ exhibits positive deviations from ideality (activity coefficients greater than 1). Thus, our calculations modeling high sanidine condensation as an ideal solute and as a pure phase bracket the actual KAlSi_3O_8 condensation temperature.

Figure 1 shows the KAlSi_3O_8 50% condensation curve over a wide pressure range. This curve was calculated assuming a high sanidine ideal solution in anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Actually, at all pressures shown the KAlSi_3O_8 50% condensation curve is 20–40°K higher than the $\text{NaAlSi}_3\text{O}_8$ 50% condensation curve. The two curves are drawn as one merely to simplify the graphical representation.

Finally, potassium may behave similarly to sodium and partition into nepheline and sodalite phases at lower temperatures. Accurate chemical equilibrium calculations

cannot be made because thermodynamic data for the potassium analog of sodalite are unavailable and activity data for the relevant solid solutions are either unavailable or highly uncertain. However, assuming ideal solution in nepheline and neglecting potassium in sodalite phases, approximately 40% of the potassium will be in kaliophillite (KAlSiO_4) at 700°K. Also, pure KAlSiO_4 becomes stable at 509°K.

THE HETEROGENEOUS ACCRETION MODEL

The pure heterogeneous accretion model, which is the extreme opposite of the pure homogeneous accretion model, assumes the rapid accretion of small particles into larger bodies, thus preventing the material within these bodies from reacting further with the gas phase. We have modeled the consequences of this process by assuming complete isolation of newly

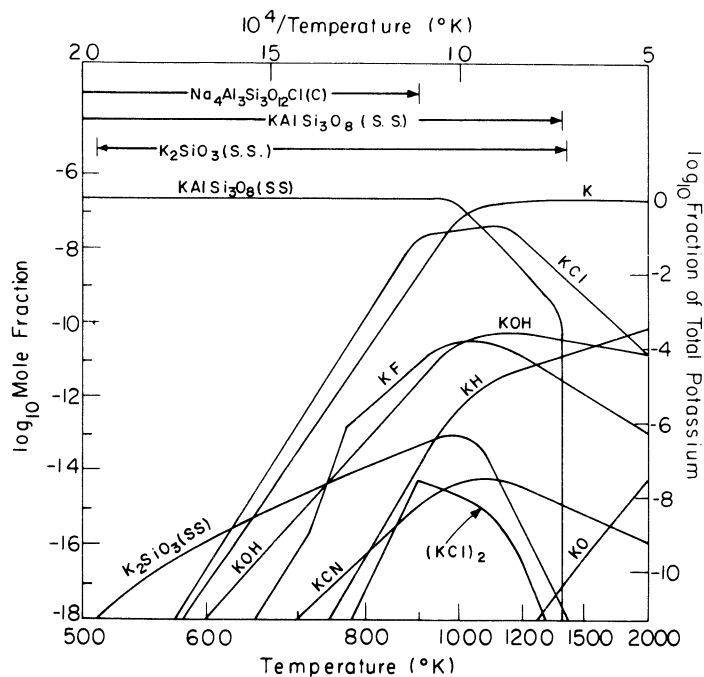


FIG. 5. The chemical equilibrium behavior of potassium-bearing compounds along the nebular adiabat. The heavy lines indicate the stability fields of the condensates. Results are shown for high sanidine ideal solution in feldspar. Potassium is 50% condensed at about 1020°K and is completely condensed by 952°K. Pure KAlSi_3O_8 condensation starts at 943°K and is essentially complete within 100°.

formed condensates from all gases and all previous condensates. Thus, as soon as an element condenses it is removed from further reactions. This chemical disequilibrium model is essentially a generalized and quantifiable, albeit extreme, version of the heterogeneous accretion model for the Earth proposed by Turekian and Clark (1969).

We have calculated how the elements Na, K, F, Cl, Br, and P would condense in the heterogeneous accretion model and present the results in Table III. The calculations apply to a solar composition gas cooled along the nebular adiabat of Fig. 1 and include newly recalculated condensation temperatures for some compounds considered in Barshay and Lewis (1976). The results in Table III plus the results in Barshay and Lewis (1976) describe the major features of the heterogeneous accretion model reaction sequence over the tempera-

ture range 2000–5°K. Finally, it is important to note that the reaction sequence in the heterogeneous accretion model is *not* path independent, and that the same results will not be obtained upon the volatilization of a homogeneous cold gas and dust mixture.

TABLE III

HETEROGENEOUS ACCRETION MODEL: CHEMICAL REACTIONS ALONG THE NEBULAR ADIABAT

T(°K)	Reaction
1520	Condensation of Fe–Ni alloy
1455	Condensation of MgSiO_3 (enstatite)
751	$2\text{Na(g)} + \text{H}_2\text{S(g)} = \text{H}_2\text{(g)} + \text{Na}_2\text{S(s)}$
747	$\text{Na(g)} + \text{HF(g)} = \frac{1}{2}\text{H}_2\text{(g)} + \text{NaF(s)}$
695	$2\text{K(g)} + \text{H}_2\text{S(g)} = \text{H}_2\text{(g)} + \text{K}_2\text{S(s)}$
261	$\text{NH}_3\text{(g)} + \text{HBr(g)} = \text{NH}_4\text{Br(s)}$
259	$\text{NH}_3\text{(g)} + \text{HCl(g)} = \text{NH}_4\text{Cl(s)}$
244	$\frac{1}{2}\text{P}_4\text{O}_6\text{(g)} + \text{NH}_3\text{(g)} + \frac{3}{2}\text{H}_2\text{O(g)} = \text{NH}_4\text{H}_2\text{PO}_4\text{(s)} + \text{H}_2\text{(g)}$
134	$\text{NH}_3\text{(g)} + \text{H}_2\text{S(g)} = \text{NH}_4\text{HS(s)}$

COMPARISON OF THE HOMOGENEOUS AND HETEROGENEOUS ACCRETION MODELS

The predictions of the homogeneous and heterogeneous accretion models about volatile element chemistry along an adiabat in the primitive solar nebula are summarized in Tables II and III. The two extreme models are seen to make very different predictions about the chemistry of the volatile elements Na, K, F, Cl, Br, P, and S in the primitive solar nebula. Some features of the heterogeneous accretion model reaction sequence such as the chalcophile behavior of the alkali metals, the failure of S and P to behave as siderophiles, and the failure of P, F, Cl, and Br to behave as lithophiles are especially noteworthy. How do these predictions compare to the limited data on abundances of these volatiles in the terrestrial planets and to the observed mineralogy of the ordinary chondrites?

First, although no observational data about volatile element abundances in the planet Mercury are available, a qualitative comparison of the planet's formation zone and the condensation curves displayed in Fig. 1 suggests that Mercury should be depleted in all the volatile elements considered in this paper. However, the (Fe,Ni)₃P condensation results of Sears (1978) imply that Mercury will retain phosphorus with approximately the solar P/Fe ratio. Second, the measured potassium abundances in very small samples of the surface of Venus (Vinogradov *et al.*, 1973; Surkov *et al.*, 1976) and the observations of HCl and HF in the upper troposphere (Connes *et al.*, 1967) are consistent with the formation of Venus within the stability fields of feldspar, sodalite, and fluorapatite. However, the observations of Cl and K are inconsistent with the predictions of the heterogeneous accretion model that Cl retention at 259°K and K retention at 695°K do not take place in the formation zone at Venus. We also note that chemical equilibrium calculations by Lewis *et al.* (1979) on the stability of various carbon-bearing species yield abun-

dances of carbon compounds similar to the observed inventories on Venus and Earth. Furthermore Barshay and Lewis (1979) find that a 10⁴-fold depletion of H₂O on Venus is entirely compatible with a 10-fold depletion of FeS and a 10- to 100-fold depletion of FeO relative to the Earth. Thus, the need for covering Venus with a veneer of volatile rich carbonaceous material and then removing all the excess water appears far from obvious.

Third, the (incomplete) data on abundances of Na, K, F, Cl, Br, P, and S in the Earth can be compared with the qualitative predictions of the homogeneous and heterogeneous accretion models. The homogeneous accretion model predicts that the bulk composition of the Earth is similar to that of the *H*-group ordinary chondrites, but is not identical to nor derived from the *H*-chondrites or any other meteorite class (Lewis, 1972). For the volatile elements considered in this study (and sulfur) the homogeneous accretion model predicts (terrestrial/chondritic) abundance ratios ≈ 1.0 for Na, K, F, Cl, P, and S and a ratio < 1.0 for Br. Using the three composition models for the Earth presented by Smith (1977) and *H*-chondrite and Cl-chondrite analytical data from Mason (1979), we calculated abundance ratios for the volatile elements under consideration and present the results in Table IV. The abundance ratio presented is the quantity $[(E/10^6 \text{ Si})_{\text{Earth}} / (E/10^6 \text{ Si})_{\text{chondrite}}]$, where $(E/10^6 \text{ Si})$ is shorthand for the elemental abundance relative to 10⁶ Si atoms. How accurate are these ratios and what do their values tell us?

First, it is necessary to realize that many assumptions about the radial distribution of elements within the Earth and about the composition of the core are necessary in the construction of any compositional models for the Earth. Smith (1977) has given a detailed discussion of the assumptions made in the construction of his models and we will not attempt to repeat all of them or to evaluate their validity. We

TABLE IV
TERRESTRIAL/CHONDRITIC ELEMENTAL
ABUNDANCE RATIOS^a

Atomic number	Element	Abundance ratio	
		(Earth/Cl chondrite)	(Earth/H chondrite)
9	F	2.1	6.5
11	Na*	3.6×10^{-2}	5.3×10^{-2}
15	P	0.56–0.76	0.68–0.91
16	S*	0.54	2.7
17	Cl*	2.1×10^{-2}	0.32
19	K*	0.19	0.20
35	Br*	1.7×10^{-2} – 2.1×10^{-2}	0.45–0.57

^a An asterisk indicates that the element is assumed by Smith (1977) to occur only in the upper 10% of the Earth's mantle. If the elements are assumed to occur throughout the entire mantle the (Cl, H) abundance ratios are Na(0.23, 0.33), S(0.55, 2.7), Cl(0.16, 2.4), K(1.1, 1.1), and Br(0.12, 3.3). *Data Sources.* Earth, Smith (1977); chondrites, Mason (1979).

can, however, illustrate the effect of two sets of assumptions on the abundance ratios calculated above. Thus, if it is assumed that Na, K, Cl, Br, and S occur throughout the entire mantle instead of only in the upper 10%, the terrestrial/*H*-chondrite abundance ratios become Na(0.3), K(1.1), Cl(2.4), Br(3.3), and S(2.7). Similarly, if iron meteorites are not used to model the composition of the core and the crustal and mantle composition alone is used for the composition of the Earth, the P and S terrestrial/*H* chondrite ratios become P(0.2) and S(0.005).

Second, it is also important to consider the quality of the analytical data for terrestrial samples and meteorites. Smith (1977) discusses the quality of the analytical data for terrestrial samples and we will briefly discuss the quality of the chondrite analytical data. The analytical data for Na, K, P, and S in Cl and H chondrites which are presented in Mason (1979) show maximum variations less than a factor of 2 and are reasonably consistent. However, the F, Cl, and Br analytical results for chondrites show considerably greater variations. Dreibus *et al.* (1979) compare their halogen analytical results with previous results for carbonaceous, ordinary (*L* group), and enstatite chondrites. The observed variations

for halogen analyses in different meteorites range from 1.1 (Ivuna Cl) to 14.5 (Mocs L6), 1.0 (Bruderheim L6) to 3.7 (Orgueil Cl), and 1.2 (Bruderheim L6) to 9 (Mocs L6) for F, Cl, and Br, respectively. Allen and Clark (1977) and Mason (1979) also present comparisons of multiple fluorine analyses by different investigators on a single meteorite. Results tabulated by Mason (1979) for fluorine analyses of the Orgueil Cl- and Allegan H5-chondrites display maximum variations of 5.5 and 5.3 times, respectively, and the data presented in Allen and Clark (1977) for the average fluorine content of *H*-chondrites show a factor of 4 maximum variation. More comprehensive comparisons of halogen analytical data for the chondrites and other types of meteorites can be found in the papers by Dreibus *et al.* (1979), Mason (1979), and the articles by Reed in Mason (1971). However, the examples given above are sufficient to illustrate the wide variations between results and the questionable accuracy of many of the data.

Now that we have a rough idea of the accuracy of the abundance ratios presented in Table IV we can discuss their implications. As we stated earlier, the homogeneous accretion model predicts terrestrial/chondritic abundance ratios ≈ 1.0 for Na, K, F, Cl, P, and S and a ratio < 1.0 for Br. The agreement between calculated abundances and predicted inventories is fairly good, especially considering the assumptions made in constructing the terrestrial composition models and the poor quality of the halogen analytical data in meteorites.

For example, the apparent Na, K, and Cl depletions largely disappear if these elements are assumed to occur throughout the entire mantle and not merely the upper 10%. The K abundance in the Earth is, however, highly controversial and Lewis (1971) has proposed that potassium may be enriched in the Earth's core. The halogen abundance ratios indicate an apparent enrichment of fluorine and apparently equal

abundances of bromine and chlorine. However, the fluorine terrestrial/chondritic abundance ratios depend strongly on which fluorine chondritic abundances are used. For example, the fluorine analytical results of Allen and Clark (1977), Dreibus *et al.* (1979), and Goldberg *et al.* (1974), which agree reasonably well with one another, all show fluorine chondritic abundances approximately two to three times lower than previously thought. The fluorine terrestrial/Cl-chondrite abundance ratios calculated using the fluorine terrestrial abundance from Smith (1977) and fluorine Cl-chondrite abundance data from either Smith (1977) or Dreibus *et al.* (1979) are 0.49 and 2.7, respectively. A high terrestrial/chondritic fluorine abundance ratio may indicate that fluorine condenses in sodalite at higher temperatures than it condenses in fluorapatite. The approximately equal Cl and Br abundance ratios may also indicate that bromine condenses as Br-bearing sodalite at higher temperatures than it condenses as bromapatite. However, as we have already stated, the bromapatite condensation results may involve a considerable uncertainty and no thermodynamic data are available for the fluorine- and bromine-bearing analogs of sodalite.

In contrast to the homogeneous accretion model, the strict heterogeneous accretion model predicts that the Earth will be devoid of any chlorine, bromine, phosphorus, and sulfur. These elements could have been added to the Earth as part of a hypothesized veneer of low-temperature volatile-rich material, which presumably would also account for the terrestrial inventories of other volatiles such as carbon, hydrogen, nitrogen, oxygen, and the rare gases krypton and xenon. However, as Lewis *et al.* (1979) point out, a comparison of the terrestrial and chondritic C, H, N, and O isotopic compositions fails to identify a particular source for the volatile elements on Earth in terms of carriers with the properties of known meteorite classes.

Fourth, sulfur, and chlorine have been detected in Martian fines by the Viking X-ray fluorescence experiments (Clark *et al.*, 1976). In the absence of any volatile element inventories for Mars we merely note that the presence of S and Cl is expected in the homogeneous accretion model but not in the heterogeneous accretion model. Retention of sulfur in the strict heterogeneous accretion model can occur only at temperatures so low that H₂O is fully condensed, a condition clearly at odds with our observational data on all the terrestrial planets.

Last, we can briefly compare the mineralogy of the ordinary chondrites, which make up ~90% of all known chondrites, with the predicted condensates in the two models. Feldspar and whitlockite are ubiquitous in ordinary chondrites (Van Schmus and Ribbe, 1968; Fuchs, 1969a). Apatite minerals found in ordinary chondrites include chlorapatite, fluorapatite, and hydroxyapatite (Van Schmus and Ribbe, 1969; Fuchs, 1969a; Curtis and Schmitt, 1979). Also, large Br and F concentrations are observed in the apatite minerals of some chondrites (Mason and Graham, 1970). Schreibersite (Fuchs, 1969a) and nepheline (Fuchs, 1969b) are also found in chondrites. It is noteworthy that feldspar, whitlockite, fluorapatite, hydroxyapatite, bromapatite, nepheline, and schreibersite are all condensates in the homogeneous accretion model but are all absent in the heterogeneous accretion model. Furthermore, the condensates containing Na, K, F, Cl, Br, and P predicted by the heterogeneous accretion model are not observed in any chondrites.

A simple chemical equilibrium-homogeneous accretion model for retention of the alkalis, halogens, and phosphorus is thus seen to be compatible with the available observations. While some variant of the heterogeneous accretion model, such as the late accretion of a layer of low-temperature volatile rich material, cannot be definitely ruled out on the basis of present observations, the need to invoke the heterogeneous

accretion model to explain these observations is far from obvious. Certainly a number of complex auxiliary hypotheses would be required in order to bring the model into agreement with observation or indeed even to render it susceptible to quantification.

CONCLUSIONS

Chemical equilibrium calculations for the elements Na, K, F, Cl, Br, and P in a solar composition system are reported for two extreme models of accretion. Condensates of these elements formed in the homogeneous accretion (chemical equilibrium) model include several phases such as whitlockite, alkali feldspars, and apatite minerals which are found in chondrites. Typical condensates formed in the heterogeneous accretion (chemical disequilibrium) model are alkali sulfides, ammonium halides, and ammonium phosphates. Available observations of the Na, K, F, Cl, Br, and P elemental abundances in the terrestrial planets and the mineralogy of the ordinary chondrites are compatible with the predictions of the homogeneous accretion model. These observations in concert with other observable properties such as planetary bulk densities, which are also explainable by the chemical equilibrium model, suggest that chemical equilibrium was closely approached in the inner parts of the solar nebula.

APPENDIX: ADDITIONAL COMPOUNDS WHICH WERE STUDIED

This Appendix lists compounds which were investigated but not included in the figures. Unstable condensates (pure solids and liquids with less than unit activity and solid solutions that are of negligible importance in an elemental mass balance sum) and minor gases (mole fractions always less than 10^{-13}) are listed. The different phases are indicated by (c) for crystalline pure solid, (l) for liquids, (ss) for solid solution, and (g) for gases. The lack of one of the above labels indicates a gas. Compounds

are listed under the least-abundant constituent element.

Na

(NaOH)₂, (NaCN)₂, NaH(c), NaOH(c, l), Na₂O(c, l), Na₂S(c, l), Na₂Si₂O₅(c, l), NaCN(c, l), Na₂CO₃(c, l), NaO₂(c), Na₂O₂(c), Na₂SO₄(c, l), NaNO₃(c, l), NaAlO₂(c).

P

P₄, P₄O₁₀(c, g), P₄S₃(c, l, g), Mg₃(PO₄)₂(c), P(white, c), P(red, c).

Cl

NaCl(c, l), Na₃AlCl₆(c), NaAlCl₄(c), POCl₃, PCl₃, PSCl₃, PCl₅, Cl₂, Ca₅(PO₄)₃Cl(c, ss), CCl, CNCl, FeCl₂(c, l), MgCl₂(c, l), NH₄Cl(c).

K

K₂, (KOH)₂, (KCN)₂, KH(c), KCl(c, l), KOH(c, l), K₂O(c), K₂S(c, l), K₃AlCl₆(c), KAlO₂(c), KAlCl₄(c), KClO₄(c), KCN(c, l), K₂CO₃(c, l), KO₂(c), K₂O₂(c), K₂SO₄(c, l), KAl(SO₄)₂(c), KNO₃(c, l).

F

F₂, NaAlF₄, (NaF)₂, NaF(c, l), Na₃AlF₆(c, l), Na₂SiF₆(c), PFS, PF₂, POF₃, PF₃, PSF₃, PF₅, (KF)₂, KF(c, l), K₃AlF₆(c), KMg₃AlSi₃O₁₀F₂(c), MgF₂(c, l, g), CaF₂(c, l, g), FeF₂(c, l, ss), NH₄F(c).

Br

Br₂(l, g), (NaBr)₂, (KBr)₂, NaBr(c, l), KBr(c, l), NH₄Br(c), FeBr₂(c, l, g), CaBr₂(c, l, g), MgBr₂(c, l, g).

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