

PRIMORDIAL RETENTION OF NITROGEN BY TERRESTRIAL PLANETS AND METEORITES

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**Abstract.** Thermodynamic calculations of the amount of dissolved nitrogen in Fe-Ni alloy in a solar composition gas were done over a wide range of temperatures and pressures. The stabilities of the nitride minerals found in meteorites, a large number of other nitrides, and ammonium aluminosilicates were also calculated in a solar gas. This thorough study indicates that equilibrium mechanisms cannot account for the nitrogen contents of the terrestrial planets and meteorites. The best available data indicate that the observed nitrogen contents of planets and meteorites are several orders of magnitude greater than the predicted nitrogen contents of condensed material in a solar gas. It is suggested that the nitrogen in meteorites was originally retained as organic compounds produced by disequilibrium mechanisms. Nitrogen retention by the terrestrial planets could be due to homogeneous accretion or to accretion of a volatile-rich veneer. However the actual mode of nitrogen accretion cannot yet be determined.

Introduction

Chemical equilibrium calculations are very useful for discussing elemental fractionations among chondrites and planets [Grossman and Larimer, 1974; Lewis, 1972a]. Recent calculations have described the thermodynamics of volatile element retention by the terrestrial planets. The results of these calculations are very interesting. For instance, Lewis [1972a] and Fegley and Lewis [1980] concluded that equilibrium mechanisms can supply the planetary inventories of water, halogens, alkalis, and phosphorus. However, Lewis et al. [1979] concluded that equilibrium mechanisms cannot supply the planetary inventories of carbon. Nitrogen is similar to carbon in many respects. Can equilibrium mechanisms supply the planetary inventories of nitrogen?

Latimer [1950] suggested that the nitrogen in the earth's atmosphere was produced by the hydrolysis of nitrides to ammonia followed by subsequent reactions. Urey [1952, 1953] developed this concept in more detail. He also suggested that nitrogen could have been retained as  $\text{NH}_4\text{Cl}$  or as ammonium silicates. Urey calculated simple reactions involving  $\text{TiN}$  or  $\text{NH}_4\text{Cl}$

which indicated the regions of P-T space in which the two nitrogen-bearing phases were stable. He concluded that nitrogen could be retained at high temperatures and low pressures as  $\text{TiN}$  and at lower temperatures as  $\text{NH}_4\text{Cl}$ . However, these reactions did not take into account the full equilibrium chemistry of solar composition matter. They cannot be directly applied to the problem of nitrogen retention by the terrestrial planets and meteorites.

Knopman (unpublished calculations, 1974) tried to quantitatively evaluate Urey's suggestion by calculating the stabilities of the three nitride minerals then known in meteorites -- sinoite ( $\text{Si}_2\text{N}_2\text{O}$ ), carlsbergite ( $\text{CrN}$ ) and osbornite ( $\text{TiN}$ ) -- along the  $10^{-3}$  bar isobar in the solar nebula. She based her work on the results of Grossman [1972] and unpublished calculations by Barshay. Her results take into account the phases which are thermodynamically stable under the P-T conditions considered in solar composition matter. Knopman found that none of the three nitrides considered was stable at  $10^{-3}$  bars.

No further quantitative calculations on the stabilities of nitrides and other nitrogen-bearing compounds have been done. One reason for this lack of progress is that until recently, very little analytical data were available on the nitrogen contents and the chemical forms of nitrogen in meteorites.

The equilibrium chemistry of nitrogen and nitrogen-bearing compounds in a solar composition system are examined in this paper. The results of this study are compared with the chemistry of nitrogen in meteorites and are used to discuss nitrogen retention by planetary bodies. Preliminary results have been presented by Fegley [1981a].

Nitrogen in Meteorites

Gibson and Moore have analyzed the nitrogen chemistry of meteorites [Gibson and Moore, 1971; Gibson et al., 1971; Moore and Gibson, 1969; Moore et al., 1969; Moore et al., 1970]. The nitrogen concentrations of the CI and CM2 chondrites are in the range of 1000-3000 ppm (by weight). They are in the range of several tens to 100 ppm for the C3V and C3O chondrites and for the ordinary (H, L, LL) chondrites. They are in the range of several hundred to 1000 ppm for the enstatite (E) chondrites. Several achondrites which were examined have nitrogen concentrations of several tens of ppm. The nitrogen concentrations of 123 iron meteorites range from a few to 200 ppm with a median nitrogen concentration of 18 ppm. Other nitrogen analyses by Kothari and Goel [1974], Shukla and Goel [1981], and Knowlton (unpublished data,

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1982) are in the same ranges as the data obtained by Gibson and Moore.

Several groups have also recently studied the isotopic compositions of nitrogen in meteorites. The most extensive data are those of Kung and Clayton [1978] who find four major isotopic groups: (1) CI and CM2 chondrites with  $\delta^{15}\text{N}$  values of +3 to +5%, (2) E chondrites with  $\delta^{15}\text{N}$  values of -3 to -4%, (3) ordinary (H, L, LL) chondrites with  $\delta^{15}\text{N}$  values of -1 to +2%, and (4) C3V chondrites with low  $\delta^{15}\text{N}$  values and large internal variations. The less extensive data of Injerd and Kaplan [1974] indicate the same isotopic groups except for group (4).

More recently several groups have examined the isotopic composition of mineral separates and of different components in carbonaceous and enstatite chondrites. Becker and Epstein [1982] and Robert and Epstein [1982] examined the soluble and polymeric organic matter in CI, CM2, and the Renazzo carbonaceous chondrites. Frick and Pepin [1981] and Thiemens and Clayton [1981] examined some different components in the Allende C3V chondrite by differential oxidation techniques and stepwise heating, respectively. Thiemens and Clayton (in press) used stepwise heating to examine clasts from the Abee E4 chondrite. Becker and Pepin [1982] have begun to examine the nitrogen isotopic compositions in iron meteorites by an oxidation technique.

The data on different components of the Allende C3V and Abee E4 chondrites and on the organic matter in CI and CM2 chondrites reveal the presence of components with unusual nitrogen isotopic compositions. The (limited) data on iron meteorites also reveal unusual isotopic components. Becker (personal communication, 1982) found a  $\delta^{15}\text{N}$  value of -5.5% for the Dayton iron meteorite. The isotopic data indicate that the nitrogen isotopic composition of the solar nebula may have been spatially and/or temporally heterogeneous. The data are interpreted by some authors to suggest the introduction of an extrasolar nitrogen component into the solar nebula. Mixing of this component with solar nebula nitrogen could have produced the observed range of isotopic variations [Geiss and Bochsler, 1982].

Several nitride minerals have also been discovered in meteorites. Osbornite, discovered by Maskelyne [1870] and verified by Bannister [1941], was the first meteoritic nitride to be found. In recent years sinoite has been found in enstatite chondrites and carlsbergite and roaldite  $[(\text{Fe},\text{Ni})_4\text{N}]$  have been identified in iron meteorites. Kung and Clayton [1978] used MgO to extract 'so-called exchangeable  $\text{NH}_4^+$ -ions' from the Murchison CM2 chondrite. Two referees have emphasized that this method does not give unambiguous evidence for ammonium salts. No specific ammonium aluminosilicate or salt has yet been identified in chondrites.

#### Method of Calculation

Elemental abundances in the solar nebula are taken from Cameron [1973] except where noted otherwise. Stability fields of high temperature condensates are taken from my unpub-

lished calculations and from other sources which are noted in the text. Thermodynamic data are taken from a variety of sources with most coming from the JANAF Tables [1971] and Robie et al. [1978]. Again, other sources are listed in the text and tables. The gas-phase composition and condensate activities for a wide range of temperatures and pressures are calculated by a computer program which considers several hundred compounds of the elements H, He, O, C, N, Mg, Si, Fe, Ni, S, Al, Ca, Na, F, Cl, Ti, and P. The activities of nitrides were calculated by this program or by hand for selected pressure-temperature points.

#### Dissolved Nitrogen in Metal

The solubility of  $\text{N}_2(\text{g})$  in  $\alpha$ -,  $\gamma$ -, and  $\delta$ -iron and in liquid iron has been measured by many investigators [Hansen, 1958, and references therein].  $\text{N}_2(\text{g})$  dissolves in iron according to the reaction



where the square brackets denote solution in the metal phase. The atom fraction of nitrogen in iron can be substituted for its activity since the solution of  $\text{N}_2(\text{g})$  obeys Henry's Law. Furthermore, at the low concentrations involved, the weight percentage can be taken as proportional to the atom fraction. Thus the equilibrium constant for reaction (1) is given by

$$K_1 = [\% \text{N}] / (P_{\text{N}_2})^{1/2} \quad (1)$$

The variation of the  $\text{N}_2(\text{g})$  solubility with temperature at a pressure of 1 atm, describes the variation of  $K_1$ . Values of  $K_1$  for the solution of  $\text{N}_2(\text{g})$  in iron metal and liquid from 873°-2273° K are given by Chipman and Elliott [1963].

The metal phase in a solar composition system is not pure iron metal, but rather a Fe-Ni alloy of variable Ni content. Grossman [1972] and Sears [1978] have performed chemical equilibrium calculations describing the composition of the Fe-Ni alloy as a function of temperature and pressure. The  $\text{N}_2(\text{g})$  solubility in  $\gamma$ -(Fe-Ni) alloys has been measured by several investigators [Wriedt and Gonzalez, 1961; Mori et al., 1963; Schenck et al., 1963]. The  $\text{N}_2(\text{g})$  solubility decreases as the Ni content of the Fe-Ni alloy increases at constant nitrogen pressure and temperature. The results of Wriedt and Gonzalez [1961], which are in excellent agreement with the work of Mori et al. [1963], cover a wide range of nickel concentrations (0-100%) and temperatures (1191°-1490° K). Their results were used to calculate  $K_1$  values for the solubility of  $\text{N}_2(\text{g})$  in Fe-Ni alloys containing up to 41 wt% Ni. The measured solubilities at higher nickel concentrations could not be used to calculate  $K_1$  values because the solubilities, which are at or below the limit of the analytical method's sensitivity, represent only upper limits.

The calculated equilibrium concentration of dissolved nitrogen in the metal ( $\alpha$  and  $\gamma$  phases)

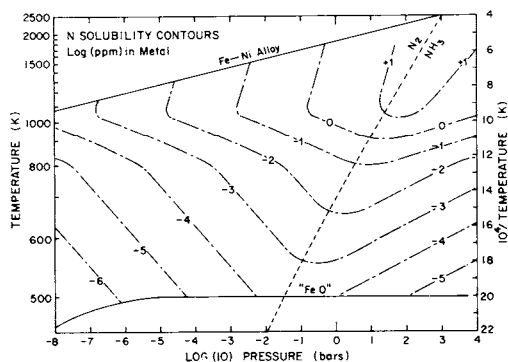


Fig. 1. Equilibrium concentrations of nitrogen dissolved in Fe-Ni alloy ( $\alpha$ - and  $\gamma$ - phases) in a solar composition system. Total nebular pressure is plotted against reciprocal temperature (K). Contours given are for  $\log_{10}$  parts per million (by weight) of dissolved N in the metal phase from  $10^{-6}$  to  $10^{+1}$  ppm. The contours are bounded at high temperatures by the condensation curve of  $\gamma$ -(Fe-Ni) alloy and at low temperatures by the endpoint for oxidation of metal to FeO dissolved in ferromagnesian silicates. The dotted line is the line where the abundances of the two major nitrogen-bearing gases are equal.

is illustrated in Figure 1. The amount of dissolved nitrogen was calculated using  $K_1$  values for  $\gamma$ -(Fe-Ni) from Wriedt and Gonzalez [1961] and  $K_1$  values for pure  $\alpha$ -iron from Chipman and Elliott [1963]. Although the effect of Ni on the (already small) solubility of  $N_2(g)$  in  $\alpha$ -iron has not been studied, it is expected to decrease the solubility as it does in  $\gamma$ -iron and liquid iron [Wada and Pehlke, 1977]. The calculations of Barshay [1981] and the Fe-Ni phase diagram of Hansen [1958] were used to calculate the amounts of  $\alpha$ - and  $\gamma$ -iron present at equilibrium. The 'FeO' curve representing the iron oxidation endpoint is from Lewis et al. [1979].

Figure 1 illustrates that the concentration of nitrogen dissolved in the metal phase is a maximum near the line where  $P_{N_2} = P_{NH_3}$ . The maximum nitrogen concentration is orders of magnitude less than the maximum carbon concentration on the same isotherm [Lewis et al., 1979]. Also, the nitrogen concentration along an isobar increases with decreasing temperature until  $\alpha$ -(Fe-Ni) alloy becomes stable at about  $1050^\circ$  K. The nitrogen concentration then decreases with further decreases in temperature. This behavior is illustrated in Figure 2 which is a diagram of the amount of dissolved nitrogen in the metal phase along the  $10^{-3}$  bar isobar.

It is important to examine the effect of two other factors to see how the presence of other alloying elements in the Fe-Ni alloy and the failure to achieve equilibrium affect the calculated nitrogen contents in Figure 1. In addition to Ni, other cosmically abundant elements which can dissolve in or alloy with Fe are H, O, C, Si, S, Co, Cr, Mn, and P. Analyses of iron meteorites [Buchwald, 1975] indicate that all of these elements except H and O are present at levels  $\geq 1$  ppm. Studies by several groups [Corney and Turkdogan, 1955; Darken, 1959; Elliott et al, 1963; Schenck et al., 1963] indicate that increasing concentrations of C, Si, S, Co

and P decrease the nitrogen solubility in metallic and liquid iron. On the other hand, increasing amounts of Cr and Mn increase the nitrogen solubility. Can these effects be quantified?

In principle, the net effect of these elements on the nitrogen solubility can be calculated by using interaction coefficients, which were developed to facilitate the thermodynamic treatment of dilute multicomponent solutions in metallurgy [Gaskell, 1973]. In practice, the lack of all the necessary interaction coefficients and their temperature and composition derivatives makes this approach unworkable. The semiquantitative information which is available indicates that the net effect of the additional dissolved elements will be to further decrease the nitrogen solubilities displayed in Figure 1. This behavior is quantitatively verified at  $1873^\circ$  K for the average iron meteorite composition tabulated by Buchwald [1975] and the interaction coefficients listed by Gaskell [1973]. More detailed calculations are not warranted at the present time.

Failing to achieve complete equilibrium will also affect nitrogen solubilities. For example, at high temperatures incomplete diffusion of  $N_2(g)$  into metal grains in the nebula will give nitrogen contents in the metal which are slightly lower than the values in Figure 1. At low temperatures incomplete nitrogen diffusion out of grains will give slightly higher nitrogen contents in the metal than indicated in Figure 1. On the other hand, there is also the possibility of partial equilibrium among the nitrogen bearing gases. Lewis and Prinn [1980], Norris [1980], and Prinn and Fegley [1981] have considered this problem by studying the kinetics of  $N_2(g)$  reduction to  $NH_3(g)$ . Lewis and Prinn [1980] and Norris [1980] showed that the reduction of  $N_2$  to  $NH_3$  will be kinetically inhibited.  $NH_3$  formation will not occur to any appreciable extent at temperatures, pressures,

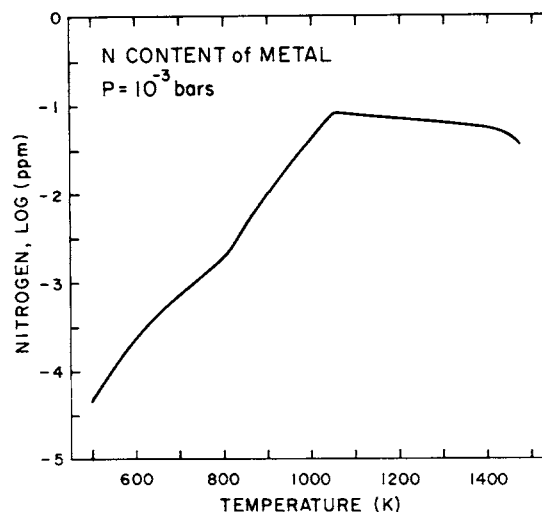


Fig. 2. Equilibrium concentration of dissolved nitrogen in the metal phase along the  $10^{-3}$  bar isobar. This diagram represents a slice through Figure 1 along the  $10^{-3}$  bar isobar in the solar nebula.

and mixing and/or cooling times appropriate to solar nebula models, e.g., Cameron [1978].

Applying these results to Figure 1 is fairly straightforward. The failure to produce appreciable quantities of  $\text{NH}_3$  leads to larger concentrations of dissolved nitrogen in the metal phase than indicated within the  $\text{NH}_3(\text{g})$  stability field. For example, at  $625^\circ \text{K}$  and  $10^{+2}$  bars, well within the  $\text{NH}_3(\text{g})$  stability field in Figure 1, the nitrogen concentration in the metal phase would increase from  $\approx 10^{-3}$  ppm to  $\approx 10^{-1}$  ppm if  $\text{NH}_3(\text{g})$  formation is inhibited. However, at pressures of  $10^{-3}$  bars and lower, which are more representative of solar nebula models, no appreciable amounts of  $\text{NH}_3(\text{g})$  are formed until temperatures below the Fe oxidation endpoint. No increase in nitrogen concentrations of the metal can be produced by the kinetic inhibition of  $\text{NH}_3(\text{g})$  formation since by the time it would form all the metal is consumed by other reactions.

Thus in the region of typical nebular temperatures and pressures the calculated nitrogen concentrations in Figure 1 are firm upper limits on the amount of nitrogen dissolved in Fe-Ni metal in equilibrium with a solar composition gas. At higher pressures within the  $\text{NH}_3(\text{g})$  stability field the calculated values may be increased by several orders of magnitude if the formation of  $\text{NH}_3(\text{g})$  is kinetically inhibited [Lewis and Primm, 1980; Norris, 1980]. These higher pressures may be of interest for models of circumplanetary nebulae [Prinn and Fegley, 1981] and of giant gaseous protoplanets [Cameron, 1978], but unless the reaction kinetics are compared with mixing and cooling times the extent to which  $\text{NH}_3(\text{g})$  formation proceeds and nitrogen concentration in the metal is enhanced cannot be calculated.

How do the calculated nitrogen concentrations from Figure 1 compare with the nitrogen concentrations of metal in meteorites? Two data sets are relevant to this question -- nitrogen analyses of iron meteorites and nitrogen analyses of the magnetic fraction of ordinary chondrites. By far the most extensive data set is the collection of iron meteorite nitrogen analyses done by Gibson and Moore [1971], Knowlton (unpublished data, 1982), Kothari and Goel [1974] and Shukla and Goel [1981]. Their work, which is summarized in Table 1, indicates that 'average' (median or mean) nitrogen concentrations in irons range from  $\approx 10$  to 30 ppm. Furthermore, only 5 of the 235 samples (not necessarily all different meteorites) analyzed by these groups have nitrogen concentrations  $\leq 1$  ppm -- Cambria (1ppm), Huizopa (0.8

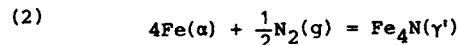
ppm), Santiago Papasquiereo (0.5 ppm), Tlacotepec (0.8 ppm), and Tobychan (0.5 ppm). Becker (personal communication, 1982) found 0.9 ppm in Hoba. Less extensive data on the nitrogen chemistry of the magnetic fraction of ordinary chondrites [Kothari and Goel, 1974] show nitrogen concentrations in the range of 5.5 to 42 ppm.

By contrast, the maximum nitrogen concentration along the  $10^{-3}$  isobar of Figure 1 is about 0.08 ppm, which is approximately two orders of magnitude less than the nitrogen concentrations of metal in meteorites. Even allowing for consistent underestimates of nitrogen solubility by a factor of two -- something which is not indicated by a comparison of several independent nitrogen solubility data sets -- the calculated nitrogen concentration is still several times smaller than the lowest reported nitrogen concentrations of metal in meteorites. In addition, lower nebular pressures, which are appropriate to nebular models such as Cameron and Fegley (in press), will lead to lower nitrogen concentrations in Fe-Ni alloy in equilibrium with a gas of solar composition.

#### $\text{Fe}_4\text{N}(\gamma')$ Stability

Buchwald [1980], Buchwald and Nielsen [1981], and Nielsen and Buchwald [1981] recently reported the discovery of an iron-nickel nitride  $(\text{Fe,Ni})_4\text{N}$ , roaldite, in the Jerslev and Youndegin iron meteorites. Roaldite is an exsolution product in the kamacite phase of the irons. It has the same structure and morphology as  $\text{Fe}_4\text{N}(\gamma')$  -- a nitride for which thermodynamic data are available. In view of this discovery it is interesting to determine the  $\text{Fe}_4\text{N}(\gamma')$  stability field.

Two independent, internally consistent evaluations of the thermodynamic properties of  $\text{Fe}_4\text{N}(\gamma')$  are available. Fast and Verrijp [1955] determined the solubility of  $\text{N}_2(\text{g})$  and  $\text{Fe}_4\text{N}(\gamma')$  in  $\alpha$ -iron by measuring the internal friction of  $\alpha$ -iron in equilibrium with  $\text{N}_2(\text{g})$  at 1 atm pressure and  $\text{Fe}_4\text{N}(\gamma')$ , respectively. The equilibrium constant for the formation of  $\text{Fe}_4\text{N}(\gamma')$  by the reaction:



is:

$$K_2 = P_{\text{N}_2}^{-1/2} = 8.0 \times 10^{-3} \exp(+1100/\text{RT}) \quad (2)$$

From a quite different investigation -- a study of the catalytic activity of iron in  $\text{NH}_3$  synthesis -- Emmett et al. [1930] measured  $(P_{\text{NH}_3})/(P_{\text{H}_2})^{3/2}$  ratios from which a value of the equilibrium constant for (2) can be determined. Their value of  $K_2$  (denoted  $K_2'$  to distinguish it from the value determined by Fast and Verrijp) is

$$K_2' = P_{\text{N}_2}^{-1/2} = 6.7 \times 10^{-3} \exp(+1150/\text{RT}) \quad (3)$$

The two equilibrium constants are in excellent agreement.  $K_2$  can be used to calculate the  $\text{Fe}_4\text{N}(\gamma')$  stability field. This calculation, which requires free energy data for  $\alpha$ -iron from

Table 1. Nitrogen Analyses of Iron Meteorites

Mean	Median	No. of Samples	Ref.
26	18	123	1
26	22	70	2
34	30	12	3
28	12	30	4

References: (1) Gibson and Moore [1971] (2) Knowlton (unpublished data, 1982) (3) Kothari and Goel [1974] (4) Shukla and Goel [1981]

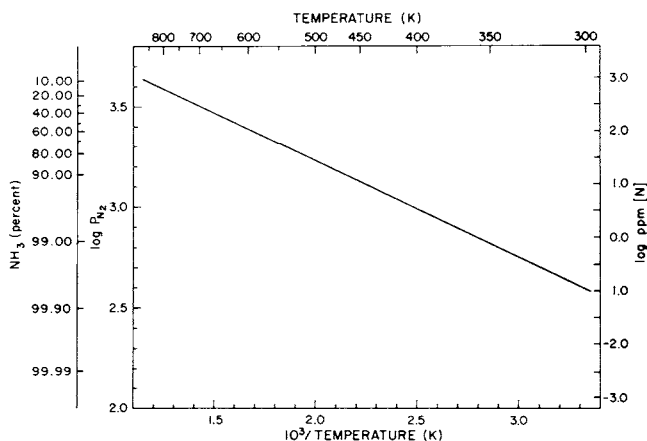


Fig. 3. The stability field of  $\text{Fe}_4\text{N}(\gamma')$  in equilibrium with  $\alpha$ -iron.  $\text{Fe}_4\text{N}(\gamma')$  plus  $\alpha$ -iron are stable above the line,  $\text{N}_2(\text{g})$  plus  $\alpha$ -iron are stable below the line. The nitrogen potential at equilibrium is given by three separate ordinates in terms of (1) the  $\text{N}_2(\text{g})$  pressure, (2) the volume percent of  $\text{NH}_3$  in a  $\text{NH}_3\text{-H}_2$  gas mixture ( $P = 1$  atm) having an equivalent nitrogen fugacity, and (3) the concentration in parts per million of dissolved N in the metal phase.

Orr and Chipman [1967], is based on the assumption that the composition of  $\text{Fe}_4\text{N}(\gamma')$  is essentially constant. Although this assumption is not strictly correct [Wriedt, 1969; Hansen, 1958] small deviations will not change the conclusions concerning  $\text{Fe}_4\text{N}(\gamma')$  stability and its contribution to dissolved nitrogen in the metal phase.

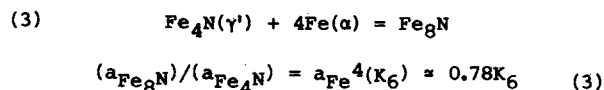
Figure 3 displays the stability field of  $\text{Fe}_4\text{N}(\gamma')$  in stable equilibrium with  $\alpha$ -iron. The three ordinates indicate the nitrogen potential at equilibrium in terms of (1) the  $\text{N}_2$  pressure, (2) the volume % of  $\text{NH}_3$  in a  $\text{NH}_3\text{-H}_2$  gas mixture ( $P = 1$  atm) with an equivalent nitrogen fugacity, and (3) the concentration (ppm) of dissolved N in the metal phase, i.e., the solubility of  $\text{Fe}_4\text{N}(\gamma')$  in  $\alpha$ -iron. As Figure 3 illustrates,  $\text{Fe}_4\text{N}(\gamma')$  and  $\alpha$ -iron can coexist at equilibrium only at extremely high  $\text{N}_2$  pressures. Equivalent nitrogen fugacities can be produced by using  $\text{NH}_3\text{-H}_2$  gas mixtures of the appropriate composition at 1 atm pressure. Furthermore, it is interesting to note that the median nitrogen concentration of 18 ppm for the 123 iron meteorites analyzed by Gibson and Moore [1971] is sufficient to precipitate  $\text{Fe}_4\text{N}(\gamma')$  at temperatures below  $\approx 480^\circ\text{K}$ .

The measurements of Fast and Verrijp [1955] show that the solubility of  $\text{Fe}_4\text{N}(\gamma')$  in  $\alpha$ -iron is considerably greater than the solubility of  $\text{N}_2(\text{g})$  at 1 atm pressure. For example, at the eutectoid temperature  $863^\circ\text{K}$  the solubility of  $\text{Fe}_4\text{N}(\gamma')$  is  $\approx 970$  ppm while the solubility of  $\text{N}_2(\text{g})$  is only  $\approx 15$  ppm. At a temperature of  $573^\circ\text{K}$ , the  $\text{Fe}_4\text{N}(\gamma')$  solubility is still relatively high -- 84 ppm -- while the  $\text{N}_2(\text{g})$  solubility is only  $\approx 2$  ppm. Hansen [1958] gives the maximum solubility of  $\text{Fe}_4\text{N}(\gamma')$  in  $\gamma$ -iron as 28,000 ppm at  $923^\circ\text{K}$ . The  $\text{N}_2(\text{g})$  solubility at the same temperature, which is calculated from the data of Corney and Turkdogan [1955], is 340 ppm.

Until now the effect of nickel (except for the slight decrease in the iron activity) has been neglected. Imai et al. [1968-1969] studied the effect of nickel on the solubility of  $\text{Fe}_4\text{N}(\gamma')$  in  $\alpha$ -iron. They found that the solubility decreases as the nickel content increases (at constant temperature). For a 4.7% Ni alloy, which was the most nickel-rich alloy studied, the solubility decreases by a factor of  $\approx 1.4$  at  $800^\circ\text{K}$  to a factor of  $\approx 5.8$  at  $500^\circ\text{K}$ . The effects of nickel on the solubility of  $\text{Fe}_4\text{N}(\gamma')$  in  $\gamma$ -iron have not been investigated. However, from the work of Atkinson and Bodsworth [1970], who have studied nitrogen solubility in Fe-Ni alloys from  $933^\circ\text{K}$ - $1083^\circ\text{K}$ , it may be surmised that nickel lowers the solubility in much the same way as it does in  $\alpha$ -iron. Other effects of nickel (such as changing the stability of  $\text{Fe}_4\text{N}(\gamma')$ ) have not been studied, and no thermodynamic data are available.

The possibility that  $\text{Fe}_4\text{N}(\gamma')$  could be a nebular condensate was also studied. The results show that  $\text{Fe}_4\text{N}(\gamma')$  is never a stable phase at chemical equilibrium in a solar composition system. The maximum activities for  $\text{Fe}_4\text{N}(\gamma')$  (which are reached near the line where  $P_{\text{N}_2} = P_{\text{NH}_3}$ ) vary from  $\approx 10^{-2.7}$  to  $\approx 10^{-4.4}$  in the  $1800^\circ\text{K}$ - $500^\circ\text{K}$  range. Maximum  $\text{Fe}_4\text{N}(\gamma')$  activities decrease with increasing temperature above  $1809^\circ\text{K}$  where liquid iron condenses and decrease with decreasing temperature below the iron oxidation endpoint at  $500^\circ\text{K}$ .

Fast and Verrijp [1955] also measured the solubility of the nitride  $\text{Fe}_8\text{N}$ , which forms as an intermediate phase in the precipitation of  $\text{Fe}_4\text{N}(\gamma')$  from a supersaturated Fe-N solution at low temperatures. The stabilities of  $\text{Fe}_8\text{N}$  and  $\text{Fe}_4\text{N}(\gamma')$  can be compared using the reaction:



Using solubility data from Fast and Verrijp [1955] to calculate  $K_3$ , it is found that  $\text{Fe}_8\text{N}$  is always less stable than  $\text{Fe}_4\text{N}(\gamma')$ . The activity ratio from (3) varies from  $\approx 0.4$  at  $300^\circ\text{K}$  to  $\approx 0.1$  at  $500^\circ\text{K}$ .  $\text{Fe}_8\text{N}$  is never stable in solar composition matter.

#### Silicon Oxynitride (Sinoite)

Andersen et al. [1964] discovered silicon oxynitride  $\text{Si}_2\text{N}_2\text{O}$ , sinoite, in the Jajh de Kot Lalu enstatite chondrite. It has subsequently been found in the Hvittis, Pillistfer, Ufana, and Yilmia enstatite chondrites [Buseck and Holdsworth, 1972; Keil and Andersen, 1965]. The observation of sinoite in the highly reduced enstatite chondrites [Keil, 1968] is of great interest because sinoite is a potential indicator of the oxidation state and nitrogen fugacity of the environment in which these meteorites formed. The presence of sinoite exclusively in the more 'metamorphosed' type II enstatite chondrites [Keil, 1968] may also prove to be of value in unravelling the genetic relationship among the type I, type II, and intermediate class enstatite chondrites.

Several authors [Herndon and Suess, 1976; Sears, 1980] have suggested that silicon oxyni-

tride can form from a gas of solar composition at high temperatures and pressures. Specifically, Sears [1980] states that silicon oxynitride can be formed at temperatures and pressures around 1900° K and 1 bar, but that it must be isolated from the gas as soon as it condenses. On the other hand, Larimer and Bartholomay [1979] argue that silicon oxynitride cannot be produced in solar composition matter. All of these studies of silicon oxynitride stability utilized limited thermodynamic data from the investigation of Ryall and Muan [1969]. Fegley [1981b] critically assessed all the available thermal and equilibrium data for silicon oxynitride and proposed an internally consistent set of thermodynamic functions (300°–2500° K) for silicon oxynitride which are more reliable than the limited data derived from Ryall and Muan [1969]. In view of this development, the stability of silicon oxynitride in a solar composition system has been reevaluated.

The hypothetical condensation curve for silicon oxynitride was calculated using the Si, N, and O elemental activities from the gas phase equilibrium program. This curve is an upper limit for the condensation temperature of silicon oxynitride in a solar composition system since the method of calculation assumes that no other Si-bearing phase condensed at higher temperature. If another Si-bearing phase does condense at a higher temperature, the thermodynamic activities of silicon oxynitride at lower temperatures will be reduced, lowering the previously calculated silicon oxynitride condensation point (where activity of silicon oxynitride = 1.0). (Grossman and Larimer [1974] illustrated this type of behavior for spinel  $MgAl_2O_4$ . Its condensation point from a solar composition gas is lowered by the prior condensation of corundum  $Al_2O_3$ .) In fact, the silicon oxynitride activities may be reduced so much by the prior condensation of more stable Si-bearing phases such as forsterite  $Mg_2SiO_4$  and enstatite  $MgSiO_3$  that silicon oxynitride may never be formed as an equilibrium product in solar composition matter.

A comparison of the hypothetical silicon oxynitride condensation curve with the forsterite condensation curve from this work and the (extrapolated) enstatite condensation curve from Sears [1980] demonstrates that silicon oxynitride never condenses before either silicate. The hypothetical silicon oxynitride condensation curve is 230°–280° K below the forsterite condensation curve in the  $10^{+3}$ – $10^{-9}$  bar region and is 510° K below the forsterite curve at  $10^{+4}$  bars. Furthermore, once forsterite condenses silicon oxynitride never forms in solar composition matter. These conclusions are not altered by the use of other (slightly different) forsterite condensation curves from Sears [1980], Trivedi and Larimer [1980], or Grossman and Larimer [1974].

Recent work summarized by Jack [1977] indicates that silicon oxynitride is soluble in corundum and that a large number of compounds, called sialons, form in the Si–Al–O–N system. Furthermore, a variety of nitrogen-containing silicate glasses in the Mg–Si–O–N system have also been synthesized [Jack, 1977]. It was

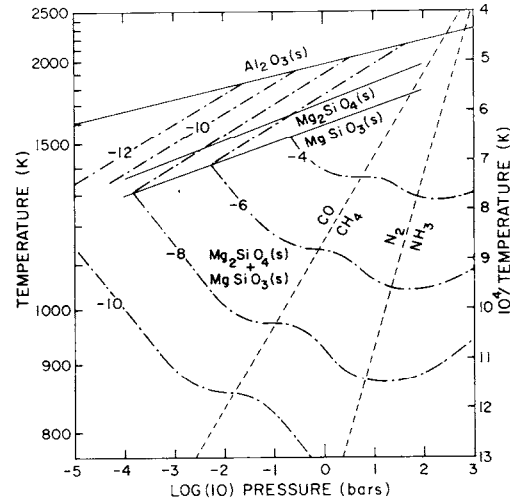


Fig. 4. Activity contours for silicon oxynitride  $Si_2N_2O$  in a solar composition system. Total nebular pressure is plotted against reciprocal temperature (K). Contours showing  $\log_{10}$  activity values for silicon oxynitride are superimposed on the stability fields of corundum  $Al_2O_3$ , forsterite  $Mg_2SiO_4$ , and enstatite  $MgSiO_3$  in a solar composition system. The forsterite and enstatite stability fields are from Sears [1980]. The dotted lines labelled  $CO-CH_4$  and  $N_2-NH_3$  are the lines in P–T space where the two major carbon-bearing and nitrogen-bearing gases have equal abundances, respectively. Silicon oxynitride is not stable in a solar composition system at total pressures up to  $10^{+4}$  bars.

therefore decided to investigate the activity of silicon oxynitride over a wide range of temperatures and pressures in the corundum, forsterite, and enstatite stability fields to determine if dissolved silicon oxynitride might be a source of nitrogen in these phases.

Figure 4 illustrates the results of the silicon oxynitride activity calculations. The calculations were done using elemental activities from the gas phase equilibrium program, the corundum stability field from this work, and the forsterite and enstatite stability fields from Sears [1980]. As Figure 4 indicates, the silicon oxynitride activities are extremely low throughout the P–T region covered, except at the highest temperatures and pressures. For example, the maximum silicon oxynitride activity along the  $10^{-3}$  isobar is only  $\approx 10^{-7.2}$  at approximately 1300° K. Assuming ideal solution of silicon oxynitride in forsterite, this activity corresponds to a dissolved N concentration of  $\approx 0.01$  ppm. By contrast, the N concentrations of the nonmagnetic fractions of several ordinary chondrites analyzed by Kothari and Goel [1974] are 20 ppm (Bruderheim, L6), 14.5–30 ppm (Farmville, H4), 33 ppm (Bjurböle, L4), 16 ppm (Ucera, H5), and 48 ppm (New Concord, L6). Unless the activity coefficients for silicon oxynitride dissolved in forsterite (and other condensed phases) are on the order of  $10^{-3}$ , it seems unlikely that dissolved sinoite is a significant contributor to the nitrogen concentration of nonmagnetic phases in ordinary chondrites.

Finally, Figure 4 also illustrates that the

silicon oxynitride activity at 1900° K and 1 bar, where it is claimed to be stable by Sears [1980], is only  $10^{-8.0}$ . A nearly identical activity value is obtained using the silicon oxynitride thermodynamic data from Ryall and Muan [1969]. The present results thus disagree markedly with the results of Herndon and Suess [1976] and Sears [1980].

#### Osbornite Stability

The mineral osbornite (TiN) was discovered in the Bustee enstatite achondrite (aubrite) by Maskelyne [1870] and was verified by Bannister [1941]. Buseck and Holdsworth [1972] identified osbornite in the Yilmia enstatite chondrite and Derham et al. [1964] found it in the Bishopville aubrite. Ramdohr [1973] observed osbornite in the Hvittis and Khairpur enstatite chondrites, the Pesyanoe aubrite, and in the Kapoeta howardite. He also reported a gold-colored mineral, which may be osbornite, in the Atlanta enstatite chondrite.

Work by several groups [Larimer, 1975; Larimer and Bartholomay, 1979; Lattimer and Grossman, 1978] indicates that osbornite is an equilibrium product in a gas of nonsolar composition (carbon to oxygen ratio  $> 0.9$ ). Herndon and Suess [1976] and Sears [1980] also suggested that osbornite is an equilibrium product in a solar composition system, but at high temperatures and pressures. Their suggestion has been disputed by Larimer and Bartholomay [1979] and by Trivedi and Larimer [1980], who claim that osbornite is not stable at pressures as great as  $10^{+3}$  bars. In view of the similar controversy about silicon oxynitride stability, a careful examination of the stability of osbornite in a solar composition system was made.

The important results are summarized in Figure 5, which displays the condensation curves of osbornite and perovskite  $\text{CaTiO}_3$  in a solar composition system. Osbornite condenses before perovskite at pressures between  $\approx 224$  bars and  $\approx 8610$  bars. These two points are determined by the intersection of the osbornite and perovskite condensation curves which are calculated assuming no previous Ca- and/or Ti-bearing condensates. The calculated perovskite condensation curve from this work is in good agreement with the (extrapolated) perovskite condensation curve of Trivedi and Larimer [1980] over the entire range from  $10^{-8}$  to  $10^{+4}$  bars.

The osbornite stability field shown in Figure 5 is very narrow because the condensation curve of perovskite is lowered only a few degrees by the prior condensation of osbornite. The dash-dot line in the figure is the perovskite condensation curve in the absence of osbornite formation while the dashed line illustrates the slightly lowered perovskite condensation curve when the prior condensation of osbornite is taken into account. These two lines are indistinguishable on the scale shown at pressures from 224-710 bars. Once perovskite condenses osbornite is not stable. It converts to perovskite.

It is important to note that the lowest temperature at which osbornite is stable is 2280° K, which is  $\approx 90^\circ$  K above the melting point of perovskite. The results shown in

Figure 5 are thus an upper limit to the osbornite stability field since the stability of osbornite is being compared to that of a crystalline phase which is less stable than the complex melt which actually forms at these pressures.

An intentionally simple calculation illustrates that the osbornite stability field is much smaller when condensation of pure liquid  $\text{CaTiO}_3$  is considered. The congruent melting point of perovskite is 2188° K [Levin et al., 1964]. The entropy of fusion for perovskite is estimated to be 2.3 cal/(gm atom K), or 11.5 cal/(mole K), by analogy with experimentally determined  $\Delta S_m^\circ$  values for lithium and sodium titanates [JANAF Tables 1971; Kelley, 1960]. The heat capacity  $C_p$  of the molten  $\text{CaTiO}_3$  is estimated to be 7 cal/(gm atom K), the value recommended by the JANAF Tables for many molten oxides, silicates, and titanates. These estimated data, plus thermal functions for perovskite below the melting point [Kelley, 1960], the heat of formation of perovskite [Robie et al., 1978], and Gibbs energy functions for the

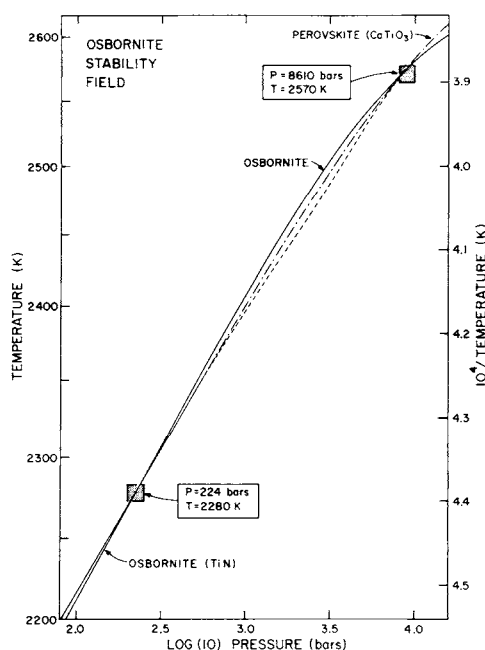


Fig. 5. The stability field of osbornite TiN in a gas of solar composition under equilibrium conditions. Total nebular pressure is plotted against reciprocal temperature (K). Osbornite condenses before perovskite  $\text{CaTiO}_3$  between pressures of  $\approx 224$  bars to  $\approx 8610$  bars. The dash-dot line indicates the condensation curve of perovskite from a solar composition gas (ignoring TiN formation). The dashed line indicates the slightly lower perovskite condensation curve after TiN formation. The two lines are indistinguishable on the scale shown at pressures of  $\approx 224$  bars to  $\approx 710$  bars. Osbornite is only stable in a narrow P-T interval between the curves. The condensation of molten phases was not considered in the construction of this figure. However, intentionally simple calculations using (estimated) data for molten  $\text{CaTiO}_3$  indicate that when condensation of complex melts is considered, the osbornite stability field completely disappears.

constituent elements in their reference states [JANAF Tables] can be used to calculate equilibrium constants for the  $\text{CaTiO}_3$  melt. These equilibrium constants can then be used to compare the stability of osbornite with that of the  $\text{CaTiO}_3$  melt. A calculation at  $2400^\circ\text{K}$  indicates that the melt is more stable than osbornite at this temperature, i.e., the melt condenses before osbornite (which does not form). Since the complex melt which forms (instead of pure liquid  $\text{CaTiO}_3$ ) is even more stable, it is fairly safe to conclude that the osbornite stability field is nonexistent when condensation of melts is considered.

#### Carlsbergite Stability

Buchwald and Scott [1971] discovered the chromium nitride mineral carlsbergite  $\text{CrN}$  in the Descubridora and Cape York iron meteorites. It has since been recognized as a minor although often ubiquitous mineral in a large number of iron meteorites [Buchwald and Scott; Buchwald, 1975].

A comparison of the condensation curves of carlsbergite,  $\text{Cr}_2\text{N}$ , eskolaite  $\text{Cr}_2\text{O}_3$ , chromite  $\text{FeCr}_2\text{O}_4$ , and daubreelite  $\text{FeCr}_2\text{S}_4$  has been made over the pressure range of  $10^{-5}$  to  $10^{+2}$  bars. The condensation of chromium in ideal and non-ideal solid solution in iron metal has also been considered. Thermodynamic data for  $\text{CrN}$ ,  $\text{Cr}_2\text{N}$ , and  $\text{Cr}_2\text{O}_3$  were taken from the JANAF Tables, data for  $\text{FeCr}_2\text{O}_4$  from Jacob and Alcock [1975], and data for  $\text{FeCr}_2\text{S}_4$  from Kessler et al. [1976]. An estimated entropy of  $48.3 \pm 1.0$  cal/(mole K) for  $\text{FeCr}_2\text{S}_4$  was also used. The estimated entropy is in good agreement with the experimental value of  $49.2 \pm 0.6$  cal/(mole K) which was published after these calculations had been completed [Khodakovskiy and Petaev, 1981]. Activity coefficients for the Cr-Fe solid solution were calculated from data in Hultgren et al. [1973].

The results of the calculations indicate that neither  $\text{CrN}$  nor  $\text{Cr}_2\text{N}$  form as equilibrium products in the P-T region studied. Chromium initially condenses in solid solution in iron metal. If equilibrium is maintained,  $\text{Cr}_2\text{O}_3$  forms at lower temperatures, and  $\text{FeCr}_2\text{O}_4$  at slightly lower temperatures. No attempt is made here to describe the condensation chemistry of chromium in detail, because the (intentional) neglect of other Cr-bearing condensates and solid solutions makes such an attempt foolish. The present calculations, however, do provide firm upper limits on the activities of the two chromium nitrides, as the condensation of more stable phases lowers these activities. The calculated upper limits for the two chromium nitrides can now be compared with calculated upper limits for the activities of many other nitrides.

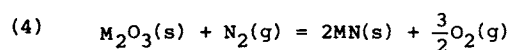
#### Stability of Other Nitrides

No other nitride minerals have (so far) been observed in meteorites, although  $\text{AlN}$  is an equilibrium product in a highly reducing gas with a C/O ratio  $> 0.9$  [Larimer and Bartholomay, 1979]. Several other main group, transition metal, and lanthanide nitrides are also known to be very stable. In addition, the solar abun-

dance of several other nitride-forming elements is large enough that retention of all or part of the elemental inventory as a nitride could account for the observed nitrogen contents of the earth, Venus, or Mars.

The activities of a large number of nitrides were calculated over various temperature-pressure ranges in order to determine if any are stable in a solar composition gas and to set upper limits on the activities of nitrides found to be unstable. The P-T range studied and the number of gases and condensed phases included in the calculation varied from element to element.

Generally, calculations for nitrides having very low activities were performed over restricted P-T ranges, since consideration of simple equilibria could be used to show that the nitride activities would remain smaller than unity outside the P-T ranges considered. For the elements Sc, Y, La, Ce, Sm, Ho, Er, Yb, and Th, calculations were done at one of two P,T points -- either  $1400^\circ\text{K}$  or  $1300^\circ\text{K}$  at  $10^{-3}$  bars. These calculations were done within the stability fields for the pure metal oxides given by Grossman [1973] and Grossman and Ganapathy [1976]. The relevant equilibrium (except for Th where an analogous equation can be written) is:



$$a_{\text{MN}} = [(K_4)(a_{\text{M}_2\text{O}_3})(P_{\text{N}_2})/(P_{\text{O}_2})^{3/2}]^{1/2} \quad (4)$$

where  $K_4$  is the equilibrium constant for (4) and the gas pressures are the equilibrium pressures in a solar composition gas. Equation (4) illustrates that  $a_{\text{MN}} \propto a_{\text{M}_2\text{O}_3}$ . The calculated nitride activities are firm upper limits, since condensation of these elements as solutes in other minerals is thermodynamically equivalent to lower  $a_{\text{M}_2\text{O}_3}$  values.

These nitride activity calculations (like the chromium condensation calculations) are not an attempt to describe completely the condensation sequences of the elements studied and should not be interpreted as such. The thermodynamic data used in the calculations are given in Table 2. The elemental abundances used are from Cameron [1973], except for zirconium (for which the lower abundance given by Cameron (in press) is used). The results of the calculations are summarized in Table 3 where the activities of various nitrides at  $10^{-3}$  bars and  $1400^\circ\text{K}$  (some at  $1300^\circ\text{K}$ ) are compared. None of the nitrides investigated are stable in solar composition matter. Nitrogen retention as pure nitride minerals is not a viable mechanism in a solar composition nebula.

#### Ammonium Aluminosilicates

The hydrated feldspar buddingtonite  $(\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O})$  occurs terrestrially. Several other  $\text{NH}_4^+$ -bearing silicates, including ammonium muscovite  $(\text{NH}_4\text{Al}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2)$  and ammonium phlogopite  $(\text{NH}_4\text{Mg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2)$  have been synthesized in the laboratory [Hallam and Eugster, 1976 and references therein]. Also, Kung and Clayton [1978] extracted so-called 'exchangeable  $\text{NH}_4^+$ -ions' from the Murchison CM2



Table 2. Thermodynamic Data Sources

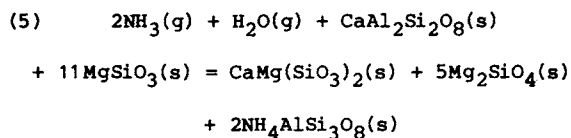
Gases	Source	Condensed Phases	Source
V	1	VN	1
VN	1	VN <sub>0.465</sub>	1
VO	1	VC <sub>0.88</sub>	2
VO <sub>2</sub>	1	VO	1
Zr	1	V <sub>2</sub> O <sub>3</sub>	1
ZrO	1	V <sub>2</sub> O <sub>4</sub>	1
ZrO <sub>2</sub>	1	V <sub>2</sub> O <sub>5</sub>	1
Hf	1	FeV <sub>2</sub> O <sub>4</sub>	3
HfO	4	V	1
HfO <sub>2</sub>	5	Zr	1
Nb	1	ZrO <sub>2</sub>	1
NbO	1	ZrN	1
NbO <sub>2</sub>	1	ZrC	1
Ta	1	Hf	1
TaO	1	HfO <sub>2</sub>	6,7
TaO <sub>2</sub>	1	HfN	8,9,10
Ni	21	Nb	1
Co	1	NbC <sub>0.98</sub>	1
Mo	1	NbO	1
MoO	1	NbO <sub>2</sub>	1
MoO <sub>2</sub>	1	Nb <sub>2</sub> O <sub>5</sub>	1
MoO <sub>3</sub>	1	Nb <sub>5</sub> Si	11
MoF	1	NbN	12,13,14
MoF <sub>2</sub>	1	Nb <sub>2</sub> N	5,15
MoF <sub>3</sub>	1	Ta	1
MoF <sub>4</sub>	1	TaC	1
MoF <sub>5</sub>	1	Ta <sub>2</sub> O <sub>5</sub>	1
Mo <sub>2</sub> F <sub>10</sub>	1	Ta <sub>5</sub> Si	11
		TaN	12,16,17,18
		Ta <sub>2</sub> N	5,15,19
		Al <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Si	20
		Al <sub>4</sub> N <sub>4</sub> O <sub>2</sub> Si	20
		Ni <sub>3</sub> N	21,22
		Co <sub>3</sub> N	2
		Mo <sub>2</sub> N	2
		AlN	1
		Si <sub>3</sub> N <sub>4</sub>	23
		ThN	2
		ThO <sub>2</sub>	7
		YN	2
		Y <sub>2</sub> O <sub>3</sub>	7
		ScN	2
		Sc <sub>2</sub> O <sub>3</sub>	7
		LaN	2
		La <sub>2</sub> O <sub>3</sub>	7
		SmN	24,25
		Sm <sub>2</sub> O <sub>3</sub>	7
		HoN	24,25
		Ho <sub>2</sub> O <sub>3</sub>	7
		YbN	24,25
		Yb <sub>2</sub> O <sub>3</sub>	7
		ErN	24,25
		Er <sub>2</sub> O <sub>3</sub>	7
		CeN	26
		Ce <sub>2</sub> O <sub>3</sub>	27

References and Notes (1) JANAF Tables [1971], (2) Kubaschewski and Alcock [1979], (3) Jacob and Alcock [1975], (4) Ackerman and Rauh [1974], (5) Schick [1966], (6) Kornilov et al. [1975], (7) Robie et al. [1978], (8) Humphrey [1953], (9) Glushko et al. [1974], (10) Litvinenko et al. [1979], (11) Larson and Elliott [1967], (12) Mah and Gellert [1956], (13) Paukov et al. [1969], (14)  $C_p$  from 298<sup>o</sup>-2500<sup>o</sup> K estimated using techniques given in (2), (15) Mah [1958], (16) Nogteva et al. [1969], (17) Kelley [1960], (18) a linear extrapolation of  $C_p$  from 800<sup>o</sup> K to the melting point was made assuming  $C_p$  at the melting point is 7.0 cal/(gm-atom K) as suggested by (2), (19) Kirpichev et al. [1976], (20) Moon et al. [1980], (21) Mah and Pankratz [1976], (22) entropy at 298<sup>o</sup> K estimated using techniques given in (2), (23) Glushko et al. [1978], (26) Gschneidner and Kippenhan [1971], (27) Gschneidner et al. [1973].

chondrite. However, no NH<sub>4</sub><sup>+</sup>-bearing minerals have yet been identified in chondrites. Fegley and Lewis [1980] showed that NH<sub>4</sub><sup>+</sup> salts form only at low temperatures (< 260<sup>b</sup> K at about 10<sup>-5</sup> bars) in a solar gas. Furthermore, formation of the NH<sub>4</sub><sup>+</sup> salts occurred only with restrictive assumptions about prior chemical reactions. Can ammonium aluminosilicates form in a solar gas and under what conditions?

The stability of NH<sub>4</sub><sup>+</sup>-feldspar (NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub>) at several temperatures along the 10<sup>-3</sup> bar isobar has been estimated using estimated ther-

modynamic data for NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> from Watkins [1981] and data for other minerals and gases from Robie et al. [1978]. The reaction studied is



As a first approximation all minerals (except

Table 3. Nitrides:  $\log_{10}$  Activity Values  
1400° K and  $10^{-3}$  bars

Nitride	$\log_{10}$ Activity
Mg <sub>3</sub> N <sub>2</sub>	-24.1
Ca <sub>3</sub> N <sub>2</sub>	-36.8
ScN	-10.5
YN	-11.2
LaN*	-10.2
CeN*	-8.0
SmN*	-8.8
HoN	-8.6
ErN	-8.2
YbN*	-6.6
ThN	-10.3
TiN	-2.6
ZrN	-6.6
HfN	-7.4
VN	-1.8
VN <sub>0.465</sub>	-1.1
NbN	-2.4
Nb <sub>2</sub> N	-3.8
TaN	-2.9
Ta <sub>2</sub> N	-7.2
CrN	-5.1
Cr <sub>2</sub> N	-6.6
Mo <sub>2</sub> N	-10.0
Fe <sub>4</sub> N	-6.1
Co <sub>3</sub> N	-16.1
Ni <sub>3</sub> N	-10.6
AlN	-5.9
Si <sub>3</sub> N <sub>4</sub>	-22.3
Si <sub>2</sub> N <sub>2</sub> O	-8.0
Al <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Si (β'-sialon)	-6.5
Al <sub>4</sub> N <sub>4</sub> O <sub>2</sub> Si (15R-sialon)	-14.7

\* Activity calculated at 1300° K and  $10^{-3}$  bars

NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub>) were assumed to be present at unit activity at the low temperatures ( $\approx 300^{\circ}$ -500° K) where the calculations were done. The resulting NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> activities vary from  $\approx 10^{-12.5}$  at 500° K to  $\approx 10^{-4.7}$  at 300° K. Extrapolation of the results indicates formation of pure NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> at  $\approx 240^{\circ}$  K.

The very low NH<sub>4</sub><sup>+</sup>-feldspar activities suggest that nitrogen retention as NH<sub>4</sub><sup>+</sup> in silicates does not occur to any significant extent at low temperatures in the solar nebula. Although the results indicate that pure NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> becomes stable at  $\approx 240^{\circ}$  K, formation of this phase probably does not occur in the solar nebula due to kinetic inhibition of NH<sub>3</sub>(g) formation [Lewis and Prinn, 1980; Norris, 1980]. The same mechanism probably also prevents the formation of NH<sub>4</sub><sup>+</sup> salts. These interpretations are in accord with the large body of evidence indicating that varying degrees of chemical reactions occurred on planetary bodies and altered carbonaceous chondrite chemistry and mineralogy [Bunch and Chang, 1980, and references therein]. Any exchangeable NH<sub>4</sub><sup>+</sup>-ions which may be found in carbonaceous chondrites could have been formed in aqueous phase reactions on the carbonaceous chondrite parent body by alteration of a preexisting nitrogen-bearing phase, rather than by chemical reactions in the solar nebula.

#### Nitrogen Retention Mechanisms in Meteorites

The formation of nitride minerals has been shown to be impossible in solar composition matter. Furthermore the amounts of N<sub>2</sub>(g) dissolved as N in the metal phase, nitrides dissolved in silicate and oxide minerals, and NH<sub>4</sub><sup>+</sup> dissolved in silicates have been shown to be much less than the observed nitrogen concentrations of meteorites. How was the nitrogen which we see in meteorites originally retained in them?

All of the mechanisms which have been examined are equilibrium mechanisms. All of them fail to provide the observed nitrogen concentrations found in meteorites. One alternative is chemical equilibrium at higher nebular pressures. Pressures on the order of 10 to 100 bars are required to provide approximately 10 ppm nitrogen in the metal phase of meteorites. These pressures are orders of magnitude greater than the pressures in recent nebular models, e.g., Cameron and Fegley (in press). I consider the high pressure nebular equilibration of chondritic matter very unlikely. I suggest that the only likely alternative is to resort to disequilibrium mechanisms for nitrogen retention in solar composition material. Several types of disequilibrium mechanisms may be responsible for nitrogen retention in meteorites. Fortunately, two types of mechanisms -- the Miller-Urey type reactions and the Fischer-Tropsch type reactions -- have been extensively studied [Hayatsu and Anders, 1981, and references therein]. The Miller-Urey type reactions, which convert simple molecules such as CH<sub>4</sub>, CO, H<sub>2</sub>O, NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>S into more complex molecules, involve free radical reactions initiated by electric discharges, UV light,  $\gamma$ -radiolysis, and other energy sources. The Fischer-Tropsch type (FTT) reactions, which operate on starting materials such as CO, H<sub>2</sub>, and NH<sub>3</sub>, are spontaneous reactions forming organic compounds in the presence of catalysts such as Fe-Ni metal, magnetite (Fe<sub>3</sub>O<sub>4</sub>), and hydrous silicates. Both types of reactions are possible mechanisms for producing the organic matter in meteorites and both produce nitrogen-bearing organic molecules. How do the reaction products from the two mechanisms compare with the nitrogen-bearing organics found in meteorites?

Hayatsu and Anders [1981] report that several purines, pyrimidines, and aliphatic amines occur in the Orgueil CI and Murchison CM2 chondrites. A large number of amino acids have also been identified in Murchison. Furthermore, pigments resembling porphyrins have been detected in several carbonaceous chondrites. The FTT reactions are successful in producing the purines, pyrimidines, and aliphatic amines while the Miller-Urey type reactions are less successful in doing so. On the other hand, the Miller-Urey type reactions are better than the FTT reactions at producing the amino acids found in carbonaceous chondrites. Both types of reactions apparently produce porphyrinlike pigments but identifications of both the reaction products and the compounds detected in the meteorites are too vague to support any close correspondence.

The nitrogen isotopic compositions of the

reaction products and organic matter in the meteorites can also be compared. Kung and Clayton [1978] found  $\delta^{15}\text{N}$  values of +3 to +5‰ for organic nitrogen in CI and CM2 chondrites. They also found that the Renazzo carbonaceous chondrite had a  $\delta^{15}\text{N}$  value of +17‰. Robert and Epstein [1982] found comparable  $\delta^{15}\text{N}$  values for organic nitrogen in CI and CM2 chondrites and also confirmed the high  $\delta^{15}\text{N}$  value for Renazzo. Robert and Epstein [1982] and Becker and Epstein [1982] also found large variations in  $\delta^{15}\text{N}$  values between solvent extractable and polymeric organic matter in carbonaceous chondrites. These variations, which are of order 10‰, can be compared with the nitrogen isotopic variations in the FTT and Miller-Urey type reactions. Kung et al. [1979] found that the products formed by the FTT and Miller-Urey type reactions had  $\delta^{15}\text{N}$  values (relative to the  $\text{NH}_3$  reactant) of only 0.3‰ and 1.0 to 1.2‰, respectively. Thus although each type of reaction can account for some of the chemical features of the organic nitrogen in meteorites, neither can account for the isotopic fractionations (starting from an isotopically homogeneous nebula). However, neither mechanism is ruled out by the isotopic data since the nitrogen isotopic composition of the nebula may have been spatially and/or temporally heterogeneous. The question of the nitrogen isotopic composition of the nebula, which is beyond the scope of this paper, has been recently reviewed by Geiss and Bochsler [1982].

Although specific mechanisms cannot yet be identified, it is nonetheless possible that the nitrogen in meteorites may have been originally retained as organic nitrogen. Subsequent processes in the meteorite parent bodies (e.g., metamorphism, melting, hydrothermal alteration) may have acted upon this material to redistribute the nitrogen in various chemical forms. These processes may have acted to different degrees in different meteorite types. For example, in the CI and CM2 chondrites, the nitrogen content of the organic matter accounts for nearly all the nitrogen in the meteorites [Kung and Clayton, 1978]. However, some nitrogen may be present as exchangeable  $\text{NH}_4^+$ -ions. The chemical form of nitrogen in the ordinary chondrites is not well known. Some of it may be present in organic matter and some may be in nitrides dissolved in the silicate minerals. The latter may have been produced during metamorphism if pyrolysis of organic matter generated the required nitrogen potentials [Fegley, 1982]. The nitrogen in iron meteorites is present as dissolved nitrogen in the metal and other phases and as exsolved metal nitride inclusions. Pyrolysis of organic matter in the meteorite parent bodies may have generated nitrogen potentials high enough to account for the observed nitrogen content of the metal and other phases. The metal nitrides, which are late-stage precipitates [Nielsen and Buchwald, 1981], formed upon cooling when the kamacite became supersaturated.

The nitrogen in the enstatite chondrites also presents an interesting problem. A substantial proportion of the nitrogen in the meteorites containing sinoite can be accounted

for by the abundance of the sinoite [Keil, 1968; Kung and Clayton, 1978]. However, some enstatite chondrites in which no nitride minerals have yet been identified also have high nitrogen abundances (several hundred ppm) [Moore et al., 1969]. The high nitrogen abundance in these chondrites may be due to the presence of several components: (1) fine-grained nitride minerals which have not yet been identified; (2) nitride inclusions, e.g.,  $\text{Si}_3\text{N}_4$ , in the metal phase; or (3) dissolved nitrides (analogous to the  $\beta'$ - and 15R-sialons) in the silicate phase. These suggestions cannot be rigorously evaluated without further work such as ion microprobe nitrogen analyses, nitrogen analyses of mineral separates, examination of the metal phase by various microscopic techniques, or calculations of nitride stabilities in nonsolar composition material. Some preliminary work -- nitrogen analyses of clasts from Abee [Thiemens and Clayton, 1982] and calculations of nitride stabilities for a limited number of nitrides [Larimer, 1975; Larimer and Bartholomay, 1979] -- has already been done along these lines, but much more work is needed to explain the nitrogen contents and chemical forms in the enstatite chondrites.

#### Nitrogen Accretion by the Terrestrial Planets

A comparison of the observed nitrogen contents of the terrestrial planets with the predicted equilibrium concentration of nitrogen in the condensed matter which accumulated to form these bodies is given in Table 4. The inputs for this comparison are: (1) the formation temperatures and pressures from Lewis [1972a] for the material which formed the terrestrial planets; (2) the calculated nitrogen solubilities from Figure 1; (3) assumed metal contents for Mercury, Venus, Earth, and Mars of 60 wt%, 33%, 33%, and 2%, respectively; (4) nitrogen inventories for Venus, earth, and Mars from Barsukov et al. [1980], Norris and Schaeffer [1982], and McElroy and Prather [1981], respectively.

Nitrogen dissolved in silicates as nitrides or  $\text{NH}_4^+$  ions is not included in the comparison. The contributions from these sources is negligible except for Mercury. Assuming ideal solution of  $\text{Si}_2\text{N}_2\text{O}$  in forsterite and that Mercury contains 40 wt% forsterite, the predicted nitrogen content increases to approximately  $10^{-7}$  g/g.

The comparison in Table 4 illustrates that the predicted nitrogen contents of Venus, earth, and Mars are orders of magnitude lower than the observed nitrogen contents. Since the observed nitrogen contents are only lower limits -- no nitrogen inventories are available for the mantles and cores of Venus and Mars or for the earth's core -- the discrepancy is greater than indicated.

The failure of any equilibrium mechanism considered to retain significant amounts of nitrogen in condensed material and the apparent necessity to retain nitrogen in meteorites as organic matter produced by some disequilibrium process have already been discussed. Lewis et al. [1979] also concluded that equilibrium mechanisms cannot retain significant amounts of

mine if the radial transport of low temperature condensates can provide some or all of the volatile element inventories of the terrestrial planets.

Anders and Owen [1977] investigated the possibility that accretion of volatile-rich meteorites provided the volatile element inventories of the terrestrial planets. They did a comparison of terrestrial and chondritic  $^{36}\text{Ar}$ ,

and models for volatile retention. Their group made explicit predictions about nitrogen inventories on the terrestrial planets.

#### Summary

A thorough study of the equilibrium chemistry of nitrogen and nitrogen-bearing compounds in solar composition matter indicates that