Ammonium Aluminosilicates: The Examination of a Mechanism for the High Temperature Condensation of Ammonia in Circumplanetary Subnebulae

by

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Signature of Author ... Department of Earth and Planetary Sciences May 15, 1981 Certified by. John S. Lewis Thesis Supervisor Accepted by Accepted by Theodore A. Madden Chairman, Department Committee FROM 1981 MITLIBRARIES Ammonium Aluminosilicates: The Examination of a Mechanism for the High Temperature Condensation of Ammonia in Circumplanetary Subnebulae

by

Hampton Watkins

Submitted to the Department of Earth and Planetary Sciences on May 15, 1981 in partial fulfillment of the requirements for the Degree of Master of Science.

ABSTRACT

The relatively high ammonia and water fugacities expected incircumplanetary subnebulae have led to an examination of the possibility of condensation of <u>ammonium aluminosilicates</u> from a gas of solar composition. Due to the paucity of reliable data on ammonium aluminosilicates, estimation of the thermochemical properties of several of these compounds was necessary. With the speculative nature of the data taken into account, it is improbable that a substantial quantity of ammonia was incorporated into the silicate fraction of the condensate, and subsequently included in bodies formed from this material. The effects of the incorporation of ammonia-rich silicates on the thermal histories of satellites is discussed.

Thesis supervisor: John S. Lewis Title: Professor of Planetary Sciences

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Finally, I must give very special thanks to Prof. John S. Lewis. Without his help and continuing encouragement I could never have successfully completed this thesis.

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CHAPTER ONE

Introduction

The study of high temperature condensation of ammonia as ammonium aluminosilicates has been prompted by two recent findings. The first of these was the preliminary work on the chemistry of the Jovian subnebula by Prinn and Fegley (1980), in which they demonstrated relatively high ammonia fugacities. The additional notable points made by Prinn and Fegley were: (1) the satellite Europa formed at a radial distance (P,T regime) which would have precluded the formation of ammonia hydrate, and (2) that none of the other ammonia-bearing compounds considered in their study would have been stable at Europa's radial distance. Thus, we conclude from their work that very little, if any, ammonia would have been incorporated into Europa from local low temperature equilibrium condensates.

The second finding that led to this work was the remarkably smooth and featureless surface of Europa reported by the Voyager Imaging Experiments (Smith, et al., 1979a; Smith, et al., 1979b). The lack of topographic relief implies a low strength subsurface/surface material of this body. One mechanism for reducing the strength of a rocky/icy material is to keep it in a partially molten state. The most attractive chemical mechanism for the maintanence of a partially molten state in an icy mixture is the incorporation of a solute capable of substantially depressing the freezing point. The most attractive solute in the case of an icy planetary body is ammonia. As an example of the effectiveness of this mechanism it should be noted that the ammonia hydrate - water eutectic at one bar is -100 C! The

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importance of the incorporation of ammonia into the interiors of icy satellites has been noted previously (Consolmagno, 1975), but it appears to have otherwise been largely ignored.

The lack of a suitable, abundant, low temperature condensate thus prompted us to examine the possibility of the retention of substantial quantities of ammonia in a high temperature silicate fraction. In this work we examine the possibility of incorporation of ammonia into Europa as ammonium aluminosilicates, particularly, ammonium feldspar and ammonium muscovite. CHAPTER TWO

Methods and Procedures

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I. DATA ESTIMATION

In pursuit of our goal of determining the condensation behavior of high temperature ammonium-bearing species we sought data on the stability of several ammonium aluminosilicate phases. We found very few reliable data published on this class of compounds. What was found were a pair of studies of the stability of ammonium muscovite $(NH_4Al_3Si_3O_{10}(OH)_2)$ and ammonium feldspar/buddingtonite $(NH_4AlSi_3O_8/NH_4AlSi_3O_8\cdot1/2H_2O)$ (Hallam and Eugster, 1976; Schultz, 1973). Additionally, some work was found on ammonium phlogopite $(NH_4Mg_3AlSi_3O_{10}(OH)2)$ (Eugster and Munoz, 1966). The data were all of low quality with inconsistencies and/or discrepancies among the works of the several authors. Therefore, an attempt was made to explain the inconsistencies and to generate relatively consistent and reasonable sets of thermodynamic properties for ammonium feldspar and ammonium muscovite.

False Starts and Dead Ends

Initially, an attempt was made at estimating the heats of formation of the ammonium feldspar and ammonium micas by the Born-Haber cycle. This technique was abandoned due to the difficulties and uncertainties in the calculation of the lattice energies of the compounds. Though this method has been demonstrated to be of some value for simple solids (Sadhukhan and Bell, 1979), after our experiences we cannot recommend its use for more complex substances.

The next attempt in earnest to estimate the thermodynamic data employed the method of Chen (1975). This largely empirical method uses the ranked cumulative sums of free energies of progressively more complex oxides, including quartz, to generate an exponential series in which the last member determines the free energy which is sought. After expending considerable energy in an attempt to implement this method, it was found that the published results were irreproducible. The method was found to depend too heavily on the subjective judgement of the individual user in the selection of the input data. In other words, if the input data set was biased to yield the desired results, it would; otherwise, it gave garbage. This method was worth far less than the effort that went into assessing it.

The Proper Path

The first success was found in an old method (Stull and Prophet, 1967). We assumed that the heat capacity of the ammonium aluminosilicates were given by the following:

 C_p (M aluminosilicate) + $C_p(NH_4X) - C_p(MX) = C_p(NH_4$ aluminosilicate) where M is an alkali metal ion and X is some cation. This is simply the assumption that the change in the heat capacity for the exchange reaction at any temperature is zero. The results

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for the estimated heat capacities are presented in Tables 1 and 2 and Figure I and II.

Next, we assumed that the free energy of exchange for the reaction:

 $K^{+}(aq) + NH_{4}$ aluminosilicate = $NH_{4}^{+}(aq) + K$ aluminosilicate

was zero for equimolar concentrations of K^+ and NH_4^+ aqueous ions. This assumption is not without basis, in that the exchange constant is known to be near unity (Jenny; 1927; Jenny and Reitemeier, 1935; Bada and Miller, 1968), and that the potassium and ammonium ions have similar radii, 1.33 and 1.43 Å, respectively (Weast, 1974).

Entropies were estimated by several methods, the most satisfactory of which was the method of Saxena (1976) in which the entropy of a silicate is correlated with its molar volume within its structural class. The correlation among the feldspar and feldspathoid minerals was shown to be very good, far better than the simple sum of the oxides. For the hydrous silicates the correlation was far weaker, but nevertheless we feel that it is adequate for our proposed estimate of the ammonium muscovite entropy.

These data were combined into our initial estimates of the thermodynamic properties of ammonium feldspar and ammonium muscovite. There is one point worth mentioning here. The ammonium feldspar is reported to possess 1/2 zeolitic water molecule per molecule of ammonia at temperatures less than 300 to 370 C

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(Erd, et al., 1964; Barker, 1964). This water is essential to the formation and stability of buddingtonite, the naturally occurring terrestrial mineral, as well as to the synthesis of the synthetic ammonium feldspar under mild geothermal conditions. Above the dehydration temperature, the molecule, ammonium feldspar, still will yield 1/2 water molecule upon decomposition. Thus, at all temperatures, the ammonium feldspar stability is dependent on both the water and the ammonia fugacities. Only the functional dependence changes with temperature. The calculations conducted in this work were for the ammonium feldspar, not for buddingtonite. Therefore, the numbers are not expected to agree with any low temperature calculations employing NH_4Al- Si₃O₈·1/2H₂O. Thus, we generated our first set of thermodynamic functions over a temperature range from 298.15 to 1400 K for ammonium feldspar and ammonium muscovite. The data generated compared reasonably well with the data for the alkali aluminosilicates.

These data were subsequently substantially improved by the addition of several constraints. Buddingtonite, NH_4AlSi_3 - $O_8 \cdot 1/2H_2O$, is known to be unstable at typical atmospheric fugacities of water and ammonia (Eugster and Munoz, 1966). A simple calculation with assumed, but reasonable, f_{NH_3} and f_{H_2O} will give a log K_f(298.15,1) of roughly, 620±3. This is in accord with our estimate from the alkali ion exchange reaction which yielded log K_f(298.15,1) of 619.6. As we will see shortly, these values are very nearly the value determined by Schultz (1973).

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The Final Estimation

The data collected by Schultz (1973) were considered to be of the highest quality of those available. The difficulty with his experimental data are that they were derived in singly buffered environments. To generate high quality data, double buffering, buffering of both H_2O and NH_3 , is necessary (Barker, 1980). Though this is the approach that Hallam and Eugster (1976) took in their work, they chose their buffers rather poorly. In their study they employed the graphite/ methane buffer, which is very slow to equilibrate (Chou, 1980) and the Cr/CrN buffer, which is literally nonexistent: at the temperatures under consideration there is an intermediate phase of the Cr - N phase diagram, Cr₂N, chromium subnitride. Thus, either their nitrogen buffer was Cr/Cr₂N or Cr₂N/CrN, but not Cr/CrN (Fegley, 1981). This may account for the large differences in the ammonia fugacities determined by Schultz (1973) and by Hallam and Eugster (1976).

Nevertheless, our constrained data agree very well with the log K_f derived by Schultz (1973). His value is 622.514, which converts to a free energy of formation from the elements of -3553.249 kJ/mol. This value combined with an estimated entropy of 242.664 J/mol K at 298.15 K and one atm, gives a heat of formation of -3857.3 kJ/mol for ammonium feldspar. The free energy, entropy and heat of formation for ammonium muscovite are -5414.9 kJ/mol, 308.057 J/mol K and -5877.77 kJ/mol, respectively. The corresponding log K_{f} (298.15,1) is 948.673.

The free energy functions, Gibbs free energies of formation from the elements and the log K_f 's are presented for ammonium feldspar and ammonium muscovite in Tables 3 and 4, respectively. These are the data that have been used in all subsequent calculations.

II. DATA APPLICATIONS

Jovian Subnebula

The adiabatic profiles employed by Prinn and Fegley (1980) for their nominal and high density cases were used in this work. The abundances of the elements H, O, C, and N were identical to theirs. Calculation of the gas phase equilibrium abundances of over 50 species was performed with a greatly modified version of the NASA chemical equilibrium code package (Gordon and McBride, 1971; Reese, 1973). The species considered in the calculations of the gas phase equilibria are listed in Table 5. The results of the calculations are plotted in Figures III and IV. The fugacities of ammonia and water in these model subnebulae were taken as their fully equilibrated abundances in all of the calculations. For the purposes of this work, we considered the silicate minerals present in the solar nebula from roughly 1200 to 400 K. The mineral data was taken from Robie, Hemingway and Fisher (1978) and all minerals considered in this work are listed in Table 6.

CHAPTER THREE

Results and Discussion

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Initially, we attempted to estimate the importance of the retention of ammonia by aluminosilicates through the use of simple mass balance arguments. This was a logical first step in that the putative importance of this mechanism could be assessed without knowledge of the stability of the ammonium aluminosilicates. In other words, unless we could find some phase capable of retaining a substantial quantity of ammonia, we ought not study the problem further. We especially ought not spend our effort on tedious thermochemical calculations if after they were completed we found that due to simple mass balance arguments our work was in vain. We thus defined three plausible cases for study: (1) ammonium feldspar is substantially more stable than alkali feldspar, (2) ammonium feldspar and alkali feldspar exhibit roughly the same activities, and (3) ammonium feldspar is much less stable than alkali feldspar.

The first case would lead to the condensation of ammonium feldspar prior to the alkali feldspar. The source of aluminum, the limiting element in our system, is plagioclase feldspar. The reaction by which we assume the ammonium feldspar to form is:

 $2NH_3 + H_2O + CaAl_2Si_2O_8 + 11MgSiO_3 = CaMg(SiO_3)_2 + 5Mg_2SiO_4 + 2NH_4AlSi_3O_8$.

If we assume that the ammonium feldspar is very much more stable than the alkali feldspar, then all of the aluminum would be consumed by the ammonium feldspar before the alkali metals would commence condensation. This is schematically illustrated in

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Figure V. The extent of the above reaction in this case would be limited only by the total aluminum abundance.

The second case is by far the most complicated and interesting of the three. Here, we assumed that the feldspar condenses as a solid solution. The amount of the various cations in the feldspar lattice is dependent on the activities of these species. The ammonium feldspar end member can range from nearly 100% to 0%. As an interesting case we have considered the possibility that most of the alkalis condense before an appreciable amount of the ammonia begins to condense. This case is also illustrated in Figure V. Here, all of the alkalis are allowed to condense before ammonia. This process consumes roughly 75% of the total Al in the system. Subsequent to the alkali reaction the remainder of the aluminum is consumed by the formation of ammonium feldspar. Thus, the amount of ammonia condensed would be roughly 25% of the Al molar abundance.

Two interesting points are worth noting here. The first is that any incorporation of ammonium in excess of the 25% limit mentioned above will alter the chemistry of the alkalis. In the mass balance sense in which we are currently working, the exclusion of the alkalis from the feldspar would lead to their condensation as either sulfides or possibly as feldspathoids. The second point of note is that once the ammonium feldspar is formed it will decompose very readily in a low $f_{\rm NH_3}$ environment. The decomposition products are vapor, Al_2SiO_5 and SiO_2 . To our knowledge, none of the Al_2SiO_5 poly-

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morphs have ever been found as meteoritic minerals. This is a weak shread of evidence against the formation of NH₄AlSi₃0₈ in the primitive solar nebula or some part thereof.

The third case considered is the trivial case in which ammonia will not condense in any high temperature phase. We mention it only for completeness, in that it is the classical solar nebula case which has been studied many times. In this case the only ammonia bearing condensate is the low temperature phase, ammonia hydrate.

From these mass balance arguments we determined that a reasonable quantity of ammonia could be retained in an aluminosilicate phase provided the activity of that phase approached unity at some point in our subnebula. In our first case approximately 7.4 g NH₃/kg rock (including Fe-Ni) could be retained. In the second case we mentioned that the quantity of NH₃ condensable ranged from nearly this value to some very small value. The interesting case mentioned in this respect would lead to the retention of about 1.8 g of ammonia/kg rock. In both of these cases the rock employed is close to that used by Lupo and Lewis (1980).

Clearly, further investigation of the stability fields of ammonium aluminosilicates was warranted by our mass balance arguments. Thus, as we described earlier (see Methods and Procedures), we estimated the thermodynamic properties of ammonium feldspar and ammonium muscovite. Before we could apply these estimates to the problem of condensation in circumplanetary subnebulae we calculated the composition of the gas phases much as

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was done by Prinn and Fegley (1980). As cited in the Data Applications section of this work, these results are illustrated in Figures III and IV. Using the gas phase species abundances and our thermodynamic property estimates, we calculated the activity of ammonium feldspar in the subnebular systems. The log of the activity of this species is illustrated in Figure VI. This calculation assumes that the solids enstatite and anorthite are initially present with the gas At low temperatures (below about 600K) even more stable phase. mineral assemblages are present than were used in the calculation of Figure VI. Thus, below 600K the activity shown is an overestimate of the real ammonium feldspar activity. Therefore, we conclude that only prohibitively high adiabats would permit ammonium feldspar to condense in an equilibrated solar composition system.

The condensation of micas from a gas of solar composition seems highly improbable, and the observed meteoritic phyllosilicates are probably the result of alteration processes on the meteoritic parent bodies (McSween and Richardson, 1977; Bunch and Chang, 1980). Thus, though we have estimated the thermodynamic properties of ammonium muscovite we have not attempted to determine its chemical behavior in circumplanetary subnebulae. It is interesting to note that the ammonium muscovite is stable under extremely low $f_{\rm NH_3}$. This species may be found as a minor component of the phyllosilicate fraction of carbonaceous chondrites. An estimate of the activity of ammonia in these objects' parent bodies could then be obtained. This

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would then enable us to add one more constraint to our models of meteoritic parent bodies.

The results of our calculations are somewhat disappointing. We had hoped to find that the ammonium aluminosilicates, particularly the feldspar, would provide a mechanism for the incorporation of ammonia into Europa. Instead we have shown that even under extreme conditions the ammonium feldspar is not stable in a system of solar composition. There may be some other silicate phase capable of retaining ammonia, but no data exists on the most probable phases, the ammonium bearing scapolites and the sodalite analogue.

Another plausible, even probable, mechanism for the incorporation of a substantial quantity of ammonia into Europa is radial mixing of material during the later stages of the accretionary process. Recently, work on radial mixing (Cox <u>et al</u>., 1978; Cox and Lewis, 1980) and its effect on planetary bulk composition (Barshay, 1981; Barshay and Lewis, 1980) has been conducted. These works demonstrate that a small, but important, quantity of material from distant orbits can be incorporated into an accreting body. If we apply these conclusions to the Jovian system, then we would expect Europa to contain a small fraction of ammonia hydrate condensed in a more distant portion of the primitive Jovian subnebula. The ammonia included in this manner may be able to account for the entire European inventory of this substance.

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CHAPTER FOUR

Conclusions

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The surface of Europa has quite clearly been completely There seem to be no satisfactory mechanisms for melted. raising the temperature of the near surface regions of this body to the melting point of pure water ice. If a small amount of ammonia is included in the body a much lower temperature would be required for melting and differentiation. In this work we have considered the incorporation of a small amount of ammonia in the form of a putative condensate, ammonium feld-After a detailed examination of the activity of this spar. species, it was concluded that it would not be found as an equilibrium condensate in a primitive Jovian subnebula. It is nevertheless important to consider the effect of ammonia on the thermal evolution on this and other icy satellites.

Finally, it must be remembered that this work is based on estimated thermodynamic data, and not on high quality measurements. It is not believed that improvement of the data would alter the conslusions presented herein. If the ammonium feldspar is somewhat more stable than the data employed here indicates, then this problem should be reexamined. Also, if the behavior of the quarternary feldspar system is examined, then the data gained might be applied to a reexamination of ammonia retention of high pressure, low temperature solar composition systems.

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CHAPTER FIVE

Suggestions for Future Investigations

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There are two particular projects which would be well worth undertaking. First, the establishment of the phase equilibria and stability fields in the system $(NH_4)_2^0$ - $Al_2^0_3 - SiO_2$ should be examined in as much detail as the comparable systems containing K_2^0 and Na_2^0 . This would be invaluable in determining with certainty the condesnation behavior of NH_3 in a solar composition gas. As a part of this work, it would also be useful to explore the solution behavior of the quarternary feldspar system: anorthite, albite, orthoclase and buddingtonite.

Second, an examination of the systems $H_2O - NH_3$ and $H_2O - NH_3 - CH_4$ at elevated pressures would provide useful information. The phase relationships and equations of state of these systems are not well known, but are important in the modelling of the thermal histories of icy bodies. With this information we could better understand the physical processes of importance within these bodies (convection vs. conduction, evolution through melting vs. evolution without melting).

These projects offer substantial physical and intellectual challenges to any individuals bold enough to undertake them.

Table l

The Estimated Heat Capacity of Ammonium Feldspar

The heat capacity of ammonium feldspar, $NH_4AlSi_3O_8$, was estimated as described in the text. The estimates were smoothed and fitted to a modified Maier-Kelley polynomial (Robie <u>et al.</u>, 1978).

Table 1 – Estimated Heat Capacity of Ammonium Feldspar	
Temperature Heat Capacity	
(Kelvin) (J/mol K)	
298.15 233.61	
300.00 234.47	
350.00 255.21 400.00 272.31	
450.00 287.03	
500.00 300.08	
550.00 311.87	
600.00 322.68	
650.00 332.70 700.00 342.05	
750-00 350-83	Comment of and
800.00 359.09	
350.00 366.89	
900.00 374.27	
950.00 381.26 1000.00 387.89	
1000.00 387.89_ 1050.00 394.17	
1100.00 400.13	
1150.00 405.76	
1200.00 411.09	
1250.00 416.13	
1300.00 420.88 1350.00 425.35	
1400.00 429.54	

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Table 2

The Estimated Heat Capacity of Ammonium Muscovite

The heat capacity of ammonium muscovite, $NH_4Al_3Si_3Q_{10}(OH)_2$, was estimated as described in the text. The estimates were smoothed and fitted to a modified Maier-Kelley polynomial (Robie <u>et al.</u>, 1978).

Table 2 –	Estimated	Heat	Capacity of	of	Ammonium	Muscovite
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Temperature	Heat Capacity
(Kelvin)	(J/mol K)
298.15 300.00 350.00 400.30 450.00 500.00 550.00 630.30 700.30 750.00 800.00 850.00 900.00 950.00 1000.00	355.39 356.95 393.07 421.15 444.43 464.56 482.44 498.60 513.35 526.91 539.39 550.88 561.44 571.10 579.91 587.86
1050.00	594.99
1100.00	601.29

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Table 3

The Thermodynamic Functions of Ammonium Feldspar

The estimated heat capacity function was integrated and combined with the entropy and heat of formation given in the text to obtain the thermodynamic functions of ammonium feldspar.

	timated inermod	ynamic Functions of	NH4 retuspar
Temperature	Free Energy	Gibbs Free Energy	Log Kf
(Kelvin)	Function	of Formation	
	(kJ/mol K)	(kJ/mol)	
298.15	242.564	- 3553.249	622.514
400.00	251.838	-3448.684	450.352
500.00	270.642	-3345.470	349.499
600.00	292.836	-3242.079	282.248
700.00	316.007	-3138.764	234.217
800.00	339.115	-3035.015	198.166
900.00	361.688	-2932.553	170.201
1000.00	383.510	-2828.902	147.767
1100.00	404.490	-2725.080	129.403
1200.00	424.600	-2621.285	114.101
1300.00	443.844	-2517.708	101.163
1400.00	462.240	-2414.221	90.076
1500.00	479.816	-2310.671	80.465

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Table 3 - Estimated Thermodynamic Functions of NH4 Feldspar

Table 4

The Thermodynamic Functions of Ammonium Muscovite

The estimated heat capacity function was integrated and combined with the entropy and heat of formation given in the text to obtain the thermodynamic functions of ammonium muscovite. Table 4 - Estimated Thermodynamic Functions of NH4 Muscovite

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Temperature (Kelvin)	Free Energy Function (kJ/mol K)	Gibbs Free Energy of Formation (kJ/mol)	Log Kf
298.15	308.057	-5414.929	948.673
400.00	320.993	- 5255. 487	686.296
500.00	348.546	-5098.093	532.594
600.00	381.071	-4940.292	430.091
700.00	414.794	-4782.291	356.859
800.00	448.076	-4623.180	301.863
900.00	480.166	-4665.365	259.163
1000.00	510.715	-4303.848	224.810
1100.00	539.568	-4140.547	196.618

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Table 5

The Species Considered in the Gas Phase Calculations

The calculation of the thermodynamic equilibrium assemblage was performed for all of the species listed. The more abundant species are plotted in Figures III and IV.

Table 5

Species being considered in this system

j	3/78	C(s)	j	3/77	N	j	9/66	c ₂ 0
j	12/67	СН	j	6/77	NH	j	6/68	c_02
j	3/61	сн ₂ о	j	6/77	^{NH} 3	j	12/69	c5
j	3/61	CH ₄	j	9/64	NO2	1	12/69	HCN
j	6/66	CNN	j	3/77	^N 2	j	12/70	HCNO
j	9/65	CO	j	12/64	N20	j	6/63	^{HNO} 2
j	12/69	с ₂	j	12/64	^N 2 ^O 5	j	3/64	но ₂
j	3/61	с ₂ н ₂	1	5/66	Ne	1	11/65	$H_2^{O(s)}$
j	5/72	^с 2 ^н 6	j	6/77	OH	j	3/61	н ₂ 0
j	3/61	C ₂ N ₂	j	6/61	03	1	5/66	He
j	12/69	с _з	j	3/78	С	j	12/70	NCO
j	12/69	C ₄	j	12/72	CH ₂	j	6/77	NH2
j	3/77	H	j	6/69	CH3	j	6/63	NO
j	12/70	HCO	j	6/69	CN	j	12/64	NO3
j	3/63	HNO	j	12/70	CN ₂	j	12/65	$^{N}2^{H}4$
j	3/63	HNO ₃	j	9/65	co ₂	j	9/64	N ₂ 0 ₄
j	3/77	^H 2	j	3/67	с ₂ н	j	12/70	^N 3
1	11/65	H ₂ 0(1)	j	9/65	C ₂ H ₄	j	3/77	0
1	2/69	H ₂ O ₂	j	3/67	C ₂ N	j	3/77	°2

j: JANAF data l: NASA/Lewis data

Table 6

The Condensed Species Considered in the Determination of Ammonium Aluminosilicate Activity

These species were considered in the calculation of the data presented in Figure VI.

Table 6

Minerals considered in this work

NH4 ^{AlSi30} 8	$NH_4Al_3Si_3O_{10}(OH)_2$
KAlSi308	KA13 ^{Si30} 10 ^(OH) 2
NaAlSi308	CaAl ₂ Si ₂ O ₈
CaMg(SiO ₃) ₂	Ca2 ^{Mg5} Si8022(OH)2
Al ₂ SiO ₅	sio ₂
MgSiO ₃	Mg2SiO4
NaAlSiO4	KAlsio ₄
NaAlSi206	KAlSi206

Figure I

Estimated Heat Capacity of Ammonium Feldspar

The heat capacity of NH₄AlSi₃O₈ was estimated as described in the text (see Methods and Procedures). Heat Capacity units are Joules/ mole K and temperature is given in Kelvins.

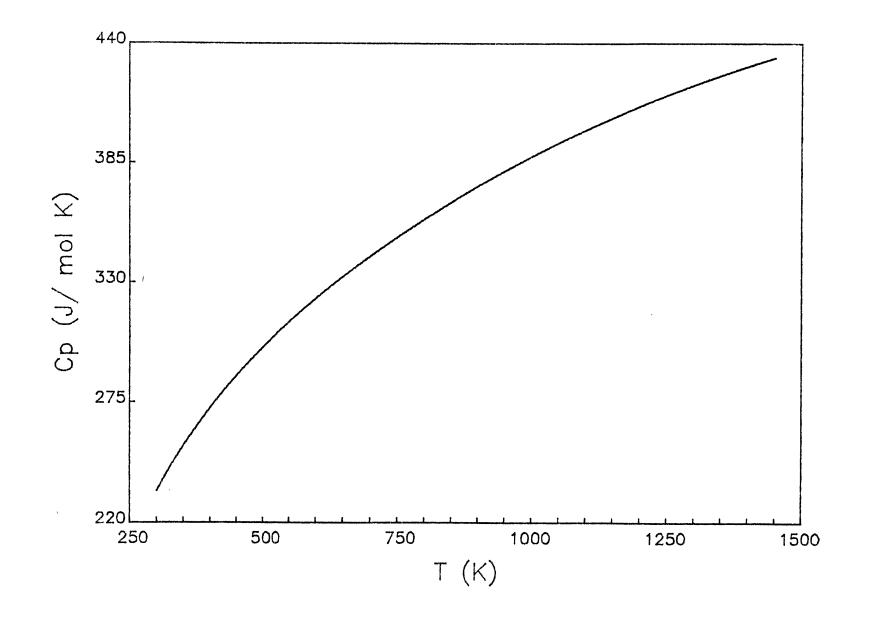
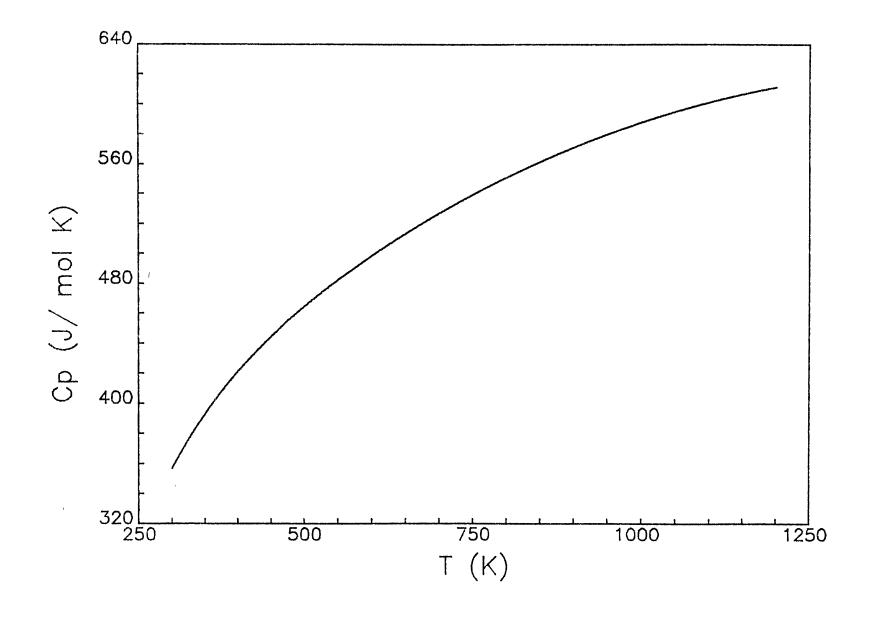


Figure II

Estimated Heat Capacity of Ammonium Muscovite

The heat capacity of NH₄Al₃Si₃O₁₀(OH)₂ was estimated as described in the text (see Methods and Procedures). Heat capacity units are Joules/mole K and temperature is given in Kelvins.



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Figure III

Gas Phase Equilibria - Nominal Adiabat

Gas phase equilibria for the elements carbon, hydrogen, nitrogen, oxygen, helium and neon along the nominal adiabat of Prinn and Fegley (1980). The elemental abundances are identical to those employed by Prinn and Fegley. The equilibrium was calculated considering all substances in Table 5 and only the more abundant species are plotted. The P_{o} pressure is 1 atm. and the T_{o} is 400 K.

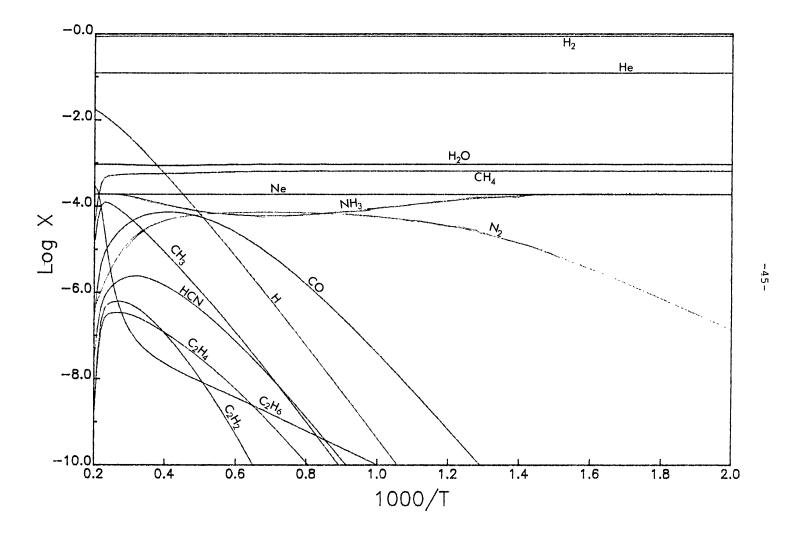
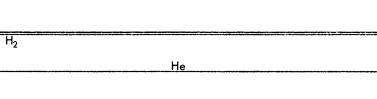


Figure IV

Gas Phase Equilibria - High Adiabat

Gas phase equilibria along the high Jovian adiabat of Prinn and Fegley (1980). Calculated in the same manner as Figure I with P_{o} equal to 200 atm. and T_{o} equal to 400 K. -0.0



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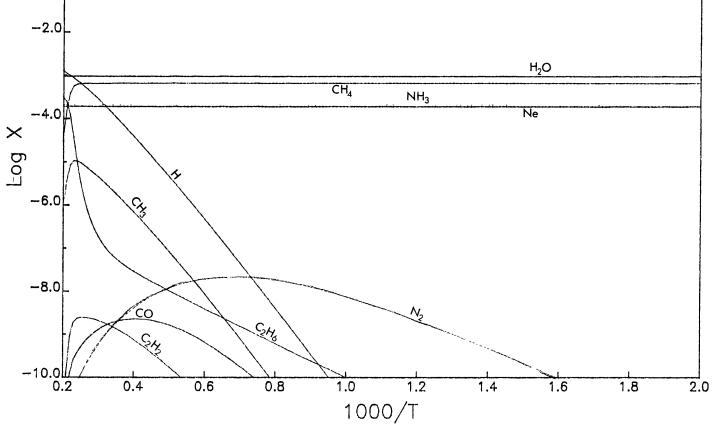


Figure V

Feldspar Mass Balance

- (A) The figure illustrates the putative condensation of ammonium feldspar prior to alkali feldspar.
 All of the aluminum is consumed by the formation of the ammonium compound before the alkalis (sodium and potassium) condense (solid line).
- (B) The figure illustrates the condensation of alkali feldspar with the additional reaction of anorthite to form ammonium feldspar. The alkali feldspar consumes roughly 75% of the total aluminum and the feldspar formation process is limited only by the total aluminum available (broken line).
- (C) The figure illustrates the solar composition case (dotted line).

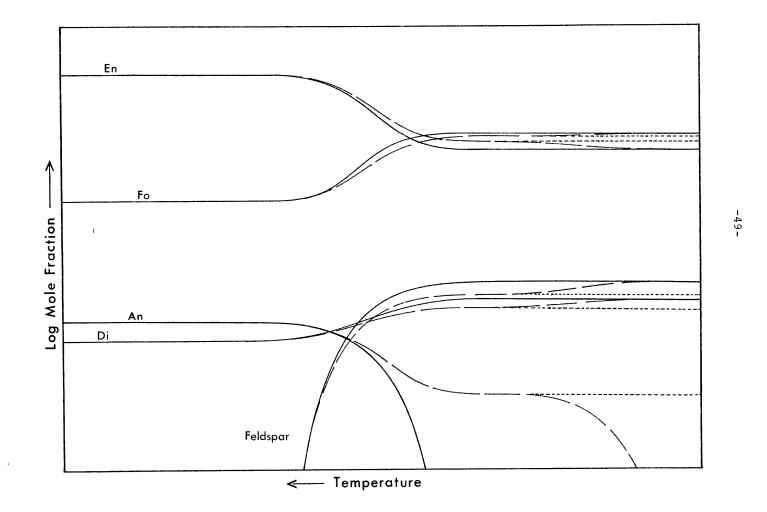
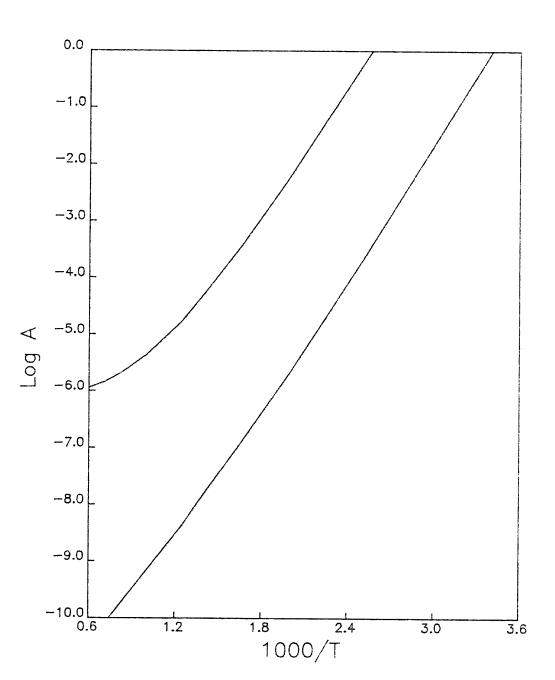


Figure VI

The Activity of Ammonium Feldspar

The ammonium feldspar activities along the nominal (right) and high (left) Jovian adiabats are illustrated. At temperatures less than approximately 600 K these activities are overestimates. See the text (Chapter III, Results and Discussion) for further discussion.



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REFERENCES

- Bada, J.L. and Miller, S.L. (1968). Ammonium ion concentration in the primitive ocean. Science, <u>159</u>, 423-425.
- Barker, D.S. (1964). Ammonium in alkali feldspars. Am. Mineral., <u>49</u>, 851-858.
- Barker, D.S. (1980). Personal communications.
- Barshay, S.S. and Lewis, J.S. (1980). Combined condensationaccretion of the terrestrial planets. Submitted to Icarus, September, 1980.
- Barshay, S.S. (1981). Combined condensation-accretion model of the terrestrial planets. Ph.D. dissertation, Massachusetts Institute of Technology.
- Bunch, T.E. and Chang, S. (1980). Carbonaceous chondrites II: Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. Geochim. Cosmochim. Acta, <u>44</u>, 1543-1577.
- Chen, C.-H. (1975). A method of estimation of standard free energies of formation of silicate minerals at 298.15K. Am. Jour. Sci., 275, 801-817.
- Chou, I.-M. (1980). Calibration of the graphite-methane buffer using the hydrogen fugacity sensor. Abstract GSA 1980 Annual Meeting 12, 402.
- Consalmagno, G.J. (1975). Thermal histories of icy satellites. S.M. Thesis, Massachusetts Institute of Technology. Cox, L.P. and Lewis, J.S. (1980). Numerical simulation of the

final stages of terrestrial planet formation. Icarus, in press.

- Cox, L.P., Lewis, J.S. and Lecar, M. (1978). A model for close encounters in the planetary problem. Icarus, <u>34</u>, 415-427.
- Erd, R.C., White, D.E., Fahey, J.J. and Lee, D.E. (1964) Buddingtonite, an ammonium feldspar with zeolitic water. Am. Mineral., 49, 831-850.
- Eugster, H.P. and Munoz, J. (1966). Ammonium micas: Possible sources of atmospheric ammonia and nitrogen. Science, <u>151</u>, 683-686.

Fegley, M.B. (1981). Private communications.

- Gordon, S. and McBride, B.J. (1971). Computer program for calculation of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman-Jouguet detonations. NASA SP-273.
- Hallam, M. and Eugster, H.P. (1976). Ammonium silicate stability relations. Contrib. Mineral. Petrol., <u>57</u>, 227-244.
- Jenny, H. (1927). Kationen- und Anionenumtausch an Permutitgrenzflaschen. Kolloid. Beihefte, <u>23</u>, 428-472.
- Jenny, H. and Reitemeier, R.F. (1935). Ionic exchange in relation to the stability of colloidal systems. J. Phys. Chem., 39, 593-604.
- Lupo, M.J. and Lewis, J.S. (1980). Mass-radius relationships in icy satellites. Icarus, <u>40</u>, 157-170.
- McSween, H.Y. and Richardson, S.M. (1977). The composition of carbonaceous chondrite matrix. Geochim. Cosmochim. Acta, 41, 1145-1161.

- 53 -

Prinn, R.G. and Fegley, B. (1980). Kinetic inhibition of CO and N₂ reduction in circumplanetary nebulae: Implications for satellite composition. Submitted to Astrophys. J.
Reese, R.L. (1973). Computed solid-vapor equilibria in multicomponent systems. M.S. thesis, University of Arizona.
Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. USGS Bulletin 1452.

Sadhukhan, P. and Bell, A.T. (1979). Theoretical estimation of $H_{f,t}$, $S_{f,t}$, and $G_{f,t}$, for $Ca(O_2)_2$. J. Solid State Chem., <u>29</u>, 97-100.

Saxena, S.K. (1976). Entropy estimates for some silicates at 298K from molar volumes. Science, <u>193</u>, 1241-1242.

Schultz, R. (1973). Bildung und Stabilitat der Ammoniumaluminumsilikate NH₄-Muskovit und NH₄-Feldspar. D. Naturwissenschaften dissertation, Universitat Karlsruhe.

Smith, B.A., Soderblom, L.A., Beebe, R., Boyce, J., Briggs, G., Carr, M., Collins, S.A., Cook, A.F., Danielson, G.E., Davies, M.E., Hunt, G.E., Ingersoll, A., Johnson, T.V., Masursky, H., McCauley, J., Morrison, D., Owen, T., Sagan, C., Shoemaker, E.M., Strom, R.M., Suomi, V.E., Veverka, J. (1979a). The Galilean satellites and Jupiter: Voyager 2 imaging science results. Science, <u>206</u>, 927-950.

Smith, B.A., Soderblom, L.A., Johnson, T.V., Ingersoll, A.P., Collins, S.A., Shoemaker, E.M., Hunt, G.E., Masursky, H., Carr,

- 54 -

M.H., Davies, M.E., Cook, A.F., Boyce, J., Danielson, G.E., Owen, T., Sagan, C., Beebe, R., Veverka, J., Strom, R.G., McCauley, J.F., Morrison, D., Briggs, G.A., Suomi, V.E. (1979b). The Jupiter system through the eyes of Voyager 1. Science, <u>204</u>, 951-972.

- Stull, D.R. and Prophet, H. (1967). in The Characterization of High Temperature Vapors. ed., J.L. Margrave. Wiley & Sons, New York. pp. 359-424.
- Weast, R.C. (1974). Handbook of Chemistry and Physics. Chemical Rubber Company, Cleveland. p. F198.