Early Chemical History of the Solar System

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The extreme antiquity and lack of evidence for significant chemical processing of the chondritic meteorites since they were formed suggest the possibility that their chemistry and mineralogy may have been established during the condensation of the solar system. By using equilibrium thermodynamics, the sequence of condensation of mineral phases from a cooling nebula of solar composition has been calculated. Applying the predictions of these theoretical models suggests that (1) the chemistry and mineralogy of Ca-Al-rich inclusions in C2 and C3 chondrites were established during condensation at temperatures >1300øK; (2) fractionation of such inclusions is necessary to account for the refractory element depletions of ordinary and carbonaceous chondrites; (3) the metal-silicate fractionation in ordinary chondrites took place in the nebula at $T < 1000$øK and $P_{\text{tot}} \sim 10^{-3}$ atm; (4) the volatile element depletion of C2 and C3 chondrites relative to C1 chondrites took place during chondrule formation; (5) the most volatile elements are depleted in ordinary chondrites because they accreted before these elements were totally condensed; and (6) many chemical features of planetary rare gases and organic material in carbonaceous chondrites could have been established during condensation. Chemical fractionation during condensation may also be responsible for the heterogeneous accumulation of the earth, the refractory element enrichment of the moon, and the varying Fe/Si ratios of the terrestrial planets.

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### A. INTRODUCTION

1. History

a. Astronomical studies of molecular equilibria and condensation. Thermodynamic calculations have long been employed by astronomers as an aid in the identification of spectral lines in stellar atmospheres. Molecular equilibria calculated for a number of different temperatures, pressures, and abundance ratios can be found in Russell [1934], Wildt [1934], Bouguet [1957], and de Jager and Neven [1957]. There also have been many attempts to use this type of calculation to predict the presence of condensate grains in stellar atmospheres and to identify the components of circumstellar dust [e.g., Wildt, 1933; Kamijo, 1963; Gilman, 1969; Fiz, 1970, 1971]. Special attention has been paid to the problem of the condensation of circumstellar graphite
b. Solar nebula thermodynamic calculations. Gaustad [1963] has examined the problem of the evaporation of interstellar dust during the collapse of a protostar of solar composition. The general problem of the condensation of phases from a solar nebula has been investigated by Lord [1965] at the highest temperatures, by Griffiths et al. [1972] at intermediate temperature, and by Lewis [1972b] at the lowest temperatures.

The specific problem of calculating the sequence of condensation of elements and compounds from a cooling nebula of solar composition has been the subject of intense research in recent years. These calculations, and their applications to meteorites, may be found in the work of Wood [1963], Eek et al. [1966], Larimer [1967, 1973], Blander and Katz [1967], Anders [1968, 1971a, 1972a, b], Larimer and Anders [1967, 1970], Swess [1969], Blander and Abdel-Gawad [1969], Blander [1971], Keays et al. [1971], Law et al. [1972, 1973], Grossman [1972a, 1973b], Grossman and Clark [1973], Grossman and Olsen [1974], and others. Because of the rapid improvement of thermochemical data and solar system abundance estimates and the widespread availability of computers, the accuracy, completeness, and sophistication of these calculations have improved with time.

The compositions and origins of the terrestrial planets have also been discussed in relation to chemical equilibrium between dust and vapor in the solar nebula. Early work on this subject may be found in Eucken [1944], Latimer [1950], and Urey [1952a, 1954]. More recent work on the subject includes that of Ringwood [1966], Larimer and Anders [1967], Shimazu [1967], Hoyle and Wickramasinghe [1968], Clark et al. [1972], Grossman [1972a, 1973b], Grossman and Clark [1973], Grossman and Olsen [1974], and others.

The purpose of the present paper is to review the recent literature on chemical fractionations during the condensation of the solar system and on their consequences to the establishment of chemical differences between the different classes of chondrites and between the planets.

2. Physical Setting

To perform the condensation calculations discussed in this paper, an understanding is required of the physical conditions that existed in the primitive solar nebula. Our only independent estimates of pressures and temperatures in the solar nebula come from theoretical models of the hydrodynamics of collapsing interstellar gas clouds and the formation of protostars. Modern treatments of this problem can be found in Higley [1960], Hoyle and Wickramasinghe [1968], and Larson [1968]. Recent short reviews of the subject have been given by Clark et al. [1972], McCrea [1972], Motel [1972], and Reeves [1972].

The problem has been attacked by Cameron in a long series of papers [Cameron, 1962, 1963, 1969, 1971, 1972a, Ezer and Cameron, 1963] that culminated in Cameron [1972b, 1973] and Cameron and Pine [1973]. Although specific features of the models arising from these papers have been criticized by Safonov [1972], the models presented by Cameron and his co-workers provide a detailed picture of the approximate temperature and pressure structure and dynamics of an evolving nebula containing two solar masses. Cameron and Pine [1973] have presented models of a disk-shaped nebula in which the pressure and temperature in the midplane fall from over 2000K and 10^5 atm at the center to below 100K and 10^-5 atm at a radial distance of 10 AU from the center. Perpendicular to the median plane, pressure and temperature also decrease rapidly. Two convective regions exist in these models, one from the center of the disk out to the vicinity of 1 AU and the other from ~2 AU to ~10 AU. Cameron [1973] has estimated that solid particles in the outer convective zone may attain velocities in excess of 1 km/s. Convection cells may thus play an important role in the transport of condensate grains.

Pressures and temperatures employed in the condensation calculations in this paper will be seen to fall in the general range of those predicted by these models for the inner solar system. It seems premature, at this stage, to anchor condensation calculations to any specific pressure-temperature model because of the remaining uncertainties in the input parameters of the hydrodynamic treatments.

3. Chondritic Meteorites

a. Description and classification of chondrites. Chondrites are composed of a coarse-grained fraction generally called chondrules and a fine-grained fraction referred to as matrix. Chondrules are irregular to spherical in shape, range from ~0.3 mm to over 1 cm in diameter and, in many cases but not all, contain unambiguous textural evidence of being the solidification products of rapidly quenched molten droplets. They are commonly composed of olivine, pyroxenes, and glass or feldspar. Table 1

<table>
<thead>
<tr>
<th>Solid Solution Series</th>
<th>Mineral</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Olivine</td>
<td>Forsterite</td>
<td>MgSiS10</td>
</tr>
<tr>
<td></td>
<td>Faydite</td>
<td>FeSiS10</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>Enstatite</td>
<td>MgSiS10</td>
</tr>
<tr>
<td></td>
<td>Ferrosilite</td>
<td>FeSiS10</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Diopside</td>
<td>CaMgSiS10</td>
</tr>
<tr>
<td></td>
<td>Tschermak's</td>
<td>CaAlSiS10</td>
</tr>
<tr>
<td></td>
<td>Ti-Alpyroxene</td>
<td>CaTiAlS10</td>
</tr>
<tr>
<td>Plagioclase feldspar</td>
<td>Anorthite</td>
<td>CaAlSiS10</td>
</tr>
<tr>
<td></td>
<td>Albite</td>
<td>NaAlSiS10</td>
</tr>
<tr>
<td>Mellilite</td>
<td>Gahlenite</td>
<td>CaAlSiS10</td>
</tr>
<tr>
<td></td>
<td>Akermanite</td>
<td>CaMgSiS10</td>
</tr>
<tr>
<td></td>
<td>Soda-mellilit</td>
<td>NaAlSiS10</td>
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<tr>
<td>Nickel-iron</td>
<td>Corundum</td>
<td>Al2O3</td>
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<tr>
<td></td>
<td>Perovskite</td>
<td>CaTiO3</td>
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<tr>
<td></td>
<td>Hibonite</td>
<td>CaO-6Al2O3 ± MgO, TiO1</td>
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<tr>
<td></td>
<td>Spinel</td>
<td>MgAlO4</td>
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<tr>
<td></td>
<td>Magnesite</td>
<td>FeO</td>
</tr>
<tr>
<td></td>
<td>Schreibersite</td>
<td>(Fe, Ni)3P</td>
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<td></td>
<td>Troilite</td>
<td>FeS</td>
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<tr>
<td>Feldspathoids</td>
<td>Nepheline</td>
<td>NaAlSiS10</td>
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<tr>
<td></td>
<td>Sodalite</td>
<td>3NaAlSiO3, NaCl</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>CaSiO3</td>
<td></td>
</tr>
<tr>
<td>Grossularite</td>
<td>CaMgSiS10</td>
<td></td>
</tr>
<tr>
<td>Cordierite</td>
<td>(Mg, Fe)3AlSiS10</td>
<td></td>
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gives the chemical formulas of minerals referred to in this
paper (see also Mason [1972]). In the more primitive
chondrites, the matrix consists of micron-sized particles of
the same minerals as appear in the chondrules, except in
the case of the type 2 carbonaceous (C2) chondrites, where
the matrix minerals are predominantly hydrated, layer-
lattice silicates [Puchta et al., 1973; Bass, 1971], and mag-
netite [Jedwab, 1971]. The type 1 carbonaceous (C1)
chondrites are similar in mineralogy to C2 chondrites but
contain no chondrules. The other major minerals of chon-
drites are nickel-iron and troilite, which occur both inside
silicate chondrules and as coarse- and fine-grained particles
in the matrix.

Table 2, after Van Schmus and Wood [1967], shows the
major chemical criteria that serve to define the differences
between the enstatite chondrites, the carbonaceous chon-
drites, and the different groups of ordinary chondrites.
Discussion of these differences can be found in the work of
Mason [1971] and Van Schmus and Wood [1967]. The
ordinary chondrites are intermediate in oxidation state
between the enstatite chondrites, the carbonaceous chon-
drites, and the different groups of ordinary chondrites.

<table>
<thead>
<tr>
<th>Class</th>
<th>Wt % Total Iron/Wt % SiO₂</th>
<th>Metallic Iron/Total Iron</th>
<th>Mole % FeO±alite in Olivine</th>
<th>Wt % SiO₂/Wt % MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enstatite or E group</td>
<td>0.77 ± 0.30</td>
<td>0.80 ± 0.10</td>
<td>0</td>
<td>1.90 ± 0.15</td>
</tr>
<tr>
<td>Carbonaceous or C group</td>
<td>0.77 ± 0.07</td>
<td>0.0 (some as high as 0.2)</td>
<td>1 (some as high as 0.05)</td>
<td>1.42 ± 0.05</td>
</tr>
<tr>
<td>Ordinary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H group</td>
<td>0.77 ± 0.07</td>
<td>0.63 ± 0.07</td>
<td>18 ± 2</td>
<td>1.55 ± 0.05</td>
</tr>
<tr>
<td>L group</td>
<td>0.55 ± 0.05</td>
<td>0.33 ± 0.07</td>
<td>24 ± 2</td>
<td>1.59 ± 0.05</td>
</tr>
<tr>
<td>LL group</td>
<td>0.49 ± 0.03</td>
<td>0.08 ± 0.07</td>
<td>29 ± 2</td>
<td>1.58 ± 0.05</td>
</tr>
</tbody>
</table>

Modified after Van Schmus and Wood [1967].
where \( P_\text{tot} \) is the total gas pressure of some region in the nebula. At high temperatures and low pressures, the ideal gas law can be used:

\[
N_{\text{H}_2} = \frac{P_{\text{H}_2}}{RT}
\]

where \( N_{\text{H}_2} \) is the concentration of \( \text{H}_2 \) in moles/liter. But where \( N_{\text{H}_2}^{\text{tot}} \) is the total number of moles/liter of \( \text{H} \) atoms. It follows that

\[
N_{\text{H}_2}^{\text{tot}} = \frac{2P_{\text{H}_2}}{RT}
\]

Then for any element \( X \),

\[
N_{X}^{\text{tot}} = \frac{A(X)}{A(H)} \times N_{\text{H}_2}^{\text{tot}}
\]

where \( N_{X}^{\text{tot}} \) is the total concentration of \( X \) atoms and \( A(X) \) and \( A(H) \) are the solar system abundances of elements \( X \) and hydrogen, respectively. Note that \( N_{X}^{\text{tot}} \) also depends on \( P \) and \( T \).

For each element \( X \) a mass balance equation can now be written at any \( T \) and \( P \) in which the constant on the right-hand side is \( N_{\text{TM}} \). The left-hand side is the sum of the concentrations due to all \( X \)-containing gaseous molecules.

For example, in the case of hydrogen,

\[
N_{\text{H}} + 2N_{\text{H}_2} + 3N_{\text{H},0} + 2N_{\text{H},0} + 3N_{\text{H}_2} + \cdots = N_{\text{H}_2}^{\text{tot}}
\]

A chemical reaction can then be written to describe the formation of each gaseous molecule from its monatomic gaseous constituent elements [Grossman, 1972a]. In the case of \( \text{NH}_3 \) for example,

\[
N_{(e)} + 3H_{(e)} \rightarrow NH_{3(e)}
\]

From the free energies of these species an equilibrium constant \( K \) can be calculated such that

\[
K = P_{\text{NH}_3}/P_N \times P_{H}_3
\]

Substituting the ideal gas law and rearranging yields

\[
N_{\text{NH}_3} = K N_X N_{H}^3 (RT)^3
\]

All expressions of this form can be substituted into (6). It now becomes evident that knowledge of the concentrations of the other monatomic gaseous component elements is necessary in order to compute \( N_{\text{H}} \). A mass balance equation like (6) is written for each element being considered. All substitutions of the form of (9) are made in each equation. The result is a system of \( n \) simultaneous, nonlinear mass balance equations in \( n \) unknowns, the concentrations of the monatomic gaseous component elements. These equations are solved by a method of successive approximations by using a computer. Grossman [1972a] considered nearly 300 gaseous species in a system consisting of the 20 most abundant elements in the solar system, excluding the noble gases. For a discussion of the thermodynamics of chemical equilibriums and of computational methods that can be applied to these systems, see Van Zeggeren and Storey [1970].

c. Treatment of condensed phases. To determine the conditions under which a vapor becomes saturated with respect to condensed phases, equilibrium constants \( K_{\text{sa}} \) were calculated for the decomposition reactions of 75 crystalline phases into their monatomic gaseous constituent elements [Grossman, 1972a]. These calculations have been extended to cover more than 100 phases, many of which are commonly found in terrestrial rocks and meteorites. The temperature variation of \( \log K_{\text{sa}} \) for corundum and spinel is shown in Figure 1. In the case of a pure element these lines are simply vapor pressure curves. For corundum the reaction is

\[
\text{Al}_2\text{O}_3(\text{s}) \rightleftharpoons 2\text{Al}(\text{g}) + 3\text{O}(\text{g})
\]

and

\[
\log K_{\text{sa}} = 2 \log P_{\text{Al}} + 3 \log P_{\text{O}} - \log A_{\text{Al},0}
\]

where \( A_{\text{Al}_2\text{O}_3} \) is the activity of aluminas. The activity of a pure crystalline phase is unity, and hence (11) reduces to the ordinate on the top half of Figure 1.

Figure 1 also illustrates a technique introduced into solar nebula condensation calculations by Grossman [1972a]. The equilibrium lines for corundum and spinel divide their respective phase diagrams into fields of vapor only and of condensate only. The system of mass balance equations was solved at very high temperatures (2000°, 1800°, and 1700°K) at 10^4 atm; the concentrations of monatomic
gaseous components converted to partial pressures and the functions appearing as the ordinates in all the phase diagrams were calculated. These functions (squares in Figure 1) are seen to be linear with \(1/T\), and all except the function for corundum at 1700*K plot in their respective fields of vapor only. Corundum was thus found to be the first condensate of the major elements.

To represent complete chemical equilibrium, however, the 1700*K equation set must be solved again, this time including terms for the concentration of crystalline corundum in the Al and O mass balance equations. The introduction of this new variable requires the addition of (11), the condition that corundum be in equilibrium with the vapor below its condensation point. This forces the gas composition to vary along the corundum equilibrium line, requiring a lower \(P_{\text{At}}\) at 1700*K than would have been the case had corundum not appeared. Thus spinel (lower half of Figure 1), which would have condensed at 1685*K if corundum had not appeared, does not condense until nearly 1500*K. Grossman [1972a] was thus able to determine the effects of high-temperature condensates on the temperatures of appearance of less refractory phases by starting at high temperatures, assuming complete chemical equilibrium, and correcting the equations each time a new condensate became stable.

d. Solid solutions. In cases where solid solutions are considered, the activity term in (11) generally does not equal one but becomes the product of a temperature- and composition-dependent activity coefficient \(\gamma\) and a mole fraction \(X\). In the case of ideal solid solutions, \(\gamma\) is unity. This simplification has been used for the condensation of trace elements in perovskite [Grossman, 1973b] and sodiophiles in iron metal [Larimer, 1967; Grossman and Olsen, 1974]. The condensation of nonideal solutions has been considered by Larimer [1973] for Bi, Tl, and In and by Grossman [1972a] for the melilites, olivines, and pyroxenes.

Because the activities of components in dilute solution are less than one, solid solution raises the condensation temperature of an element above that of the pure component.

e. Limitations of condensation models. Aside from the possibility that important gaseous molecules or crystalline phases may exist for which thermodynamic data are lacking, the quality of the thermal data themselves imposes errors on the calculation of condensation temperatures.

Fortunately, most of the important species in these calculations are quite stable under laboratory conditions and have been well studied. The year to year fluctuations in their reported free energies yield maximum errors of \(\pm 50^\circ\). More important is the effect that such fluctuations would have on the sequence of crystallization of phases that have similar condensation temperatures and the effect that this, in turn, would have on the appearance or disappearance of later phases in the condensation sequence.

The standard compilations of thermodynamic data routinely list error estimates on the tables for each species.

Important errors can also be introduced through the elemental abundances. The condensation temperature of a phase changes by 50°-100° if the abundance of one of its component elements is altered by a factor of 10. Anders [1971b] argued, however, that the abundances of the elements in the solar system [Cameron, 1968] are known to within a factor of 2 for most elements and within a factor of 5 for some groups of trace elements. More serious effects can be produced by less severe alterations in the ratios of certain critical elements, such as C/O. This ratio controls the oxidation state of the system and the availability of oxygen to condensed phases. New solar spectral data [Cameron, 1974] yield a C/O ratio within a few percent of older data [Cameron, 1968].

In the calculations described here it is assumed that phases appear at their equilibrium condensation points and that they remain in complete thermal and chemical equilibrium with the vapor at lower temperatures. These assumptions are made in order to facilitate theoretical treatment and can be tested by comparing theoretical predictions with observations in meteorites. Blander and Katz [1967] and Blander and Abdel-Gawad [1969] have argued that kinetic barriers led to the condensation of iron from a supersaturated gas and to the condensation of magnesium silicate chondrules as subcooled liquid droplets. Troilite could have condensed at higher-than-equilibrium temperatures owing to these effects [Blander, 1971]. Arrhenius and Alfven [1971] and Arrhenius [1972] have suggested that condensation took place from a plasma at 10*°K and <10 atio pressure. Under these conditions, they argue that the equilibrium condensation sequence will be disrupted owing to ionization effects and the lack of thermal equilibrium between grains and vapor.

The theme of this paper is to see how far equilibrium condensation calculations can be used to satisfactorily explain the chemistry and mineralogy of chondrites and to determine what sorts of disequilibrium processes need to be postulated to account for the deviation of theory from observation.

2. Condensation Sequence

The condensation sequence of a gas of solar composition [Cameron, 1968] at 10* atm total pressure is shown in Figure 2, patterned after earlier versions by Larimer [1967] and Anders [1968, 1971a, 1972a, b]. The curves are based on the data of Grossman [1972a, 1973b], Grossman and Clark [1973], Larimer [1973], and Grossman and Olsen [1974]. The detailed condensation relations in specific temperature ranges will be discussed in later sections.

The general features of the condensation sequence are described.

Under equilibrium conditions the first condensates from a cooling solar nebula will consist of a group of refractory trace elements, such as Os, Re, and Zr. These condense well above 1679*K, the condensation point of Al₂O₃, the first condensate containing any major element. By 1500*K, all the Ti and most of the Ca have condensed as CaTiO and CaAl₂SiO₆, respectively. The rare earth elements U, Pu, Th, Ta, and Nb can condense in solid solution in CaTiO₂. In contrast to Ca, Al, and Ti, less than 10% of the total Mg and Si are condensed until CaMg₁₋₂SiO₃ appears at 1373*K. Similarly, metallic Fe only begins to condense at 1373*K, carrying with it Ni and Co. At 1350*K, iron-free Mg₃SiO₄ appears, condensing most of the Mg. It later reacts with the vapor to form Mg₃SiO₄ and MgO. Total Mg₃SiO₄ is classified here as the refractory elements.

Below this temperature, Cu, Ge, and Ga condense in solid solution in the metal. At about 1200*K, Na, K, and Rb condense in the form of solid solutions with previously condensed CaAl₂SiO₆. The alkali metals should be totally
condensed by 1000°K. Ag is 100% condensed by 750°K. These elements, among others, are referred to as the normally depleted elements, in reference to their abundance patterns in chondrites. They all condense in the interval between 1300°K and 650°K. Metallic iron begins to oxidize significantly only after the temperature has fallen below 750°K, at which point MgSiO and MgSiO₃ contain about 1 mole % of the iron end members of their respective solid solution series. At lower temperatures, their Fe⁺⁺ content rises rapidly. Troilite (FeS) becomes stable at 700°K and forms by the reaction of gaseous HS with metallic iron.

The strongly depleted elements Pb, Bi, In, and Tl condense between 600° and 400°K. Magnetite appears at 405°K, and magnesium silicates react with gaseous H₂O to form hydrated silicates below 350°K. Below 200°K, not shown in Figure 2, argon, CH₄, NH₃, HO, and methane hydrate condense, according to Lewis [1972b].

The details of particular temperature regions in Figure 2 will be examined in the following sections.

C. REFRACTORY ELEMENTS

1. Predictions From Condensation Calculations

This section deals with the elements that condense above 1300°K at a solar nebular pressure of 10⁻⁴ atm. They can be divided into two groups: the highest-temperature condensates, primarily Ca-Al-Ti-rich oxides and silicates, and the lower-temperature condensing metallic iron and magnesium silicate assemblage.

a. Ca, Al, and Ti. The first suggestion that Ca, Al, and Ti might be the earliest-condensing major elements in a gas of solar composition appeared in the work of Lord [1965], who found that, among other compounds, Al₂O₃, TiO₂, CaO, MgAl₂O₄, CaAl₂Si₂O₈, and CaTiO₃ were near saturation under high-temperature solar nebular conditions. Later work by Larimer [1967], Gilman [1969], and Fix [1970] confirmed this.

Grossman [1972a] presented the first calculations showing the effect of high-temperature condensates on the composition of the vapor phase and on the ensuing path of condensation. This work superseded the condensation sequence listed in Clark et al. [1972]. Figures 3 and 4 give the sequence of condensation and reaction of the highest-temperature condensates of the major elements at 10⁻⁴ atm total pressure. Corundum condenses first at 1758°K, followed by perovskite at 1647°K. Ti is rapidly removed from the vapor by the latter phase, but only a small fraction of the Ca is removed because the Ti/Ca ratio is only 0.03. The major sink for Ca at high temperature is mellitite, which begins to form by the reaction of corundum with the vapor at 1625°K. For over 100°, Al was the only major element condensed in the solar system. Excess corundum reacts with the gas to form spinel at 1513°K. The first-formed mellitite is the pure gehlenite end member. Significant quantities of akermanite dissolve in the mellitite only below 1550°K, when Ca is more than 90% condensed. This reaction requires the inward diffusion of Mg and Si and the outward movement of Al, which is precipitated as corundum above 1513°K or as spinel below this temperature. Mellitite disappears by reaction to form diopside plus spinel at 1450°K. At this temperature the akermanite content reaches 81 mole % for an ideal solution or 43 mole %, according to a nonideal solution model. Grossman and Clark [1973] have calculated that no more than 2 X 10⁻⁴ mole % of soda-mellitite is soluble in this phase under these conditions. Perovskite reacts to form diopside plus spinel at 1393°K. At 1362°K. Na begins to condense in solid solution in anorthite at about 1250°K.
Fig. 3. The distribution of Ca between crystalline phases and vapor in a cooling gas of solar composition at 10^{-3} atm total pressure. Ca first condenses as perovskite at 1647°K, but the major sink for Ca at high temperature is melilite, which condenses at 1625°K. The reactions of melilite to form diopside and spinel at 1450°K and diopside plus spinel to form anorthite at 1362°K are also shown. [From Grossman, 1972a.]

Grossman and Clark [1973] have reestimated the composition of the first pyroxene to be 67 mole % diopside, 12% CaAl_2SiO_6 and 21% CaTiAl_2O_6 rather than the pure diopside, above. In this calculation the initial Ti content is an upper limit. Solid solution raises the pyroxene's temperature of appearance to 1455°K and probably causes perovskite to disappear at this temperature, allowing melilite to persist to lower temperatures and to increase its akermanite content. It is also quite possible that this pyroxene contains Ti^4+. Although pure TiO_2 is not stable until 1393°K, it could dissolve in pyroxene at higher temperatures. Since thermodynamic data are lacking for the postulated pyroxene components, the composition of the pyroxene has not been calculated as a function of temperature. Because of this the details of the reactions shown in Figures 3 and 4 are not well known below 1455°K.

Grossman and Clark [1973] have estimated the pressure variation of the condensation temperatures of these phases from 10^{-9} to 10^4 atm. The condensation sequence is constant over this pressure range, as is seen in Figure 5.

b. Fe, Mg, and Si. Fe, Mg, and Si are the most abundant nonvolatile elements in the solar system. Figure 6, however, shows that the bulk of these elements only begins to condense at significantly lower temperatures than Ca, Al, and Ti. At 10^{-2} atm, metallic Fe begins to condense at 1471°K. Its initial Ni content is 13.4 mole %, the Co con-
tent is 0.74 mole %, and the Cr content is 0.32 mole % [Grossman and Olsen, 1974]. With falling temperature, the Ni and Co concentrations decrease to 5.2 and 0.26 mole %, respectively, whereas the Cr concentration rises to 0.98% by 1375°K. Before the first appearance of forsterite at 1444°K, 46% of the iron has condensed. Phosphorus condenses as schreibersite by the reaction of condensed metal with gaseous P2 at 1416°K. At 1349°K, forsterite begins to react with the vapor to form enstatite. The early olivine and pyroxene remain iron free until the temperature falls another 500° below their condensation points.

At 10⁻⁴ atm, the initial Ni, Co, and Cr concentrations in the metal become 14.9, 0.81, and 0.30 mole %, respectively. The effect of pressure on the relative condensation temperatures of metal and magnesium silicates is shown in Figure 7. Iron condenses before forsterite at pressures in excess of 7.1 × 10⁻⁴ atm.

c. Trace elements. In general, condensation temperatures for the refractory trace elements are less well determined than those of the major elements because of the lack of thermodynamic data for condensates and gaseous molecules containing these elements, the poor quality of the existing data, and uncertainty regarding their solid solution behavior. Some calculations have recently been performed by Clark et al. [1972] and Grossman [1973a, b]. Table 3 gives condensation temperatures at two different total pressures for a number of refractory trace elements. For each element, Table 3 shows the gaseous species assumed to be present in order of decreasing abundance and lists the crystalline phases whose condensation temperatures were investigated. For each element the condensation temperatures refer to the italicized phase that is the first to condense of those listed. The temperatures given are for condensation of the pure phases, except in the case of the rare earth oxides that are assumed to go into solid solution in perovskite, although they can also condense as pure oxides above 1450°K at 10⁻⁴ atm. Similarly, Ta and Th may begin to condense at 1647°K in perovskite, which is higher than the temperatures listed. This is probably also the case for PuO₂, UO₂, and Nb₂O₅, which would otherwise condense as pure oxides below 1450°K. By 1400°K, Be may be 100% condensed in spinel [Cameron et al., 1973]. Sr and Ba are
also likely to condense in solid solution in the high-temperature Ca minerals, although detailed calculations for these elements have not been performed.

2. Evidence for Ca-Al-Rich Condensates in Chondrites

a. Mineralogy. Spinel-bearing aggregates in carbonaceous chondrites have been known since the study of Kaba (C2) by Srtrókay et al. [1961]. The first report of the occurrence of melilitc in meteorites was made by Fredriksson and Reid [1967] in a carbonaceous clast in Shars, and perovskite was first reported by Christophe [1968] in Vigarano (C3). Ca-Al-Ti-rich inclusions were later studied by Christophe [1969] in Lancé and Felix (both C3) and by Keil et al. [1969] in Leoville (C3). Attention focused on these objects after the fall of Allende (C3) in February, 1969. Over two tons of this meteorite have been recovered [Clarke et al., 1970] and melilitc-spinel-bearing white inclusions comprise about 8% of it by volume [Marvin et al., 1970]. Mineralogical and electron microprobe studies of the inclusions in Allende have been performed by Fuchs [1969, 1971], Clarke et al. [1970], Keil and Fuchs [1971], Malissa et al. [1972], Fuchs and Blander [1973], and Marvin et al. [1970], who also observed spinel-bearing aggregates in Grosnaja, Ornans, and Warrenton (all C3).

Ti-Al-rich pyroxene was first identified in Allende by Fuchs [1969], in Lancé by Frost and Symes [1970], and in Vigarano by Christophe et al. [1970]. Dowty and Clark [1973] have presented evidence for the presence of trivalent Ti in the Ti-Al-rich pyroxene. Pure Al₂O₃ was first found by Kurat [1970] in Lancé, and hibonite was first found by Fuchs et al. [1970] in Murchison (C2). Hibonite has since been described in inclusions in Leoville and Allende by Keil and Fuchs [1971] and in Murchison by Fuchs et al. [1973]. The mineralogy of the inclusions in the C3 chondrites is dominated by a virtually alkali-iron-free melilitc averaging 85 mole % gehlenite and a nearly Fe-Cr-free spinel. Fe-free clinopyroxenes, either pure diopside or Al-Ti₄⁺-rich pyroxene, are common. Perovskite is a frequent accessory mineral, particularly in the absence of the titaniferous pyroxene. Relatively rare minerals include plagioclase having a composition of An₄₅-An₄₀, hibonite and feldspathoids. Corundum is very rare. Grossularite, rhönite, cordierite, Al-enstatite,

TABLE 3. Relationships Between the Condensation Temperatures of the Refractory Trace Elements and Those of the Major High-Temperature Minerals

<table>
<thead>
<tr>
<th>Gaseous Species</th>
<th>Crystalline Phases</th>
<th>10⁻³ atm</th>
<th>10⁻⁴ atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>Os</td>
<td>1925</td>
<td>1840</td>
</tr>
<tr>
<td>WO, W</td>
<td>W</td>
<td>1885</td>
<td>1798</td>
</tr>
<tr>
<td>ZrO₂, ZrO₃</td>
<td>Zr, Zr₂O₃</td>
<td>1840</td>
<td>1780</td>
</tr>
<tr>
<td>Re</td>
<td>Re</td>
<td>1839</td>
<td>1759</td>
</tr>
<tr>
<td>HfO₂</td>
<td>Hf, Hf₂O₃</td>
<td>1719</td>
<td>1652</td>
</tr>
<tr>
<td>VO, Y</td>
<td>Y, Y₂O₃</td>
<td>1719</td>
<td>1646</td>
</tr>
<tr>
<td>Sc₂O₃, Se</td>
<td>Sc, Se₂O₃</td>
<td>1715</td>
<td>1644</td>
</tr>
<tr>
<td>Mo₂, MoO₄</td>
<td>Mo₂O₃</td>
<td>1684</td>
<td>1603</td>
</tr>
<tr>
<td>HfO₂</td>
<td>Hf, Hf₂O₃</td>
<td>1758</td>
<td>1679</td>
</tr>
<tr>
<td>REO, RE₂⁺</td>
<td>RE, RE₂O₃</td>
<td>1647</td>
<td>1571</td>
</tr>
<tr>
<td>Ir</td>
<td>Ir</td>
<td>1629</td>
<td>1555</td>
</tr>
<tr>
<td>Ru</td>
<td>Ru</td>
<td>1614</td>
<td>1541</td>
</tr>
<tr>
<td>VO, V</td>
<td>VO₂, V, VO₂</td>
<td>1534</td>
<td>1458</td>
</tr>
<tr>
<td>Spinel (Mg₂Al₂O₆)</td>
<td>Mg₂Al₂O₆</td>
<td>1513</td>
<td>1444</td>
</tr>
<tr>
<td>TaO₂, Ta</td>
<td>Ta, Ta₂O₃</td>
<td>1499</td>
<td>1452</td>
</tr>
<tr>
<td>ThO₂, Th₂O₄</td>
<td>Th₂O₄, Th</td>
<td>1496</td>
<td>1429</td>
</tr>
<tr>
<td>Diopside (CaMgSi₂O₆)</td>
<td>CaMgSi₂O₆</td>
<td>1450</td>
<td>1387</td>
</tr>
</tbody>
</table>

* The condensation temperature of the italicized crystalline phase. For each element, this is the highest-condensing phase of those listed.

† Rare earth.
and wollastonite have been reported occasionally. The striking resemblance between the observed mineralogy and mineral compositions and the predicted high-temperature condensate phase assemblage is truly remarkable. Marvin et al. [1970] and Larimer and Anders [1970] were the first to notice the similarity between the chemistry of these aggregates and the chemistry of the highest-temperature condensates predicted by Lord [1968]. Kurat [1970] suggested that the aggregates may be vaporization residues.

b. Textural features. Grossman [1972a] pointed out how the textural relations reported by Fuchs [1969] and Kurat [1970] are consistent with the same sequence of reactions predicted by his condensation model: hibonite in the cores of spinel grains that are intimately intergrown with melilite containing 5–35 mole % akermanite, perovskite grains scattered throughout the assemblage, and pure diopside rims around entire inclusions or surrounding cavities in their interiors. Thermodynamic data are lacking for hibonite, but its similarity in composition to corundum and its occurrence suggest that it may take the place of corundum in the condensation sequence. In terms of the condensation model the observed assemblages are not at equilibrium but contain relics of high-temperature minerals surrounded by incompatible lower-temperature eutectics that stopped equilibrating with the vapor at 1450°K at 10 atm.

Recently, Fuchs and Blander [1973] called attention to the fact that some inclusions exhibit textural relations unlike those expected from the postulated condensation sequence. These are inclusions in which high-temperature perovskite and hibonite surround minerals calculated to be lower-temperature condensates. Such assemblages may represent accumulations of condensate grains or aggregates, each of which at one time was suspended independently in the gas. Different aggregates may have approached equilibrium to different degrees and perhaps at slightly different pressures and temperatures before they were incorporated in no particular order. The absence of gehlenite and the abundance of hibonite and perovskite in Murcison inclusions suggest that these were formed under different conditions from those in Allende. Some peculiarities of the textural features of Allende inclusions may also be due to subsolidus reactions at much lower temperatures than the condensation temperatures of the phases.

Melting is another possible mechanism for producing textures indicative of a different crystallization sequence than the sequence expected from condensation. Evidence for melting is cited in many of the references listed above, including the presence of near-spherical inclusions [Clarke et al., 1970; Grossman and Clark, 1973; Fuchs and Blander, 1973], occasional glass [Marvin et al., 1970], and rare eutectic intergrowths of diopside and anorthite or gehlenite and anorthite [Fuchs and Blander, 1973]. In addition, there are some exceptionally fine-grained white aggregates in Allende that appear to have been squeezed into shapes conforming to surrounding ferromagnesian chondrules, suggesting that these aggregates were in a plastic, near-molten state during compaction of the parent body. The suggestion that some of the Allende inclusions were once liquid opens the door to the possibility that some may be the solidification products of primary liquid condensates. Grossman and Clark [1973] outlined the physical conditions required for the equilibrium condensation of phase assemblages of these compositions as liquids. They concluded from the absence of critical liquidus phases and assemblages that the inclusions had not originated as liquid condensates. Such evidence for condensate liquids, however, may have existed at one time but may have been destroyed during later subsolidus reactions. Fuchs and Blander [1973] suggested that the inclusions may have condensed as subcooled liquids.

Both of these mechanisms are unable to account for the coexistence of plastic high-temperature condensates and ferromagnesian silicates that must have equilibrated with the vapor at ~700°K. If the Ca-Al-rich aggregates condensed as liquids at about 1500°K, they would have had to travel very great distances to reach a part of the nebula having a temperature of only ~700°K. It is unlikely that they could do so without cooling to temperatures far too low for them to remain plastic. Thus the evidence seems to point to the melting of solid condensate aggregates in the nebula during local high-temperature events in the vicinity of the Allende parent body, perhaps the same events responsible for the production of chondrules of all compositions [Whipple, 1966, 1972; Cameron, 1966, 1973]. Glass-free, coarse-grained inclusions have the same composition as fine-grained, molded types [Clarke et al., 1970; L. S. Walter and R. T. Dodd, Jr., unpublished data, 1973], but the exact relationships between the two varieties are as yet unknown. There seems to be some evidence for melting of some of the coarse-grained inclusions and some evidence for condensate textures in some of the fine-grained inclusions.

c. Major element composition. In view of the possibility of later melting events, perhaps the best evidence that the inclusions represent high-temperature condensates is their bulk major and trace element composition rather than their mineralogy or texture. Table 4 compares the bulk chemical compositions of a coarse-grained and a fine-grained inclusion [Clarke et al., 1970] with those predicted for the equilibrium condensate assemblages at 1500°K and 1450°K. Again, the similarity is striking. The high Na content is the only serious discrepancy.

d. Trace element composition. A remarkable story is unfolding regarding the trace element characteristics of the Allende inclusions. Gaet al. [1970] first reported rare earth element enrichments in one of the inclusions by a factor of 15 relative to chondrites, and Ehmann and Rebagly [1970] measured Zr and Hf enrichments by factors of 2 or more relative to the bulk meteorite. Kurat [1970] noted percent levels of Zr and Y in perovskite from a Laced Ca-Al-rich inclusion and attributed these refractory element enrichments to a vaporization process. Warren et al. [1971] reported high Sc, V, Sm, Eu, and Ir concentrations in Ca-Al-rich chondrules from Allende. High Nb relative to the bulk meteorite was found in a mellitie-rich chondrule from Allende by Graham and Mason [1972]. Enhanced Sc and Eu abundances have been measured in Ca-Al-rich Allende chondrules [Menainga et al., 1973]. Grossman [1972b, 1973a, b] determined the abundances of Sc, Ir, La, Sm, Eu, and Yb in 16 individual Allende inclusions. These elements were found to be enriched by factors of 18.3 (Sm) to 25.7 (La) relative to C1 chondrites. Grossman attributed these high refractory element contents to a high-temperature condensate origin for the Ca-Al-rich minerals because all the refractory elements reported to be enriched in the inclusions have condensation temperatures in the same range as those of their major mineral phases (see Table 3). Wänke
et al. [1973] have reported the results of trace and major element analyses of a single Allende inclusion. These results have confirmed the trend of refractory element enhancements, adding Sr, Ba, U, Ta, Mo, W, Os, Re, Ru, and Pt to the list of enriched refractories. Relative to Cl chondrites, these elements are enriched by factors of 10 (Mo) to 21 (Re). These elements span a wide range of geochemical behavior: Al, Ca, Ti, rare earths, and Sc are lithophile; Mo is chalcophile; Ir, Re, and Ru are siderophile. The only property common to all of them is that they condense from a gas of solar composition at very high temperatures, strongly suggesting that it is this behavior that has brought them all together into the Ca-Al-rich inclusions.

Grossman [1973a, b] suggested that the inclusions represent ~4.46 wt % of the total condensate matter, assuming a disequilibrium assemblage at 1450°K and 10⁻⁴ atm. If collection of the refractory trace elements by the major mineral phases were 100% efficient, enrichment factors of 100/4.46 = 22.4 relative to Cl chondrites are expected. Although many elements are enriched to this degree, the work of Wänke et al. [1973], in particular, shows that many other trace refractories, such as Nb, Zr, and Hf, are not so concentrated. This would seem to imply that the collection efficiency was not the same for every element. This may be understandable in terms of the different mechanisms by which different elements must have found their way into the white aggregates. Some probably acted as nuclei for the major phases, others probably nucleated upon the major phases, and still others had to condense in solid solution in the major phases [Grossman, 1972a, 1973a, b].

Wänke et al. [1973] reported that their inclusion is depleted in Pd by a factor of 0.15 relative to Cl chondrites. This is particularly anomalous because the same inclusion is enriched by factors of 12–20 in Ru, Os, Pt, and Ir. As platinum metals, all these elements are noted for their cosmochemical behavior that has brought them all together into the Ca-Al-rich inclusions. Wänke et al. [1973], in particular, shows that many other trace refractories, such as Nb, Zr, and Hf, are not so concentrated. This would seem to imply that the collection efficiency was not the same for every element. This may be understandable in terms of the different mechanisms by which different elements must have found their way into the white aggregates. Some probably acted as nuclei for the major phases, others probably nucleated upon the major phases, and still others had to condense in solid solution in the major phases [Grossman, 1973a, b].

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TABLE 4. Comparison Between High-Temperature Condensate Compositions at 10⁻³ atm and Compositions of Allende Inclusions

<table>
<thead>
<tr>
<th>Calculated Condensate Composition at 1500°K, percent</th>
<th>Coarse-Grained Inclusion,* percent</th>
<th>Fine-Grained Inclusion,† percent</th>
<th>Calculated Condensate Composition at 1450°K (Excluding Fe), percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>24.42</td>
<td>26.76</td>
<td>21.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>37.88</td>
<td>31.61</td>
<td>26.6</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.60</td>
<td>0.99</td>
<td>1.3</td>
</tr>
<tr>
<td>MgO</td>
<td>6.73</td>
<td>10.82</td>
<td>13.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19.57</td>
<td>29.79</td>
<td>33.7</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>99.97†</td>
<td>96.3§</td>
</tr>
</tbody>
</table>

* Clarke et al. [1970], type a chondrule National Museum of Natural History sample 3529.
† Clarke et al. [1970], single aggregate NMNH 3510.
§ Also contains 0.37% FeO and 0.11% NaO.
Also contains 0.1% CrO₃, 2.3% FeO, and 1.1% NaO.

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erved similar enrichments in Na and K. The data of Podosek and Lewis [1972] show that the I-Xe age of the Allende inclusions is not unlike the ages of equilibrated chondrites. Furthermore, the lack of I-Xe isochronism was interpreted to indicate that the inclusions began to retain 130Xe over a 4-m.y. time span. Under the assumption that Cl and I entered the inclusions at the same time, this means that the Cl-bearing sodalite, and probably the other feldspathoids, formed over this same interval of time, which, as Grossman [1973b] pointed out, is probably 10–100 times longer than the condensation time of the solar system. Such evidence thus points toward a late origin for the feldspathoids by reactions that occurred inside the parent body at about the same time that the equilibrated chondrites began to retain their 130Xe. The 130Xe content implies an initial 130Pu/238U ratio nearly 3 times higher than in any other meteoritic material. Although Podosek and Lewis [1972] suggested that this was due to fractionation of Pu from U during the formation of the inclusions, it can also be interpreted, at least in part, in terms of a greater age for the inclusions, which is consistent with a condensation origin [Turekian et al., 1973].

Gray et al. [1973] have reported the lowest 87Sr/86Sr ratio ever measured in meteorites from a Ca-rich chondrule in Allende. This suggests that Rb-poor, Ca-rich inclusions are among the most primitive objects in the solar system. Other inclusions, with higher Rb/Sr ratios, were reported by them and by Wetherill et al. [1973]. Gray et al. [1973] saw evidence in the Rb/Sr systematics of late addition of Rb to the inclusions, some as late as the last 3.6 by. Assuming that Na entered the inclusions at the same time as Rb, this is further strong evidence for the production of feldspathoids by reactions inside the parent body long after condensation was over.

g. Oxygen isotopes. The oxygen isotopic compositions (δ18O) of three gehlenite-spinel-bearing Allende inclusions have been measured by Onuma et al. [1972] to be in the range −9.7 to −11.5‰, relative to SMOW. Such compositions imply temperatures of equilibration with the nebular gas as low as 800°K or else very low δ18O for that part of the solar nebula where the inclusions formed. These temperatures are much lower than those implied by the texture and mineralogy of the inclusions. The meaning of this discrepancy is under active investigation.

h. P-T implications. As was stated above, the presence of diopside rims on some of the Ca-rich inclusions implies that reaction between the condensates and the vapor ceased at about 1450°K, under the assumption of 10^4 atm for the total pressure. The major element contents of the inclusions of Table 4 point to equilibration temperatures between 1500°K and 1450°K at 10^4 atm. The absence of forsterite from the inclusions requires their isolation at temperatures above 1444°K. Anorthite is sometimes found inside the inclusions, indicating equilibration temperatures in such cases as low as 1382°K at 10^4 atm, although this temperature is uncertain by about 30° owing to the complex solid solution relationships of the coexisting pyroxene. On the other hand, anorthite may be one of the crystallization products of melted condensate aggregates.

Metallic iron should have begun to condense at 1471°K, above the formation temperature of the diopside rims at 10^4 atm, yet no iron has been observed inside the inclusions. This may be a clue to the pressure in the region of the nebula where the inclusions formed. At 10^4 atm, for example, the diopside rims should form at 1387°K, iron at ~1377°K, and forsterite at 1370°K. Because of the mineralogical and textural evidence for disequilibrium condensation [Grossman, 1972a], diopside may have formed slightly below its equilibrium condensation temperature [Grossman and Clark, 1973], making 10^4 atm an upper limit to the pressure in the part of the nebula where the inclusions formed. This pressure will allow inclusions having the same mineralogy, textural features, and major and trace element chemistry as those observed to form just before metallic iron and forsterite condense. The model requires transport of these nodules away from their condensation site at this stage before they become coated with the later condensates. The previous lowest value for the upper limit to the pressure in this part of the nebula was 2.2 × 10^4 atm [Grossman and Clark, 1973] and was based on the lack of evidence for the condensation of partial melts.

i. Fractionation of refractory condensates. Ca-Al-rich condensates must have accreted to form centimeter-sized nodules and must have begun moving away from where they condensed before iron or magnesium silicates appeared; otherwise they would have been coated by these later condensates. The absence of these phases also suggests that transport of the refractory aggregates through parts of the nebula where condensation was still going on had to be rapid compared with the condensation rate. Finally, they must have reached cooler regions where condensation was nearly complete and where they were accreted along with lower-temperature condensates into the C2 and C3 chondrite parent bodies. Cameron and Pine [1973] have computed physical models of the solar nebula that suggest that convection cells could have carried grains further away from the center of the nebula, through the required temperature difference, on a time scale of several years.

The separation of Ca-Al-rich materials from Mg-Fe-rich materials seems to have been a widespread process in the solar nebula. Larimer and Anders [1970] suggested that fractionation of early condensates in the form of these aggregates was responsible for the lithophene element depletions in ordinary and enstatite chondrites, respectively, relative to the carbonaceous chondrites. Grossman [1973a, b] also emphasized this process, pointing out that many of the same refractory elements that are relatively uniformly depleted in these chondrites are also relatively uniformly enriched in the Allende inclusions.

There is reason to believe that partial condensation of refractories was not restricted to the solar nebula. The interstellar gas is underabundant in Ca, Al, and Ti, but the abundances of Na and K are normal. Herbig [1970c, d] suggested that much of the material in the interstellar medium has been processed through stellar nebulae, with Ca, Al, and Ti being returned in the form of grains and Na and K remaining in the gaseous state.

3. Evidence for Metal and Magnesium Silicate Condensates in Chondrites

Type 2 carbonaceous chondrites contain Ca-Al-rich aggregates and hydrous layer-lattice silicate minerals as well as coarse-grained aggregates of ferromagnesian silicates that have been called chondrules. The Ca-Al-rich aggregates are very similar to those described from Allende and other C3 chondrites and are probably primitive refractory conden-
sates. The layer-lattice silicate has been ascribed a condensation origin at very low nebular temperatures [Larimer and Anders, 1967]. What evidence is there for the presence of phases with condensation temperatures intermediate between these two?

Grossman and Olsen [1974] noted that only a small proportion of the total olivine and pyroxene in C2 meteorites possesses textural features that unambiguously indicate that these phases are the solidification products of once-molten droplets. Although they have been called chondrules in the past because of their rounded shapes and coarse crystallinity, the olivine-pyroxene aggregates may be direct high-temperature condensates from the solar nebula. Onuma et al. [1972] also suggested this on the basis of their oxygen isotopic compositions.

The olivine and pyroxene of interest is in the form of loose clusters of euhedral crystals or single, broken crystals surrounded by layer-lattice silicates. Most of them contain 99–100 mole % of the magnesium end members [Fuchs et al., 1973], thus indicating that they have not suffered massive alteration at low temperature. They frequently contain blebs of Ca-Al-rich glass of obvious chemical affinity with Allende type inclusions.

The compositions of metal grains enclosed by the silicates can also be understood in terms of a condensation model if early Ni-Co-rich metal were transported away from the site where later metal grains condensed [Grossman and Olsen, 1973]. Later metal grains and Ca-Al-rich glass may have acted as nuclei for lower-condensing forsterite. The aggregates are depleted in Fe relative to Mg, whereas the reverse is true for the hydrated silicate matrix, compared with C1 chondrites. Because the bulk Fe/Mg ratio of a C2 is only slightly less than that of a C1, this interpretation would require that most of the metal lost from the high-temperature fraction had been oxidized and incorporated into the low-temperature fraction before being agglomerated together with the forsterite and enstatite just prior to accretion. Textures and compositions of metal grains suggest that condensation of the high-temperature fraction took place near 10^4 atm and that this metal/silicate separation accompanied condensation.

D. SIDEROPHILE ELEMENTS

1. Meteorite and Planetary Metal Variations

The abundance of iron in the solar system was uncertain for many years and was the source of considerable controversy. Up until 1969 the iron abundance in the solar photosphere appeared to be a factor of 5-10 less than in chondrites or in the solar corona. This discrepancy has now been resolved with the discovery of a 10-fold error in the oscillator strengths of the FeI lines used in photospheric abundance determinations [Garz and Kock, 1969]. All abundance values from the sun now agree with meteoritic values to within experimental error, about a factor of 2.

Controversy persists, however, over the apparent variation in metal/silicate ratio among the planets and satellites and the indisputable fact that in primitive chondrites the Fe/Si ratio is variable (Table 2). In the case of planets and satellites the Fe/Si ratio must be inferred from the measured densities [Urey, 1952a]. But density differences could conceivably be due to other factors. For example, Ringwood [1966] suggested that most planetary bodies have the same Fe/Si ratio and that density differences are the result of variable proportions of metallic iron/iron oxide and metallic silicon/silicon dioxide. On the other hand, Lewis [1972a] argued that the density differences are the result of variations in iron oxide, sulfur, and volatile content. Such factors can be involved in the case of Venus, the earth, and Mars, whose densities are relatively similar. But variations in oxidation state and volatile content do not explain the extremely high density of Mercury, the low density of the moon, or the variations in Fe/Si ratios observed in chondrites. Some mechanism, perhaps several, must have been operative that produced bodies with different total iron contents.

2. Metal/Silicate Fractionation in Chondrites

Urey and Craig [1953] first drew attention to the systematic variation in Fe/Si ratio among chondrites. Other siderophile elements such as Ni and Co follow the same pattern as Fe. Neither gravitational separation during partial melting in a parent body nor accretion prior to complete condensation of metal and silicate material can explain these data. Partial melting some time after accretion is ruled out because (1) independent of the size of the body, and hence of the gravitational field, the segregation of molten metal from silicate is an extremely efficient, all-or-nothing process that takes place on a time scale of years or less [Fish et al., 1960], and (2) unequilibrated chondrites that obviously have not partially melted since accretion display variations in siderophile element content that parallel those of their equilibrated counterparts [Dodd et al., 1967]. Accretion before complete condensation of metal or silicate is also ruled out because chondrites contain abundant FeS and other volatiles that condense at a much lower temperature than the bulk of the metal (Fe and Ni) or the silicates (MgSiO_3 and MgSiO_3). Evidently the metal-silicate fractionation took place after the bulk of the metal and silicate condensed but before accretion. A fractionation of metal and silicate grains while dispersed in space is implied.

Larimer and Anders [1970] have attempted to infer from chemical data the direction, extent, temperature, and redox conditions at the time of fractionation. Following Anders [1964] we can write

\[
\text{Fe}^+ = \text{Fe}^{+2} + \text{Fe}^0 \tag{12}
\]

where the symbols Fe^0, Fe^{+2}, and Fe^{+3} denote total iron, iron in the metal phase, and iron in the silicate plus sulfide phases, respectively. In principle, if FeS was present, it could have followed either the metal or the silicate during the fractionation. However, S contents in chondrites do not parallel metallic iron abundances; it is therefore assumed that, if it was present, FeS followed the silicates. If metal is lost or added, it is convenient to define \( \beta \) as the fraction of metal present after fractionation. Thus

\[
\text{Fe} = \text{Fe}^{+2} + \beta \text{Fe}^0 \tag{13}
\]

where Fe is the total iron after fractionation. Analogous relations can be written for Ni, but they are simplified since most of the Ni presumably resided in the metal:

\[
\text{Ni} = \beta \text{Ni}^0 \tag{14}
\]

These equations must now be normalized to a suitable reference element. For present purposes, Mg is used rather
than the conventional Si because the Fe/Mg ratio depends more directly on oxidation state than the Fe/Si ratio, which also depends on the proportion of olivine to pyroxene. Combining (13) and (14) and normalizing to Mg, we obtain

$$\text{Fe}/\text{Mg} = \left(14.90 \pm 0.50\right)\text{Ni}/\text{Mg} + (0.14 \pm 0.015)$$  \hspace{1cm} (16)

A similar plot for the enstatite chondrites is also shown in Figure 8a [cf. Yavne1, 1966]. The least squares line through these points is

$$\text{Fe}/\text{Mg} = \left(15.3 \pm 1.2\right)\text{Ni}/\text{Mg} + (0.00 \pm 0.07)$$  \hspace{1cm} (17)

Both the slope and the intercept of the enstatite chondrite line differ from the slope and intercept of the pooled carbonaceous and ordinary chondrite line by statistically significant amounts. Evidently conditions were more strongly reducing during metal-silicate fractionation of the enstatite chondrites.

Indeed, the fact that the enstatite chondrite line passes through the origin indicates that there was essentially no Fe$^{+2}$ present as either silicate or sulfide. The intercept of the ordinary and carbonaceous chondrite line, however, indicates that in these cases either silicate or sulfide or both were present. Larimer and Anders [1970] argued that sulfide was not present, but a portion of their arguments (those based on the Fe$^{+2}$ contents of the silicates as a function of temperature) are no longer valid, owing to a large relative error in the thermodynamic data [Grossman, 1972a].

a. Direction of fractionation: Primordial composition. In principle, the metal-silicate fractionation may represent the loss of silicates from iron-poor material (e.g., L chondrites [Urey and Craig, 1953]) or loss of metal from iron-rich material (C1 chondrites). Anders [1964] suggested that the convergence of the evolutionary tracks on a plot such as Figure 8a pointed to the primordial composition. The lines defined by (16) and (17) converge at Fe/Mg = 0.74, close to the high-iron end of the spectrum. However, when the uncertainties in the position of the lines are taken into account, the intersection could fall anywhere between Fe/Mg = 1.55 and Fe/Mg = 0.21. Hence none of the known chondrite classes can be disqualified as the starting material on this basis. Opinion currently leans toward the view that C1 chondrites represent the primordial material because they alone appear to have escaped all other fractionation processes. Now that the discrepancy between solar and C1 iron abundances has been eliminated, there is no compelling reason not to accept this view.

The Fe/Mg and Ni/Mg ratios from E chondrites seemingly suggest that some have been depleted and others enriched in metal relative to C1 chondrites (Figure 8a). These ratios are misleading, however, because appreciable amounts of Mg, our normalization standard, apparently were lost during refractory element fractionation (see section C). When a correction for this effect is applied (Figure 8b), all chondrites have lower Fe/Mg ratios than C1 chondrites. The fractionation thus seems to have been unidirectional, involving only loss, not gain, of metal. The maximum loss appears to have been \textasciitilde 50%.

b. Temperature and mechanisms of fractionation. The temperature during fractionation can be delimited from known abundances of other siderophile elements of increasing volatility by using their predicted condensation temperatures as a guide. The reasoning is that, for an element to be depleted along with Fe and Ni, it must have condensed onto the metal grains prior to the fractionation event. It turns out that Ir, Co, Au, Pd, and Ge are systematically less abundant in L chondrites than in H chondrites by an average factor of 0.64 (Table 5). An upper limit of $T \leq 1000^\circ$K is inferred (at $P_{\text{sat}} = 10^5$ atm) because elements less volatile than Ge correlate with Fe and Ni, but more volatile elements (Ga) do not. Similarly, a lower limit of about 650$^\circ$-700$^\circ$K is implied because the amount of S condensed as FeS at the time of fractionation could not have exceeded about 10% in the case of enstatite.
chondrites and about 20–30% for ordinary and carbonaceous chondrites, as is deduced from the intercepts of the evolutionary tracks. A variety of mechanisms have been proposed for the metal-silicate fractionation on the basis of density, brittleness, volatility, and magnetism [Urey, 1952a, b, 1954; Wood, 1962]. Of these factors, volatility and magnetism are of special interest here. As was discussed earlier (section C), at high pressures (>7 x 10⁷ atm), metal condenses before the bulk of the silicates. If accretion took place during condensation [Turekian and Clark, 1969], the innermost regions of a planet that accreted at higher pressures would consist largely of metal, and if pressure increased toward the center of the nebula, as might be expected, the metal contents should increase correspondingly, as is observed. For chondrites, however, a different mechanism suggests itself, which may or may not be applicable to the planets. The upper temperature limit inferred from chondrite compositions, T ≤ 1000°K, falls close to the ferromagnetic Curie point of Fe/Ni grains with the predicted compositions. This may simply be a coincidence, but perhaps it is essential, the fractionation being triggered by the onset of ferromagnetism in the metal grains. There is a growing body of independent evidence that metal and magnetite grains in meteorites were subjected to weak magnetic fields, probably while still dispersed in the nebula [Brecher, 1972; J. M. Herndon, unpublished data, 1972].

The complete picture of metal-silicate fractionation is still unfolding. Larimer and Anders [1970] pointed out that the initial metal condensate is predicted to be enriched in refractory siderophile elements (e.g., Pt and Ir). Some iron meteorites are enriched in these elements [Nichiporuk and Brown, 1965; Wasson and Kimberlin, 1967; Cobb, 1967] and perhaps could be derived from this early condensate. Ehmann et al. [1970] and Müller et al. [1971] pointed out that Ir/Ni ratios among different groups of chondrites vary in a systematic fashion. Possibly this implies that the extent to which the early metal condensate was lost differed in the parent material of each group, a possibility that is expanded on by Grossman and Olsen [1974]. Wasson [1972] presents an alternative view: he argues that the metal-silicate fractionation was a continuous process beginning at high temperatures with the loss of Ir continuing through Au and other less volatile elements. However, the data (Au/Ni ratios) on which the model is based are far from complete, and the scatter is so large that it completely obscures the trends that are alleged to exist (Ehmann et al. [1970]; see also Table 5).

E. VOLATILE ELEMENTS

Urey [1952a, b, 1954] first suggested that volatile trace elements (e.g., Cd, Zn, and Hg) might be used as 'cosmothermometers' to estimate the accretion temperatures of meteorites and the earth. On the basis of the data available at that time, which showed no evidence that these elements were deficient, Urey concluded that both the earth and the meteorites accreted at T ≈ 300°K. The concept of 'cold accretion' has since become rather firmly entrenched in planetary cosmogony.

The situation has changed considerably in subsequent years, however. More precise trace element determinations, largely by neutron activation analysis, indicate that nearly all volatile elements are depleted in most chondritic me-
is that carbonaceous chondrites are a mixture of two components: a high-temperature, volatile-deficient component and a low-temperature, volatile-rich component [Wood, 1963; Anders, 1964]. The trend (C1:C2:C3=1:0.5:0.3) can then be explained by postulating ~100, ~50, and ~30% low-temperature material in the three types of chondrites. Considerable circumstantial evidence exists in favor of the model. Carbonaceous chondrites indeed seem to be comprised of at least two types of material, which, broadly speaking, can be referred to as high-temperature (olivine, pyroxene, metal) and low-temperature (hydrated silicates, S, FeS, FeO) materials. The observed amounts of these minerals seem to vary in roughly the postulated proportions. Moreover, the high-temperature minerals are found in chondrules or chondrule-like objects, and the low-temperature minerals are found in the matrix. There is also direct experimental evidence that the chondrules are depleted in volatiles such as Na and Ga relative to the matrix [Schmitt et al., 1965; Chou and Cohen, 1970]. Oxygen isotope ratios also differ, and these differences have been interpreted to indicate that the matrix formed at a much lower temperature (~350⁰K) than did the chondrules (>1000⁰K) [Onuma et al., 1972].

Among ordinary chondrites a slightly different trace element pattern is observed. Some nine elements (Ag, Cu, F, Ga, Ge, S, Se, Sn, and Te) are depleted relative to C1 chondrites by a factor of 0.227 ± 0.027 [Krähenbühl et al., 1973]. These nine elements obey the same trend as was observed in the case of all volatile elements in C chondrites, the only difference being the larger depletion factor, which implies a larger percentage of the high-temperature component. These nine elements are referred to as 'normal' elements [Anders, 1964]. However, most of the remaining volatile elements are depleted by even larger factors, a factor of up to 10⁴ for the most volatile (e.g., In and Tl). These elements are referred to as 'strongly depleted.' To explain these depletions, some explanation other than mixing components must be found. We shall return to this point momentarily.

2. Formation of Chondrules and Matrix

There have been numerous suggestions as to how chondrules formed in the nebula. The models may be divided into two broad categories: primary and secondary.

a. Primary models. In primary models both chondrules and matrix are thought to be original condensates produced via two different condensation paths: vapor to solid, yielding submicron-sized dust grains (matrix) and vapor to liquid, yielding millimeter-sized droplets (chondrules) by coalescence [Wood, 1962, 1963]. The chondrules would be relatively inefficient collectors of volatiles because, having radii 10⁵ times that of the matrix grains, they would have a surface area 10⁶ times smaller and would take 10⁴ times as long to reach diffusional equilibrium. Qualitatively, this model accounts for the observed textural and compositional relations. Quantitatively, there are problems, however. Vapor to liquid condensation of Mg₂SiO₄ or MgSiO₃ and Fe-Ni grains from a cosmic gas requires pressures of 10 to 10⁵ atm [Suess, 1963; Wood, 1963], much higher than those expected in the nebula (<1 atm). However, there may be ways to circumvent this problem while still retaining the basic framework. Wood [1963] proposed that transient, high-pressure shock waves might occur during the T Tauri stage of solar evolution. Alternatively, Blander and Katz [1967] pointed out that liquids are prone to nucleate before solids even in the stability field of solids. Some of the silicate and metal might therefore condense as liquid droplets even at low pressures.

b. Secondary models. In secondary theories the original condensate is assumed to consist entirely of dust (matrix), some of which is later reheated to form chondrules. Whipple [1966] and Cameron [1966] proposed that lightning discharges might be common in the nebular gas-dust cloud and might provide a suitable reheating mechanism. If such events occurred shortly before accretion but after the bulk of silicates and metal had condensed, time sufficient for the refractory element and metal/silicate fractionations could have elapsed [Larimer and Anders, 1970]. More recently it has been suggested that high-velocity (~1 km/s) impacts between dust grains would be sufficiently energetic to partially melt and outgas the original dustlike condensate to form chondrules [Whipple, 1972; Cameron, 1973b]. At least one chondrule found in the Ngawi meteorite displays evidence of an impact event that partially melted it [Lange and Larimer, 1973]. In further support of a reheating model, Onuma et al. [1972] pointed out that oxygen isotope ratios of separated chondrules and matrix in ordinary chondrites are similar, thus suggesting that both ceased to exchange oxygen with the gas at about the same temperature (~450⁰K), which is quite close to the estimated accretion temperature (section E3). They note that reheating experiments on silicate material on a time scale of hours cause little change in the isotopic ratio.

It should be noted here that only in the idealized form of the two-component model is the high-temperature fraction assumed to be completely devoid of volatiles. In reality, whatever the mechanism of formation, elements of intermediate volatility might be only partially outgassed or condensed. Indeed, several elements (e.g., As, Au, Rb, and Sb) have anomalous depletion factors of 0.9–0.4 or so in some chondrites [Laul et al., 1973; Case et al., 1973]. These elements, referred to as 'partially depleted,' might be partially retained in the high-temperature fraction. The P–T conditions under which the high-temperature fraction formed (or the initial composition, if formed by reheating) presumably varied from place to place in the nebula, and this may explain why some elements, such as the partially depleted elements and Na, K, and Mn, behave as volatile elements in C chondrites and as partially depleted or non-volatile elements in ordinary and E chondrites [Larimer and Anders, 1967; Laul et al., 1973].

3. Temperature and Pressure

Whatever their mode of origin, one can attempt to deduce a 'condensation temperature,' defined as the temperature at which the material ceased to equilibrate with the gas, for the two components. In C chondrites the high-temperature fraction contains magnesium silicates and metal but is depleted in alkalis and all other more volatile elements. The temperature range at which material of this composition ceased to equilibrate with the gas is inferred from Figure 2 to be about 1200⁰ to 1300⁰K. In the case of the high-temperature fraction in ordinary and E chondrites the alkalis and Mn, along with such elements as As and Au, are either not depleted or are only partially depleted, thus
implying a slightly lower temperature or higher pressure of equilibration with the gas.

a. Accretion conditions. The composition of the matrix provides information that may be of far greater significance than the composition of the chondrules. The temperature at which this material ceased to equilibrate with the gas, as deduced from elemental abundances, presumably is close to the temperature at which the meteorites accreted. There is, of course, the possibility that some elements were redistributed after accretion during metamorphism [Dodd, 1969]. This will be considered an alternative working hypothesis that will be tested by comparing the observed abundances to those predicted from the condensation calculations.

The matrix in C chondrites contains its full complement of volatile elements (Pb, Bi, Tl, and In) plus hydrated silicates and magnetite. A condensate of this composition would be stable in a cosmic gas only at temperatures less than about 400° to 350°K (Figure 2). Thus, as was pointed out by Urey [1952a, b], these meteorites must have accreted at rather low temperatures. The condensation temperatures of the volatile elements as well as the formation temperature of the hydrated silicates (which, incidentally, is not well established) are dependent on pressure. But the formation temperature of FeO, which is well established, is independent of pressure; hence the upper limit of 400°K is firm. Anders [1972b] has reviewed the formation temperatures of CI chondrites on the basis of data from a variety of thermometers, both pressure-dependent and independent (Table 6). The results are remarkably concordant, especially considering that each thermometer involves assumptions that, although they are individually vulnerable, were not made with a conscious effort to achieve concordancy.

The fact that the nine so-called normal elements are depleted by constant factors in ordinary chondrites, whereas the remaining volatiles, in general, have larger and variable depletion factors, was somewhat of a puzzle to Anders [1964]. Constant depletion factors are, of course, explicable in terms of the two-component models; variable depletion factors are not. Moreover, the extent of the depletions, ranging up to 10° for Bi, In, and Tl, was especially bothersome. This problem was at least partially resolved by Larimer [1967], who noted that the strongly depleted elements are among the most volatile in a cosmic gas and that the extent of depletion is correlated with the predicted condensation temperatures.

Ordinary chondrites contain their full matrix complement of S as FeS. On the other hand, few contain FeO, of indisputable extraterrestrial origin. Both the formation temperature of FeO, (~700°K) and that of FeO, (~400°K) are pressure independent (at the expected low pressures, <1 atm). Thus, ordinary chondrites containing FeS but not FeO, must have formed below 700° and above 400°K. The upper limit is also consistent with the abundances of all the normal elements, whose condensation temperatures are known, because they are all 100% condensed at 700°K. Strongly depleted elements such as Pb, Bi, In, and Tl, however, are predicted to condense at 500° ± 100°K (at P<sub>atm</sub> = 10° atm), consistent with the presence of FeS and lack of FeO. These elements, which are depleted by up to 3 orders of magnitude in ordinary chondrites, may thus have been condensing as accretion was taking place [Larimer and Anders, 1967].

At about the time that attention was drawn to the poten-tial use of these volatiles as cosmothermometers, Dodd et al. [1967] published a survey of unequilibrated ordinary chondrites. This was followed by the classification scheme of Van Schmus and Wood [1967], who suggested that chondrites could be classified into groups on the basis of their major element chemistry and that, within each group, textural and mineralogical features could be used to rank the meteorites according to what were considered progressive stages of metamorphism. Accordingly, the so-called unequilibrated ordinary chondrites could be placed into the H, L, or LL group on the basis of their total iron content. They were therefore considered to resemble their equilibrated counterparts in all respects but two: their silicate minerals contain variable amounts of iron, and their bulk volatile content seems higher. These observations prompted a large number of studies aimed at determining the volatile element content of ordinary chondrites as a function of increasing metamorphic grade.

It soon became apparent that the noble gases [Marti, 1967; Heymann and Mazor, 1968; Zähringer, 1968], carbon [Moore and Lewis, 1967], lead [Huey, 1972], and bismuth, indium, and thallium [Tandon and Wasser, 1968; Keays et al., 1971; Laud et al., 1970a, b, 1973; Santoliquido and Ehmann, 1972] all drop off in abundance with increasing metamorphic grade. There have been numerous suggestions made to explain these trends, and the issue is not completely resolved. Here, we shall follow the philosophy outlined earlier in this paper and explore the possibility that condensation calculations with equilibration assumed are meaningful. Accordingly, the fine-grained dust (matrix, low-temperature fraction) in the evolving nebula is thought to acquire progressively greater amounts of volatiles with decreasing temperature. Accretion takes place simultaneously, so that the meteorites that accrete last are richest in volatiles and reside nearest the surface of their parent body. There, at the most shallow depths, they are subjected to the least metamorphism. Thus a strict but noncausal relationship between metamorphic grade and volatile content is predicted [Larimer and Anders, 1967].

Condensation curves for Pb, Bi, In, and Tl are shown in Figure 10. For each element the curve is divided into two segments: (1) a linear, high-temperature segment where the elements are predicted to condense as alloys or solid solutions in previously condensed major phases, metal and troilite; and (2) an almost vertical, low-temperature segment where the pure phase condenses. The point of intersection denotes the limit of solubility of the pure phase in the solution. The elements Pb, Bi, and Tl are predicted to behave as metals in the highly reducing cosmic gas. In contrast, the stable gaseous form of indium is predicted to
Fig. 10. Condensation curves of Bi, In, Tl, and Pb. Linear portions at high temperatures represent condensation as alloys or solid solution. After solubility limit is reached (inflection point) elements condense as pure phases. The solid solution portion of the InS curve is less steep than those of the other elements.

**be InS, and its stable condensed form is InS** [Larimer, 1973]. This gives rise to a subtle but significant difference between the predicted condensation behavior of In and that of the other volatiles. The slope of the solid solution portion of the InS curve is distinctly less steep than the slope of the other curves. This means that both the absolute and the relative amounts of the elements are predicted to vary. For example, in the case of In versus Tl the abundance of Tl is predicted to rise rapidly at first relative to In. But at some point \( T \sim 455^\circ\text{K} \) the abundance of In should increase relative to Tl by about 2 orders of magnitude. At lower temperatures the Tl content will continue to rise, whereas the In content levels off.

The analytical data for In and Tl in L chondrites is shown in Figure 11. Superimposed on these data are the predicted trends inferred from the calculations as shown in the previous diagram (Figure 10). Each of the seemingly unique features apparent in the plot of the data follows the predictions of the condensation calculations. This strongly suggests that the trace element contents were indeed established at the time of accretion and were little altered by any later metamorphic event.

Laul et al. [1973] analyzed the trace element data for some 54 chondrites and found that, in general, the analyses are consistent with the equilibrium condensation reactions. However, in a few cases (~7% of the meteorites) enrichments of Ag, Bi, and Tl are observed (Figure 12). The fact that only three volatiles, all predicted to be siderophile, are involved suggests that an unusual phase is present in variable amount, for which Laul et al. coined the term 'mysterite.' It was first discovered in Supuhee, a light-dark-colored, brecciated H chondrite. Mysterite has yet to be actually separated from a meteorite, and hence its reality is still debatable. However, Laul et al. offer the plausible suggestion that it is a late condensate that was mixed into chondritic material, perhaps during the impact event that caused the brecciation.

The element pair Bi-In are of considerable interest because their condensation curves switch positions relative to one
another at pressures slightly higher than $10^4$ atm [Larimer, 1973]. At lower pressures, In condenses before Bi; at higher pressures the reverse is true. Thus meteorites that accrete from dust that has equilibrated with the gas at lower pressures are predicted to contain more In than Bi. Meteorites that form at higher pressures would contain more Bi than In. Interestingly, the data from H and L chondrites display rather large differences in their Bi/In ratios (Figure 13). L chondrites that contain 1–10 ppb Bi have Bi/In ratios distinctly less than 1, whereas H chondrites with similar Bi contents frequently have Bi/In ratios of the order of 100 or more. This can most simply be interpreted as indicating that the H chondrites accreted under slightly higher pressures than L chondrites, or slightly higher than $10^4$ atm.

The elements Bi, In, and Tl have now been measured in about 100 ordinary and enstatite chondrites. From these data, 'accretion temperatures' can be calculated. Histograms showing these results are presented in Figure 14. The calculated temperatures are based on assumed pressures of $10^4$ (L and LL chondrites) and $10^5$ (H and E chondrites), in keeping with the pressure estimates discussed above. The calculated temperatures are remarkably concordant for all three elements. This provides additional support for the assumption that the trace element contents were established at the time of accretion. A large majority of the members in each group appear to have accreted over a rather narrow temperature interval. Exactly how narrow an interval is debatable; conceivably some chondrites could represent a mixture of materials formed at different temperatures, and the resulting trace element content would be simply an average. However, the pieces could not have formed at grossly different temperatures (>10° to 15° apart) and have been mixed together to yield the type of trends observed in Figures 11, 12, and 13 [Laul et al., 1973]. The averaged temperatures are about 450° to 460°K for the L and LL chondrites and 470° to 480°K for the H and E chondrites (at Ptot = $10^4$ and $10^5$ atm, respectively).

Accretion temperatures quite similar to these have been inferred from oxygen isotope studies [Onuma et al., 1972]. In fact, when the temperatures inferred for individual meteorites from $^{18}O$/$^{16}O$ measurements are compared with those based on trace element contents, the agreement almost exceeds expectations (Table 7).

In further support of these arguments, Onuma et al. pointed out that if a large percentage of each chondrite family accreted over a fairly narrow temperature range, the quantized oxidation states might be explained. The oxidation state of silicates in equilibrium with a cosmic gas can be obtained from the relation [Larimer, 1968, 1973]:

$$\log N(Fe_3SiO_8) = 1550 \pm 20 - 0.92 \pm 0.5 - \log H_2/H_2O$$  \hspace{1cm} (18)$$

where \(N(Fe_3SiO_8)\), the mole fraction of fayalite in olivine, is virtually equivalent to the Fe/(Fe + Mg) ratio of the silicates. Substituting the observed \(N\) values of 0.19 for H chondrites and 0.25 for L chondrites, along with the predicted \(H_2/H_2O\) ratio of 0.40 [Grossman, 1972a], temperatures of 515°–518° and 485°–498° deg are calculated. The large absolute error arises from uncertainties in the thermodynamic data, but the difference in temperature, 20° ± 5°, is subject to a smaller error and almost exactly corresponds to the difference inferred from the oxygen isotope measurements. The arguments for assuming that the trace element contents can be used as cosmothermometers are thus reinforced by two independent thermometers as well as by their own internal consistency.

4. Other Models

Several other points of view have been developed in which volatile content is not considered a useful guide to accretion temperature. However, none of these models offer quantitative predictions such as are offered by the model outlined here, making their validity difficult to judge on the basis of available data.

a. Metamorphism. Dodd [1969] summarized the arguments for redistribution of volatiles during metamorphism. The model currently provides no means of predicting correlations between element pairs, except that volatiles are expected to be more thoroughly outgassed and hence more strongly depleted in the most highly metamorphosed chondrites. The problem is that the outgassed volatiles should recondense in the cooler regions of the body, and therefore the lesser metamorphosed meteorites should have volatile...
Fig. 13. Bi/In ratios frequently drop to \(<\) 1 in L group chondrites but never in the H group. Evidently, pure InS condensed first in the region where L group chondrites formed, and pure Bi condensed first in the region where the H group formed. This implies a slight pressure difference, L group at \(P_{\text{tot}} \leq 10^{-5}\) atm and H group at \(P_{\text{tot}} \geq 10^{-4}\) atm. In most cases, the observed data tend to parallel the predicted curves. The one L6 chondrite that falls below the curves is a weathered sample (Modoc), and the H5 chondrites that fall below the solid curve are light-dark structured breccias that may contain mysterite. Symbols as in Figure 11.

Contents greatly in excess of their cosmic abundance [Larimer and Anders, 1967]. But such enrichments are not observed. To avoid this difficulty, Wasson [1972] proposed that the parent bodies were heated externally. The most highly metamorphosed meteorites thus are thought to reside near the surface of their parent bodies, where the outgassed volatiles can escape into the surrounding nebula, which is heating rather than cooling. No independent evidence exists to support such a model, and there are obvious difficulties in heating the nebular gas-dust cloud several hundred degrees in this stage of its evolutionary history. But regardless of the physical setting hypothesized, the validity of the heating and outgassing model hinges on its ability to account for the observed elemental and isotopic correlations. So far, no quantitative analysis of this problem has been attempted.
b. Constrained equilibrium, multicomponent model. Bland and Abdel-Gawad [1969] have proposed a model in which the gas must be supersaturated with respect to an element or compound before it condenses. Accretion in this model takes place in a cooling nebula through a progression of steps from grains to chunks of ever increasing size. The formation of chunks effectively isolates the material from the surrounding gas over a range of temperatures. The final elemental and isotopic composition of a meteorite thus reflects the proportion of chunks to fine-grained material. There are at least two problems that confront this model. First, it predicts that the observed trace element contents should bear, at most, only a superficial resemblance to predictions based on complete equilibration. Its validity thus rests to some extent on the failure of the equilibrium condensation model discussed above, where the agreement between prediction and observation was good to excellent. Second, if chunks were separated from the gas over a range of temperatures and contained chondrules that formed at even higher temperatures (> 1000°K), oxygen isotope ratios should display large variations. But they do not; each group of ordinary chondrites has its own rather narrow range of \(^{18}O/^ {16}O\) ratios [Onuma et al., 1972], which is more consistent with the chunkless, equilibrium condensation models.

### Table 7. Trace Element and \(^{18}O/^ {16}O\) Based Accretion Temperatures

<table>
<thead>
<tr>
<th>Meteorite*</th>
<th>Average Trace Element In Content (^{18}O/^ {16}O)†</th>
<th>P(_{\text{tot}}) = 10(^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tieschitz H3</td>
<td>445 ≤ 445 ≤ 445</td>
<td>448</td>
</tr>
<tr>
<td>Allegan H5</td>
<td>478 ± 02 476</td>
<td>475</td>
</tr>
<tr>
<td>Beardsley H5</td>
<td>478 ± 03 475</td>
<td>460</td>
</tr>
<tr>
<td>Pantar H5</td>
<td>490 ± 20 478</td>
<td>465</td>
</tr>
<tr>
<td>Pultusk H5</td>
<td>490 ± 20 478 461</td>
<td></td>
</tr>
<tr>
<td>Richardson H5</td>
<td>470 ± 10 478 480</td>
<td></td>
</tr>
<tr>
<td>Khojar L3</td>
<td>450 ± 06 456 449</td>
<td></td>
</tr>
<tr>
<td>Bjurbolle</td>
<td>L4</td>
<td>457 457 455</td>
</tr>
<tr>
<td>Farmington L5</td>
<td>458 ± 03 458 458</td>
<td></td>
</tr>
<tr>
<td>Harleton L6</td>
<td>465 ± 10 458 458</td>
<td></td>
</tr>
<tr>
<td>Holbrook L6</td>
<td>458 458 455</td>
<td></td>
</tr>
<tr>
<td>Soko Banja LL4</td>
<td>457 457 455</td>
<td></td>
</tr>
<tr>
<td>Olivenza LL5</td>
<td>456 456 456</td>
<td></td>
</tr>
</tbody>
</table>

* Italicized meteorites are breccias, contain mysterite, or both. Mysterite does not contain In; these temperature estimates are perhaps more reliable than estimates based on Bi or Ti. † Reuter et al. [1965]; Onuma et al. [1972]. Italicized values are based on matrix.

F. ORGANIC MATTER

The origin and nature of organic matter in the early solar system is naturally of great significance from a biological viewpoint. Extensive recent reviews on the nature [Hayes, 1967] and origin [Anders, 1971a] of organic matter in meteorites provide the source of much of the material in this section. We are primarily concerned here with the types of compounds that might be expected in the nebula and what is actually preserved in primitive meteorites.

The study of organic material in primitive meteorites presents formidable analytical problems owing to the possibility of terrestrial contamination. Carbonaceous chondrites contain appreciable carbon, up to 4%, mostly in the form of an insoluble, aromatic polymer similar to coal. Some carbon also exists as carbonates and a variety of other compounds. Ordinary chondrites contain little carbon (0.01-2.0%, according to Moore and Lewis [1967]), which is of largely unknown chemical form, although this carbon too may be mostly an aromatic polymer [Hayes and Biemann, 1968]. The abundance pattern of carbon in chondrites can best be described as a general decrease in carbon content with increasing petrologic type. But there are numerous exceptions [Dodd, 1969] suggesting that the geochemical
history of carbon is complex, as might be expected. Hayes [1967] has attempted to explore the possibility that the types of compounds found vary with petrologic type. But except for an interesting but unexplained variation in the proportion of \( n \) alkanes/\( C_n \text{H}_{2n} \), isoprenoids, the data are insufficient to draw generalizations.

Anders [1971a] pointed out that a significant feature of the identifiable hydrocarbons in C chondrites is that the compound distribution is not random. Instead, straight chain hydrocarbons dominate; they are far more abundant than their branched chain counterparts. The straight chain configuration, however, represents only one out of \( 10^9 \)-10 \( \) possible configurations for molecules with 15-20 carbon atoms. This suggests a highly selective mechanism of formation. Also, in C chondrites the carbon present as carbonates is 7-8% richer in \( ^{13} \text{C} \) than the organic carbon [Clayton, 1963; Briga, 1963; Krouse and Modzeleski, 1970; Smith and Kaplan, 1970]. Although fractionalizations of this magnitude are theoretically possible in nature at very low temperatures (<273 °K), they are never observed.

When comparisons are drawn between the observed carbon compounds and those predicted by a model, it is necessary to bear in mind that even the primitive carbonaceous chondrites may have experienced a mild metamorphism [DuPrese and Anders, 1962]. The chemistry of carbon during metamorphism is not well understood. Conceivably, there may be some degradation of the original compounds or more complex compounds such as the coallike polymer may be produced. In fact, thermodynamic calculations [Dayhoff et al., 1964] confirmed experimentally [Eck et al., 1966] show that complex aromatic compounds form metastably when the H/C ratio drops below a critical value.

Nonetheless, it is of interest to attempt to understand the behavior of carbon in the nebula. The thermodynamics of carbon in a gas of cosmic composition has been studied extensively [Urey, 1953; Suess, 1962; Dayhoff et al., 1964]. At high temperatures, CO is the dominant carbon-bearing compound, but it becomes progressively less stable on cooling and transforms to \( \text{CH}_4 \) according to the reaction

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (19)
\]

This reaction is pressure dependent, proceeding to virtual completion at 450°-750°K at pressures of \( 10^{-5} - 10^{3} \) atm. But if the reaction had gone to completion in the nebula, methane would not have condensed until the temperature dropped to 100°K or less. There would thus be no carbon in the inner solar system. Since there is a fair amount of evidence to the contrary, it is necessary to deviate from our assumption of complete chemical equilibrium in the nebula. This is not an unexpected development because, as Urey [1953] pointed out, the reaction (19) probably would not proceed smoothly in the absence of a suitable catalyst. Instead, the reaction path followed may have involved less volatile intermediaries such as graphite and other complex carbon compounds. Presumably, the compounds found in carbonaceous meteorites represent such intermediaries or possibly their reaction products.

Anders [1971a] developed a strong case for the nebular formation of hydrocarbons by catalytic reactions. Studier et al. [1965, 1968, 1972] have attempted to determine experimentally how CO and \( \text{H}_2 \) behave in the presence of natural catalysts expected in the nebula, e.g., nickel-iron, magnetite, and hydrated silicates. Hydrogenation of CO in the presence of an iron or cobalt catalyst is known industrially as the Fischer-Tropsch reaction. Significantly, it produces mainly straight chain or slightly branched hydrocarbons of the general formula \( C_n \text{H}_{2n} \), according to reactions such as

\[
10\text{CO} + 21\text{H}_2 \rightarrow C_{10}\text{H}_{22} + 10\text{H}_2\text{O} \quad (20)
\]

The hydrocarbon distribution produced in these experiments resembles that found in C chondrites (Figure 15) as well as that in certain oil shales and natural gases [Friedel and Sharkey, 1968]. It has also been shown that these catalytic reactions produce a fractionation of carbon isotopes in just the right direction and magnitude at 400°K [Lancet and Anders, 1970]. This temperature is significant because it is close to that predicted for C chondrite accretion (section 2b). Moreover, when \( \text{NH}_3 \) is added to the system, various nitrogen compounds are formed, including many of biological significance, such as amino acids and adenine, guanine, and cytosine, the constituent bases of DNA and RNA [Hayatsu et al., 1968, 1971; Yoshino et al., 1971]. Most of the compounds produced have been observed in C chondrites [Kvenvolden et al., 1971; Hayatsu et al., 1968, 1971; Yoshino et al., 1971].

But there is still some uncertainty as to whether such reactions occur in the nebula or in the parent bodies during metamorphism. The experiments have been conducted with \( \text{H}_2/\text{CO} \) ratios (~500) much lower than those expected (~1000) and at pressures much higher than those predicted for the nebula. In fact, when the pressure is dropped to \( 10^{5} \) atm, no reaction occurs. Conceivably, the original compounds were formed by a different mechanism. The most likely alternative is the Miller-Urey reaction involving irradiation of \( \text{CH}_4, \text{NH}_3, \) and \( \text{H}_2\text{O} \) by UV, \( \gamma \) rays, etc. [Miller, 1953]. Since irradiation produces free radicals that link randomly, this reaction lacks the selectivity required to produce straight chain molecules. Nor does it provide a straightforward means of explaining the fractionation of carbon isotopes. But since a two-step process is possible, the chemistry of carbon in the nebula is still somewhat uncertain.

G. Noble Gases

In this section we shall consider the problem of how the noble gases came to be incorporated into the condensed solid material in the nebula. Both isotopic ratios and absolute abundances of these elements have long been regarded as important clues to the origin of meteorites as well as of the earth and its atmosphere.

The first problem is to identify that fraction of the gases which is 'primordial.' In all accessible solid material from the solar system, including meteorites and lunar and terrestrial rocks, the noble gases are strongly depleted by factors of \( 10^6 \) to \( 10^9 \) or more relative to their predicted abundance in the solar system. Moreover, in some cases a large fraction of the noble gases present are the result of radioactive decay (e.g., \( \text{U}, \text{Th} \rightarrow \text{He}, ^{19} \text{K} \rightarrow ^{20} \text{Ar} \)) or cosmic-ray-induced nuclear reactions. This portion of the gases must, of course, be subtracted to obtain the primordial gas content. In most cases this is accomplished routinely on the basis of isotopic ratios. The remaining gas, however, commonly contains not one but two varieties of primordial gas. In one fraction, called 'solar,' the noble gases apparently were incorporated in their solar proportions and with solar ratios. Such gas is
Fig. 15. Gas chromatogram of hydrocarbons in the range C₁₅ to C₁₆. The synthetic product (S3D) was made by a Fischer-Tropsch reaction. The sample from Nonesuch shale (1.1 × 10⁹ years old) is an n-heptane eluate from a silica gel column. The Murray sample is a volatile fraction, distilled from the meteorite at 200°C [Studier et al., 1968]. Only 6 of the ~10⁴ isomeric hydrocarbons with 16 C atoms are present in appreciable abundance; 5 of these (underlined) are common to all three samples. [After Studier et al., 1972.]

found in all types of meteorites, generally associated with shock and brecciation. It also constitutes the bulk of the noble gases in lunar soils and breccias. This gas is thought to represent implanted and trapped solar wind particles. The second fraction, called 'planetary,' may be of more ancient origin, incorporated at the time of formation. It is this fraction that is of prime importance here (see Pepin and Sigmar [1965] for a detailed review).

Three properties of the planetary gas need to be explained: the amounts, the elemental ratios, and the isotopic ratios [Anders, 1971a]. As was discussed earlier (section E3), the amounts of planetary gas correlate with petrologic type or apparent degree of metamorphism. Absolute abundances of Ar, Kr, and Xe rise by 3 orders of magnitude from type 6 to Cl chondrites [Marti, 1967; Zähringer, 1968; Mazor et al., 1970]. Helium and neon, on the other hand, are found only in carbonaceous and a few of the type 3 ordinary chondrites. The elemental ratios of Ar/Kr and Ar/Xe remain constant to within a factor of 6 over the 3 order of magnitude range in absolute abundance. Although there have been suggestions that all the noble gases are isotonically fractionated in the planetary component relative to the solar component [e.g., Manuel et al., 1972], the strongest evidence is in the case of He and Ne. The solar component, presumably reflecting the composition of the sun, is relatively enriched in the light isotopes: \(^{4}\text{He}/^{3}\text{He} = (3.79 ± 0.40) \times 10^{-5}, {^{20}\text{Ne}}/{^{22}\text{Ne}} = 12.5 ± 0.2.\) In comparison, the ratios in the planetary component are:

\[(1.43 ± 0.4) \times 10^4 \text{ and } 8.2 ± 0.4 \text{ [Jeffery and Anders, 1970; Black and Pepin, 1969].}\]

There is evidence, though not entirely unambiguous, for other types of neon, with \(^{20}\text{Ne}/^{22}\text{Ne} < 3.4, {^{22}\text{Ne}}/{^{20}\text{Ne}} = 11.2, \text{ and } {^{20}\text{Ne}}/{^{22}\text{Ne}} \geq 14 \text{ [Black and Pepin, 1969; Black, 1970].}\]

The suggestions put forth to explain these differences in isotopic ratios have been summarized by Anders [1971a]. The most obvious explanation, mass fractionation by gravity or diffusion, is deemed unlikely because the expected correlations in elemental abundance and isotopic ratios are not observed [Pepin, 1967; Jeffery and Anders, 1970]. One possible explanation for the low \(^{20}\text{Ne}/^{22}\text{Ne} \text{ ratio in planetary gas is that 2.6-year } ^{21}\text{Na} \text{ was formed in the silicates by a charged particle irradiation in the nebula and decayed to } ^{21}\text{Ne} \text{ [Jeffery and Anders, 1970]. The variation in } ^{22}\text{He}/^{20}\text{He} \text{ might reflect a gradually increasing } ^{20}\text{He} \text{ content at the} \]
solar surface with time (E. Shatman, quoted by Eberhardt et al. [1970]) or may be due to differential acceleration of the two isotopes in the solar wind (Geiss et al., 1970).

The incorporation of the planetary fraction into solid grains in the nebula may have proceeded by adsorption, partial solubility equilibrium, or perhaps some combination of the two mechanisms. The reported experimental data are limited. Fanale and Cannon [1972] have reported adsorption data for the noble gases on crushed C chondrite (Allende) material in experiments conducted at 113°K. They find that the heavier noble gases are preferentially adsorbed, just as is required to explain the enrichment of the heavier gases in planetary gas relative to the solar or cosmic gas. But the experimental temperature is rather low, which is possibly appropriate for carbonaceous chondrites but not for ordinary chondrites. Perhaps adsorption was the first step, followed by grain growth and trapping or partial solubility equilibrium.

The reported data on the solubility of noble gases in pertinent mineral phases is limited to studies on silicate melts at T = 1800°K (Gerling and Levsiku, 1956; Kirsten, 1968) and on solid magnetite at T = 450°K [Lancet and Anders, 1973]. This latter study is of special interest because FeO occurs in C chondrites and the experimental temperatures are close to the predicted accretion temperatures. Moreover, whereas the earlier high-temperature experiments on silicate melts indicated very limited solubility of the heavy noble gases (Ar, Kr, and Xe), the low-temperature experiments on magnetite indicate extensive solubility. This, in part, solves a perplexing problem, because if the solubility were as low as is indicated for silicate melts, enormous partial pressures of the gases (~10^6 atm) were required to account for the observed abundances for solubility equilibrium to be a feasible mechanism. The data are far from complete, however. Magnetite occurs only in C chondrites, and no solubility data have been reported for other minerals. Data for Xe would be particularly interesting, because to account for the amounts in type 3 chondrites seemingly will require an enormous distribution coefficient between solid and gas (~10^4). This would imply a strong bond between Xe and the host phase, corresponding to a heat of solution of about ~20 kcal/mole. The Xe content of chondrites correlates with the content of the other volatiles, e.g., In. It is therefore of interest to predict the variation of Xe content in the condensate as a function of decreasing temperature on the assumption that the heat of solution (ΔH_s) is ~20 kcal/mole or that adsorption and grain growth accomplished the same effect. The predicted and observed amounts of Xe and In can then be compared in a manner analogous to our previous comparisons of volatiles. The data are compared with predictions based on this assumption in Figure 16. As can be seen, the fit to the theoretical curves is far from impressive. However, the data do not fit any other simple trend, either. Tandon and Wasson [1968], on the basis of fewer data, argued that there was a linear correlation between these elements, but this is clearly no longer the case. The scatter in the data could arise from a variety of factors, such as redistribution of Xe during metamorphism, incomplete equilibration, or the fact that the model may be deficient in that the noble gases may not bear a simple relation to accretion temperatures.

H. Conclusions and Implications

1. Chondritic Meteorites

Many of the chemical, mineralogical, and textural features of chondritic meteorites can be explained by processes
that occurred in the solar nebula prior to and during accretion. A relatively small number of fractionation processes (at least four) are required to explain the abundances of nearly all the elements. The processes presented in outline form are:

1. Highly refractory material rich in such elements as Ca, Al, and Ti moved around in the inner solar system, becoming preferentially depleted in some types of chondrites (enstatite and ordinary) and possibly enriched in the outer regions of the earth and moon. Some fraction of metal, also rich in refractory siderophiles, may have been involved.

2. A major fractionation of metal from silicate grains took place between 1000ø and 700øK. This event certainly affected the parent material of chondrites and may in part account for the density differences among the planets. This upper temperature limit is close to the ferromagnetic Curie point of the metal (950ø to 900øK), suggesting that the onset of magnetism may have triggered the event.

3. Some time just prior to accretion a fraction of the dustlike condensate was flash-heated, possibly by electric discharges or by collisions between dust grains, to produce volatile-deficient chondrules.

4. The unaltered dust continued to equilibrate with the gas, becoming gradually enriched in volatiles (e.g., In, Tl, and Xe). This dust (matrix) accreted together with varying amounts of chondrules at \( T = 450° \pm 50°K \) and a pressure of about \( 10^{-8} \text{ atm} \) for ordinary chondrites and \( T = 350° \pm 50°K \) and a pressure of about \( 10^4 \text{ atm} \) for C chondrites. Each group of ordinary chondrites accreted over a fairly narrow temperature range (\( \pm 10° \text{ to } 20°K \)), the H group forming near 470°K and the L and LL groups near 450°K.

2. Application to the Chemistry of the Planets

The study of chondritic meteorites tells us that chemical fractionations occurred at high temperatures during the condensation of the solid matter of the solar system. There no longer seems to be any compelling reason to postulate that the bulk composition of any particular planet is the same as that of the nonvolatile fraction of solar system matter, an assumption that dominated many earlier theories [e.g., Ringwood, 1966].

a. Inhomogeneous accretion of the earth. Homogeneous accretion models are defined as those in which the starting materials that accumulate to form the planet have the same bulk composition throughout the formation process. Inhomogeneous accretion models are those in which protoplanetary materials vary in composition at different stages of the accumulation process.

Eucken [1944] proposed the first inhomogeneous accretion model to make use of chemical fractionation during condensation. He proposed that the iron of the earth's core condensed and began to accrete before the condensation of the magnesium silicates. Larimer and Anders [1967] and Anders [1968] suggested that the earth can be thought of as being composed of a high-temperature, volatile-free interior coated with a volatile-rich veneer that formed at lower temperature in the nebula. Inspired by these papers, Turekian and Clark [1969] and Clark et al. [1972] proposed that the entire earth accreted materials in their order of condensation at \( 10^5 \text{ atm} \) as the nebula cooled. This produced a zoned primitive earth, with the ratio of metallic iron to magnesium silicates decreasing from the core outward. The earth heated up during this process, causing liquid iron to sink into the core, separating itself completely from the silicates and perhaps incorporating elemental silicon. Finally, as the earth cooled, volatile-enriched material was added as a veneer composing up to 20% of the mass of the earth. The model was suggested to avoid some of the outstanding geochemical difficulties of the Ringwood [1966] model. Since the core was not produced by in situ reduction of iron oxide, no massive primitive atmosphere of CO was produced. Because the outer 20% of the earth was never in contact with the iron in the core, its high siderophile element content and oxidized nature are no longer the serious problems that they were for Ringwood [1966].

b. Two-component model: Accretion temperatures. The success of the model used to account for the elemental and isotopic composition of chondrites naturally suggests that it might be applicable to the planets as well. Of course, at the present state of knowledge there is no reason to expect both large and small bodies to be equally affected by the same processes. Nonetheless, it is instructive to explore the possibility.

Laul et al. [1972] have estimated accretion temperatures for the earth, moon, and various groups of differentiated meteorites on the basis of volatile element content and oxygen isotope ratios [cf. Anders, 1972b]. First, it is necessary to estimate the proportions of high- and low-temperature fractions. Laul et al. note that igneous differentiation processes evidently do not cause appreciable fractionation in the case of K/U, Rb/U, and Cs/U ratios. Since U is considered a nonvolatile element and the alkalis are considered 'normal' elements, these ratios, which are nearly constant in all lunar and terrestrial rocks, may give the proportion of low-temperature material in a nonhomogeneous planetary body. Moreover, Ti/Rb and Tl/Cs ratios are also constant in both lunar and terrestrial igneous rocks. These ratios should then yield the proportion of the Tl condensed into the low-temperature fraction.

The results, presented in Table 8, are rather surprising. All the various types of meteorites, both differentiated and undifferentiated, as well as the earth and moon, yield quite similar temperatures. If these values are accepted uncritically, they would seem to imply that only a very slight thermal gradient existed across the inner solar system during accretion.

Of course, the interpretation must be tempered somewhat since the temperatures deduced may be only averages for the low-temperature component. If this is the case, then the temperatures have little significance except as a curious coincidence. Such arguments, however, can be used to place severe constraints on the relative amounts of high- and low-temperature condensates incorporated into planetary-sized objects.

c. Composition and origin of the moon. The enrichment of the lunar soils, breccias, and igneous rocks in refractory elements and their depletion in volatiles is now well documented. See, e.g., Ganapathy et al. [1970], Taylor et al. [1971], and Wänke et al. [1973]. A figure from Ganapathy et al. [1970, Figure 17] illustrates the 10- to 100-fold enrichment of Ca, rare earths, Zr, Hf, Ta, and other refractories in Apollo 11 igneous rocks, as well as the depletion of alkalis, halogens, and volatile transition metals (Bi, Tl, and Hg) relative to Cl chondrites. This general
pattern has been observed in the rocks of later missions except for some relatively minor local deviations. Gast et al. [1970] suggested that even the source regions of the Apollo 11 lavas are enriched in refractories and depleted in volatiles and that this is due to preferential lunar accretion of high-temperature condensates. Gast and McConnell [1972] proposed that the outer 20–30% of the moon is enriched in refractories by at least a factor of 5 owing to the late accretion of a refractory condensate-rich outer layer. Anderson [1972, 1973] postulated that the entire moon is composed of preiron condensates like the Allende inclusions, except for perhaps a very minor, late-stage chondrite veneer. Anderson attributed the moon’s anomalous composition to its accretion from material that condensed above the median plane at lower pressure than did the material that formed the earth. Cameron [1972c] argued for lunar accretion inside the orbit of Mercury, at very high temperatures, to account for this postulated composition. Wänke et al. [1973] have suggested a moon containing 63% high-temperature condensates and 37% chondrites.

Examination of Figure 17, however, shows that the enrichment of the lunar surface rocks in refractory elements is not uniform, and some additional chemical constraints can be specified. Thermodynamic calculations suggest, and the Allende inclusions confirm, that the high-temperature condensates are enriched in the refractory siderophile elements (Re, Os, and Ir) as well as the lithophiles. As was pointed out by Ganapathy et al. [1970], Figure 17 shows that these elements are dramatically depleted in the lunar rocks. If the moon is nearly 100% high-temperature condensates [Anderson, 1972, 1973], these elements must also be en-

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**TABLE 8. Accretion Temperatures**

<table>
<thead>
<tr>
<th>Object</th>
<th>Heliocentric Distance, AU</th>
<th>$P_{\text{tot}}$, atm</th>
<th>Low-T Material, percent</th>
<th>Temperature, °K</th>
<th>$^{18}O/^{16}O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earth (oceanic basalts)</td>
<td>1.00</td>
<td>$10^{-4}$</td>
<td>11</td>
<td>468</td>
<td>450–470</td>
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<tr>
<td>Earth (continental basalts)</td>
<td>1.00</td>
<td>$10^{-4}$</td>
<td>11</td>
<td>456</td>
<td>450–470</td>
</tr>
<tr>
<td>Moon</td>
<td>1?</td>
<td>$10^{-4}$</td>
<td>1.5</td>
<td>494</td>
<td>455</td>
</tr>
<tr>
<td>Shergottites</td>
<td>2–3?</td>
<td>$10^{-4}$</td>
<td>21</td>
<td>433</td>
<td>455</td>
</tr>
<tr>
<td>Nakhlites</td>
<td>2–3?</td>
<td>$10^{-4}$</td>
<td>40</td>
<td>438</td>
<td>460</td>
</tr>
<tr>
<td>C1 chondrites</td>
<td>&gt;3?</td>
<td>$10^{-4}$</td>
<td>&gt;85</td>
<td>&lt;394</td>
<td>360</td>
</tr>
<tr>
<td>C2 chondrites</td>
<td>&gt;3?</td>
<td>$10^{-4}$</td>
<td>55</td>
<td>&lt;394</td>
<td>380</td>
</tr>
<tr>
<td>Eucrites</td>
<td>2–3?</td>
<td>$10^{-4}$</td>
<td>0.5</td>
<td>432</td>
<td>475</td>
</tr>
</tbody>
</table>

After Anders [1972b].

* Laul et al. [1972].

† Onuma et al. [1972].

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**Fig. 17.** Lunar surface rocks are depleted in volatiles (Na, Bi, In, Tl) compared with C1 chondrites. They are enriched in the lithophile refractories (Ca, La, Zr, Ta) but are depleted in the siderophile refractories (Re, Os, Ir). (Modified from Ganapathy et al. [1970].)
enriched in the total moon by the same factors as the refractory lithophile elements. Their absence from the surface rocks would suggest their efficient removal during melting and density separation of liquid iron. The postulate that the moon is 100% high-temperature condensates thus seemingly leads to the conclusion that it cannot have this composition, but that it also accreted metallic iron which is now at depth in the moon. At the nebular pressures (10^4 atm) required by Anderson [1972, 1973], massive amounts of forsterite should have been incorporated with this iron (see Figure 7). The geochemical evidence thus seems to favor mixtures of high- and lower-temperature condensates rather than pure Ca-rich Allende inclusions.

Clayton et al. [1973] pointed out the difficulty of satisfying the isotopic composition of the moon (8°O ~ +6%) if it is largely composed of Allende white inclusions. These have 8°O ~ −10.5% [Onuma et al., 1972]. As was mentioned earlier, this value is inconsistent with their postulated high-temperature origin. Calculations suggest that, if the Ca-rich aggregates stopped equilibrating their oxygen isotopic composition with the nebular gas at 1400°K, they should have a 8°O no greater than ~−2%. Even if we use this theoretical value rather than the measured one, the chondritic component in the model of Winkie et al. [1973] would have to have an average 8°O of ~+20%. The only meteoritic materials in this range are carbonates from C1 chondrites, the most volatile-rich meteorite type. There is no indication that the total moon has a volatile content as high as 0.37 that of C1 chondrites (see Table 8). The model of Gust and McConnell [1972] requires a mean 8°O of +8.0 to +9.4% for the nonhigh-temperature condensate fraction of the moon. Condensate assemblages having this value (C2 chondrites) have a volatile element content equal to 0.5 that of C1 chondrites. The total moon would again be predicted to have volatile element abundances equal to 35–40% those of C1 chondrites. Thus the requirement that the moon be composed largely of high-temperature condensates to account for its refractory element content necessitates the incorporation of lower-temperature condensates to balance the oxygen isotopic composition. This in turn leads to intolerably high volatile element contents.

4. Compositions of the terrestrial planets. From the densities of the planets, Urey [1967] estimated that the Fe/Si ratio of Mercury is a factor of 3 greater than that of the earth and 5 times that of Mars. This can be understood in terms of inhomogeneous accretion models [Grossman, 1972a] if pressure and temperature decreased outward from the center of the solar nebula [Hoyle and Wickramasinghe, 1968; Cameron and Pine, 1973]. (See also section D1.) Mercury probably formed from materials that condensed at higher pressure and temperature than those comprising the earth. At the time the nebula was dissipated, all the iron and only a small fraction of the silicates may have condensed on Mercury, whereas the earth may have accumulated an assemblage having a much higher silicate/metal ratio. The bulk of the material of Mars may be low-temperature condensates. Grossman [1972a] and Lewis [1972a] have both commented on the suitability of the postulated temperature and pressure gradients for this process. Alternatively, the ferromagnetic properties of the metal grains, as suggested by the meteorite studies, may have been an important contributing factor.

Lewis [1972a] has stressed that the density differences between Venus, the earth, and Mars may be attributable to different oxidation states of iron and varying sulfur contents rather than to different mean Fe/Si ratios of the planets. This model differs from that of Ringwood [1966] in that the planetary oxidation states are established by condensation equilibrium in a nebular temperature gradient rather than by internal reduction processes. Specifically, the model predicts that S is a major component in the earth's core.

In spite of the differences between the theories discussed here, it is clear that present-day models are moving away from planets made of a particular meteorite type and are moving toward planets made up of varying proportions of the components found in chondritic meteorites.

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