Chemical Processes in the Early Solar System, as Inferred from Meteorites

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Meteorites are the only extraterrestrial samples of matter accessible to man. They are also the oldest. Radioactive dating methods have consistently shown them to be 4.5–4.7 AE ($= 10^9$ years) old, as old as Earth itself and at least 1 AE older than the oldest rocks found on Earth thus far. Meteorites thus contain an ancient archeological record whose counterpart has been destroyed on Earth by geologic processes. The challenge to the cosmochemist is to decipher this record. The clues available to him are chemical and isotopic composition, structure, and mineralogy of meteorites.[1,2] From these he must deduce environmental variables, such as temperature, pressure, oxidation potential, pH, etc., and their variation with time. Meteorites may thus be regarded as the "poor man's space probe."[3]

A great stimulus for this work has come from the recent realization that some meteorites are even more primitive than had been supposed. Some of their properties seem to date back to the time when meteoritic and planetary matter was still dispersed in the solar nebula, a disk of gas and dust from which the planets accreted. Thus there is hope of reconstructing the very earliest history of planetary matter, up to the time when its evolution diverged from that of meteoritic matter.

Classification

Meteorites are divided into three broad classes, differing in their ratio of metal to silicate: irons, stones, and stony irons (Figure 1). Stones comprise 92% of the 778 known falls and are divided into two subclasses: chondrites, characterized by millimeter-sized globules of silicate ($=$ chondrules, after the Greek work $\chi o\nu\delta\rho o\sigma$,

grain), and achondrites, chondrule-free stones differing from chondrites in both texture and composition. Each of these classes is further subdivided on the basis of various secondary criteria, such as structure and Ni, Ca, or Fe^{2+} content (Figure 1).

Chondrites occupy the highest place in the hierarchy of meteorites, being not only the most abundant (84% of all known falls), but also the most primitive in composition. If a sample of solar matter were freed of its volatile elements (H, He, C, and the excess O not required to form metal oxides) the residue would closely resemble the chondrites in composition. On paper, at least, the other classes of meteorites can be derived from chondrite-like material by chemical differentiation. Partial melting would give a metal layer corresponding to the irons and two silicate fractions, corresponding to the Ca-rich and Ca-poor achondrites: a low-melting fraction enriched in Ca and Al and a high-melting residue enriched in Mg. The composition of the products would also be affected by redox conditions. Under strongly reducing conditions, iron would go largely into metal, giving a nickel-poor metal phase (hexahedrites) and iron-free silicates (aubrites). Oxidizing conditions would yield more Ni-rich metal and Fe-rich silicates. Age determinations, though incomplete, support this hierarchy: chondrites seem to be 10^8 years older than achondrites or irons.[4] Hence we shall focus our attention on chondrites.

Chondrites are divided into five subclasses on the basis of their degree of oxidation, as reflected in the chemical state of their iron (Figure 1). All chondrites contain 20–30% Fe, partitioned between *metal* (Ni, Fe), *troilite* (FeS), and the silicates *olivine* [$(Fe,Mg)_2SiO_4$] and *pyroxene* [$(Fe,Mg)SiO_3$]. At one end of the spectrum, *enstatite chondrites* are highly reduced, containing iron mainly as metal or troilite. Their principal silicate, enstatite ($MgSiO_3$), has less than 0.1 mol % Fe^{2+} in

(1) The following books and the review in ref 2 provide further background information: (a) F. Heide, "Meteorites," University of Chicago Press, Chicago, Ill., 1963; (b) B. Mason, "Meteorites," John Wiley & Sons, Inc., New York, N. Y., 1962; (c) J. A. Wood, "Meteorites and the Origin of Planets," McGraw-Hill Book Co., Inc., New York, N. Y., 1968.

(2) E. Anders, *Space Sci. Rev.*, **3**, 583 (1964).

(3) E. Anders, paper presented at the 126th Annual Meeting of American Association for the Advancement of Science, Chicago, Ill., Dec 30, 1959.

(4) C. M. Hohenberg, M. N. Munk, and J. H. Reynolds, *J. Geophys. Res.*, **72**, 3139 (1967).

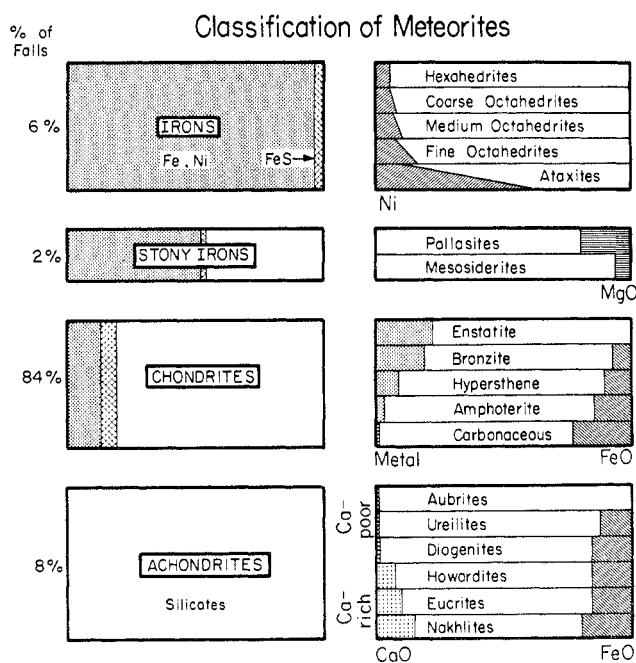## Classification of Meteorites

Figure 1. Meteorites are divided into four broad classes (left) on the basis of their ratio of metal (shaded) to silicate (white). Further subclassification (right) is based on various compositional or structural criteria.

solid solution. At the other end of the spectrum, *carbonaceous chondrites* are highly oxidized. They contain sulfur largely as S_8 or SO_4^{2-} and little or no metal. Most of their iron is present as Fe^{2+} (silicates) or even Fe^{3+} (Fe_3O_4, Fe_2O_3(aq)). Both enstatite and carbonaceous chondrites are quite rare, only ~40 being known.

The broad middle ground is occupied by the *ordinary chondrites*. They are subdivided into three groups, differing in both their state of oxidation and total iron content. The *H-group* chondrites (H = highest in Fe) contain ~27 weight % Fe, with 18 ± 2 mol % Fe^{2+} in their olivine. The *L* and *LL groups* are progressively lower in total Fe (22 and 20%), but higher in Fe^{2+} (24 ± 2 and 29 ± 2 mole % Fe^{2+} in olivine). With less iron to go around and a larger amount taken up by the silicates, the metal content decreases in the sequence H > L > LL from ~19 to ~3% by weight.

Most people believe that meteorites come from the asteroids, small planets situated between Mars and Jupiter. Other sources have been proposed, however: the moon, by Urey,[5] and comets, by Öpik.[6] Both are distinct possibilities for some of the rarer types of meteorites (calcium-rich achondrites, carbonaceous chondrites), but neither seems satisfactory for the common types, irons and ordinary chondrites.[2]

Chemical Composition of Chondrites

Most of the early work in this field served to establish the major element composition. Although some inter-

esting trends emerged from these data, I shall confine myself largely to the more recent measurements, dealing with trace elements.

The first such measurements were done in the 1930's by the Noddacks[7] and by Goldschmidt[8] using X-ray and optical emission spectroscopy. A real breakthrough came in the 1940's with the advent of neutron activation analysis. A wealth of data has been turned out by Ehmann, Goles, Lovering, Reed, Schmitt, Smales, Wasson, and others. Recent reviews were given by Ehmann,[9] Urey,[10] and Larimer and myself.[11]

One of the first trends established in this work was the primitive composition of chondrites. It led to their acceptance as representative samples of nonvolatile cosmic matter and as the basis of the cosmic abundance curve. There are two reasons for this acceptance: the abundances in chondrites resemble those in the sun,[7,12-14] and they seem to be a smooth function of mass number.[13,14] But the latter rule had its exceptions from the very beginning. In 1947, when Suess[13] attempted to construct a cosmic abundance curve on the basis of Goldschmidt's[8] meteoritic data, he noted that certain elements (Se, Te, Ga, In, Tl, Zn, Cd, Hg, and Re) were underabundant relative to their neighbors by factors of up to 100. Since most of these elements were congeners in the periodic table, he suggested that chemical rather than nuclear factors were responsible for their depletion. Subsequent work by Brown and Goldberg[15] showed some of these measurements (Ga, Re) to be erroneous, and for a while it was believed that all such discrepancies would eventually disappear. Urey noted in a series of classic papers[16-19] that volatile metals (Hg, Cd, etc.) in the earth and meteorites might serve as "cosmothermometers," indicating the temperature that prevailed during their accretion from the primitive solar nebula. A careful analysis of the data then available showed no clear-cut evidence of substantial depletion. Urey therefore concluded that the earth and meteorites accreted at a temperature of ~300°K, low enough to allow quantitative condensation of volatile metals.

But the situation changed in subsequent years. Precision measurements by neutron activation analysis showed that some elements were indeed grossly underabundant. Moreover, Reed, *et al.*,[20] made an im-

(5) (a) H. C. Urey, *J. Geophys. Res.*, **64**, 1721 (1959); (b) H. C. Urey, *Science*, **147**, 1262 (1965); (c) H. C. Urey, *Monthly Notices Roy. Astron. Soc.*, **131**, 199 (1966); (d) H. C. Urey, *Icarus*, **7**, 350 (1967); (e) H. C. Urey, *Naturwissenschaften*, **2**, 49 (1968).

(6) (a) E. J. Öpik, *Mem. Soc. Roy. Sci. Liège*, **575** (1965); (b) E. Öpik, *Advan. Astron. Astrophys.*, **4**, 301 (1965).

(7) (a) I. Noddack and W. Noddack, *Naturwissenschaften*, **18**, 758 (1930); (b) I. Noddack and W. Noddack, *Svensk Kem. Tidskr.*, **46**, 173 (1934).

(8) V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo, I, Mat. Naturv. Kl.*, No. 4 (1937).

(9) W. D. Ehmann, *J. Chem. Educ.*, **38**, 53 (1961).

(10) H. C. Urey, *Rev. Geophys.*, **2**, 1 (1964).

(11) J. W. Larimer and E. Anders, *Geochim. Cosmochim. Acta*, **31**, 1239 (1967).

(12) A. E. Ringwood, *Rev. Geophys.*, **4**, 113 (1966).

(13) (a) H. E. Suess, *Z. Naturforsch.*, **2a**, 311 (1947); (b) H. E. Suess, *ibid.*, **2a**, 604 (1947).

(14) H. E. Suess and H. C. Urey, *Rev. Mod. Phys.*, **28**, 53 (1956).

(15) H. Brown and E. D. Goldberg, *Phys. Rev.*, **76**, 1260 (1949).

(16) H. C. Urey, "The Planets," Yale University Press, New Haven, Conn., 1952.

(17) H. C. Urey, *Geochim. Cosmochim. Acta*, **2**, 269 (1952).

(18) H. C. Urey, "Plenary Lectures," XIII IUPAC Congress, London, 1953, p 188.

(19) H. C. Urey, *Astrophys. J. Suppl.*, **1**, [6], 147 (1954).

(20) G. W. Reed, K. Kigoshi, and A. Turkevich, *Geochim. Cosmochim. Acta*, **20**, 122 (1960).

portant observation: elements which are depleted by factors of 10–1000 in ordinary chondrites (*e.g.*, Hg, Tl, Pb, and Bi) often occur in nearly their predicted, "cosmic" abundances in carbonaceous' and enstatite chondrites. Type I carbonaceous chondrites, in particular, tend to match solar composition[12] and are now widely regarded as the best surviving examples of primitive cosmic matter. (Carbonaceous chondrites are divided into three types on the basis of volatile content: C, H, S, and O contents decrease from type I to type III.)

Abundance Patterns. Gradually a pattern emerged:[2,11] 48 elements, mostly in the transition groups of the periodic table (Figure 2), were well-behaved. Their abundances were nearly constant from one class of chondrites to the next and generally matched solar or "cosmic" abundances. But a sizable group of "depleted" elements, some 31 at last count, fell out of line. Their abundances were variable and often fell far below solar or "cosmic" levels.

Let us examine the abundances of depleted elements in *carbonaceous chondrites* (Figure 3). The elements are listed in somewhat unconventional order, based on their depletion pattern in ordinary chondrites. Abundances of the first 26 elements are normalized to those in type I carbonaceous chondrites, which in turn are virtually identical with cosmic abundances. Data for the last five, highly volatile, elements are normalized to cosmic abundances.

It is significant that the abundances decrease consistently from type I to type III.[21] Moreover, they decrease by *constant factors*, as shown by the parallelism of the curves. This parallelism extends even to the last five elements on the chart whose absolute depletion is very much greater. Mean relative abundances for the three meteorite types are 1, 0.55, and 0.32.

Ordinary chondrites show a somewhat different pattern. The points in Figure 4 represent means; error bars indicate the observed range of variation. Manganese and the alkalis (except Cs) show little or no depletion. The next nine elements parallel the type II and III carbonaceous chondrite curves. Deviations from horizontality match in both figures, which suggests that they are due to errors in the type I carbonaceous chondrite data used for normalization. The mean depletion factor is 0.28.

The remaining elements show markedly greater depletion, to a factor of 0.002 for In and Tl. They also tend to be more variable. We shall refer to these elements as "strongly depleted," in contrast to the preceding, "normally depleted," group.

Fractionation Mechanisms. Let us focus our attention on the carbonaceous chondrite pattern, as the simpler of the two. The only property shared by all depleted elements is volatility. Two opportunities exist in the history of meteorites for volatility-dependent fractionations: accretion of meteorite parent bodies from the solar nebula, during which they lost

ELEMENTS DEPLETED IN METEORITES

Figure 2. With the exception of Mn, all depleted elements (shaded) are situated in the main groups of the periodic table. Their only common property is volatility.

their complement of gases (H₂, He, etc.), and subsequent reheating in these bodies. The separation of dust from gas during accretion of the planets was the first, and probably largest, chemical fractionation in the solar system.[22] Let us therefore see whether the trace element depletion could have occurred at the same time.

We can at once dismiss the simplest explanation: that the constant depletion factors resulted from partial condensation or partial volatilization of the elements in question. Conditions for fractionation in a cooling solar nebula were discussed by Urey[16–19] and more recently by Lord[23] and by Larimer.[24] Briefly, an element E remains gaseous if its vapor pressure P_e exceeds its partial pressure in the nebular gas; otherwise it condenses.

It can be shown that the condition for partial condensation of some fraction $(1 - \alpha)$ is

$$P_e(T) = 2\alpha P_t(E/H) = \alpha E \cdot \text{const}$$

where E and H are the atomic abundances of element E and hydrogen, and P_t is the total pressure.

If the fraction condensed is to remain constant for a series of elements, the ratio of vapor pressure to cosmic abundance, P_e/E, likewise must remain constant. Cosmic abundances of many trace elements in Figure 3 lie within the narrow range of 0.1–1 atom per 10^6 Si atoms, but their vapor pressures vary by much larger factors. There exists *no single temperature* at which the ratio P_e/E is the same for any 5 of these elements, let alone 26.

The only way to account for the observed pattern is to assume that the meteorites are a mixture of two materials: a high-temperature fraction that lost all its volatiles and a low-temperature fraction that retained them. To explain the observed depletion factors, one can postulate that type I carbonaceous chondrites contain 100% low-temperature fraction, type II, 55%, and type III, 32%.

There exists some circumstantial evidence favoring this model. Broadly speaking, the minerals of carbonaceous chondrites can be divided into two groups: high-

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(21) Apparent exceptions occur at Au, Cl, Br, and Bi, but past experience suggests that these may be due to sampling or analytical errors. Some points are based on only one or two measurements.

(22) H. Suess, *Ann. Rev. Astron. Astrophys.*, **3**, 217 (1965).
(23) H. C. Lord, III, *Icarus*, **4**, 279 (1965).
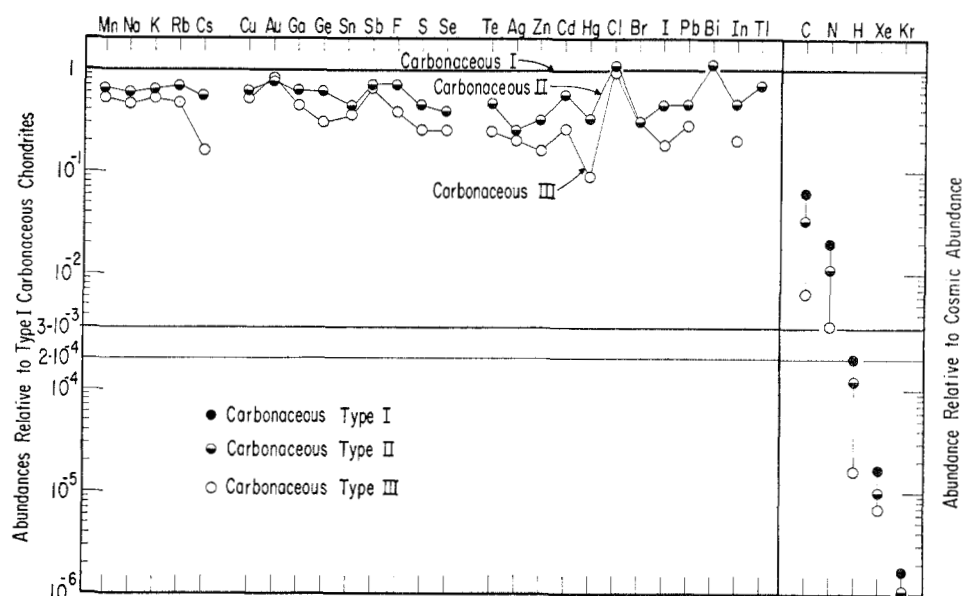(24) J. W. Larimer, *Geochim. Cosmochim. Acta*, **31**, 1215 (1967).

Figure 3. Depleted elements are underabundant in type II and III carbonaceous chondrites by nearly constant factors. Even for the strongly depleted elements C to Kr, relative abundances in types I, II, and III stand in nearly constant ratio (1:0.6:0.3) (data from ref 11 with minor revisions).
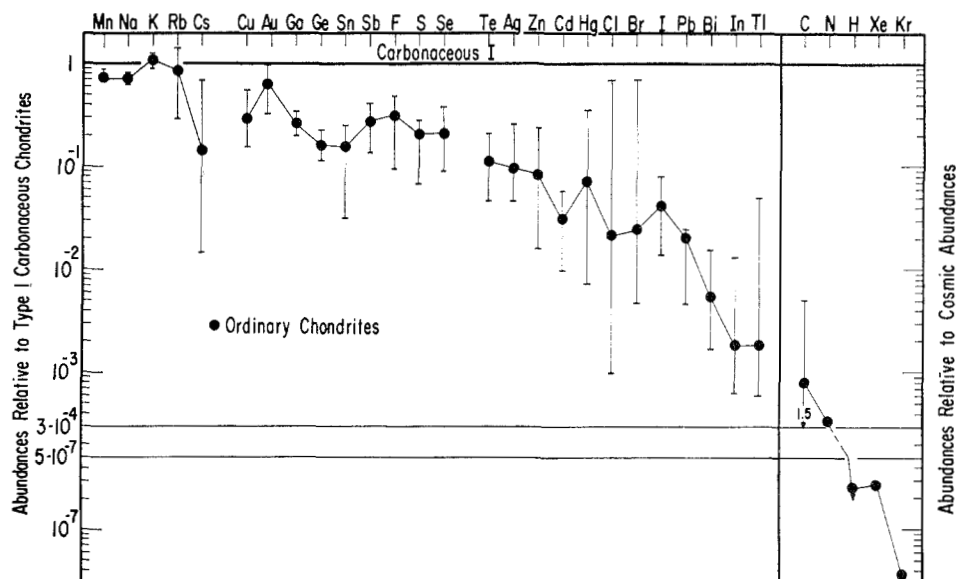

Figure 4. Abundances in ordinary chondrites show a more complex pattern. Mn and alkalis (except for Cs) are not significantly depleted. The next nine elements, Cu to Se, are depleted by a nearly constant factor of ~0.28. Irregularities in this curve segment parallel those in Figure 3, which suggests that the fault may lie with the type I carbonaceous chondrite data used for normalization. The remaining elements show increasingly greater depletion. Error bars indicate the total observed range of variation (data from ref 11 with minor revisions).

temperature (olivine, pyroxene, metal) and low-temperature (hydrated silicates, $MgSO_4$, S, FeS, Fe_3O_4).[2,25] Significantly, the *observed* content of low-temperature minerals in the three types agrees quite well with the *postulated* content of low-temperature fraction, and so does the ratio of matrix to chondrules. Type I consists entirely of a fine-grained matrix of low-temperature minerals; type III consists mainly of chondrules of high-temperature minerals. Furthermore, Schmitt, *et al.*,[26]

have shown that the chondrules are depleted in Na and Mn relative to the matrix. This suggests that the low-temperature fraction may be identical with the matrix, and the high-temperature fraction, with the chondrules and metal particles.

The data for ordinary chondrites look less straightforward (Figure 4). The nine "normal" elements from Cu to Se again are depleted by nearly constant factors. This seems to call for a two-component model. But the

(25) E. R. DuFresne and E. Anders, *Geochim. Cosmochim. Acta*, **26,** 1085 (1962).

(26) R. A. Schmitt, R. H. Smith, and G. G. Goles, *J. Geophys. Res.*, **70,** 2419 (1965).
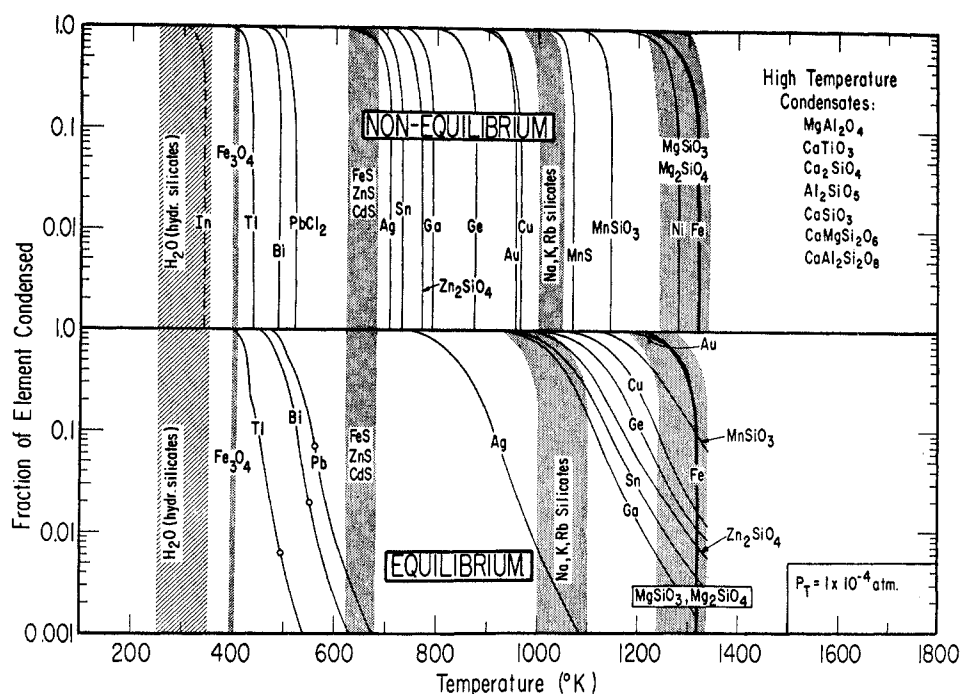
Figure 5. Condensation sequence of a gas of cosmic composition, at a total pressure of 1×10^{-4} atm.[27] "Equilibrium" sequence assumes diffusional equilibrium between grain surfaces and interiors, with formation of solid solutions, while "non-equilibrium" sequence corresponds to decomposition of pure elements or compounds, without interdiffusion. Shaded areas represent condensation or chemical transformation of major constituents. The formation range of hydrated silicates is poorly known. Abundances in ordinary chondrites (circles) suggest an accretion temperature of $\sim 550°K$ for meteorites of this class.

remaining elements depart from the pattern: Mn, Na, K, and Rb are not depleted at all, while the Te–Tl group shows progressively greater depletion. Both trends can be explained by *ad hoc* assumptions, *e.g.*, a lower condensation temperature of the chondrules which allowed Mn and the alkalis to condense, and a higher accretion temperature of the matrix which inhibited condensation of the more volatile elements. (Here we are tacitly assuming that the strongly depleted elements Te–Tl are indeed more volatile than the rest.)

Condensation Sequence of the Elements. Larimer[24,27] has made a quantitative study of the condensation process in order to clarify some of these problems. The situation becomes more involved if the condensed phase is not the free element, but a compound: oxide, sulfide, silicate, or chloride. Pertinent chemical equilibria must then be considered. A further complication is the formation of solid solutions between a trace element and a major phase, *e.g.*, Mg_2SiO_4, Fe, or FeS. The activity of the trace element is lowered, resulting in a higher condensation temperature. Activity coefficient data were not available for most systems of interest, and Raoult's law was therefore assumed to be valid in cases of complete miscibility. Cases of partial miscibility were more troublesome.[27] For most trace metals of interest, low-temperature solubilities in iron or nickel–iron of cosmic composition (6% Ni) were unavailable and had to be extrapolated from high-temperature data, sometimes on related systems. The activity of the saturated solution was set equal to 1 and the activity

at lower concentrations found from Henry's law.

Kinetic factors must also be considered. Formation of a solid solution requires interdiffusion between surface and interior of the grain. Hence it is useful to consider two limiting cases: *nonequilibrium*, where pure elements and compounds condense on each grain in successive layers without interdiffusion, and *equilibrium*, with complete interdiffusion.

Condensation sequences for these two limiting cases are shown in Figure 5. The total pressure is 1×10^{-4} atm, a value appropriate to the center of the asteroid belt.[28]

Let us follow the condensation sequence of a cosmic gas, using the *nonequilibrium* diagram for illustration (Figure 5). Near 2000°K, a few refractory substances condense: platinum metals, silicates, and spinels.[28] At 1340–1240°K, two major phases appear: nickel–iron and magnesium silicates. Together, they account for some 90% of all condensable material. Manganese and the alkalis come next, followed by a series of trace metals, Cu to Ag. At 680°K, metallic iron begins to react with H_2S, giving FeS as the third major phase. Several elements still in the gas phase which tend to form stable sulfides or iron compounds, respectively (Cd, Zn, Se, and Te), may be expected to condense at this stage. The cosmic abundance of Fe is somewhat greater than that of S, so that some metallic iron is left over. The four elements Pb, Bi, Tl, and In are the last to condense, owing to their low heats of vaporization.

(27) J. W. Larimer, to be published.

(28) (a) A. G. W. Cameron, *Icarus*, **1**, 13 (1962); (b) A. G. W. Cameron, *ibid.*, **1**, 339 (1963).

(The In curve is not well determined, owing to complexities introduced by the gaseous species In_2S.[24] The true In curve may lie closer to the Tl curve.)

At 400°K, another chemical reaction sets in: conversion of the remaining Fe to Fe_3O_4 by reaction with water vapor. Finally, at about 300–350°K, olivine transforms to hydrated silicates. The exact temperature cannot be determined for lack of thermodynamic data. As noted by Urey, an upper limit for magnesium silicates can be obtained from $Mg(OH)_2$ ($T \approx 300°K$,[16]) which holds water more tenaciously than do hydrated magnesium silicates (e.g., talc, $T \approx 250°K$[11,29]). Temperatures for iron-bearing silicates should be somewhat higher.

The *equilibrium* case (Figure 5) is similar to the nonequilibrium case insofar as the major phases are concerned. However, owing to the formation of solid solutions the trace elements condense more gradually and at higher temperatures. The shift in condensation temperature is smallest for those four elements that show limited solubility in iron: Ag, Pb, Bi, and Tl. (In is probably similar, but is omitted for lack of solubility data.) In fact, the last three elements show a marked break in their condensation curves, corresponding to the point where the available nickel–iron has become saturated. Below this point, these elements condense as pure metals, as in Figure 5. Of course, these curves are based on *estimated* low-temperature solubilities and may be in error by 50° or more. A threefold increase in solubility would also eliminate the break.

To decide whether the equilibrium or nonequilibrium case is appropriate to the solar nebula, we must know diffusion coefficients, cooling times, and grain sizes. The last two, in particular, are rather uncertain. Let us therefore proceed empirically and see which diagram best explains the observed fractionation patterns in Figures 3 and 4.

Interpretation of Abundance Patterns. The *high-temperature fraction of carbonaceous chondrites* seems to have lost all its volatiles: Mn, alkalis, and the elements Cu to In. This pattern agrees well with the nonequilibrium sequence for a condensation temperature between 1150 and 1240°K. It does not agree with the equilibrium sequence; here the elements Cu to Ga condense ahead of the alkalis.

The *low-temperature fraction of carbonaceous chondrites* must have accreted at a temperature no higher than ~350°K, judging from the presence of magnetite ($\leq 400°K$) and hydrated silicates (approximately $\leq 350°K$). The trace element content does not provide any more restrictive limits. All elements from In on up are present in nearly cosmic proportions, which implies accretion at ≤ 340 or $\leq 400°K$ according to either the nonequilibrium or the equilibrium sequences.

The data for *ordinary chondrites* also seem to fit the condensation sequence, supporting our previous speculations. A lower condensation temperature of the *high-temperature fraction* (970–1000°K according to the non-

equilibrium sequence) would indeed account for the non-depletion of Mn, Na, K, and Rb. Again, the equilibrium sequence does not fit the observed pattern: the *depleted* elements Cu, Ge, Zn, Sn, and Ga condense ahead of *undepleted* Na and K.

The *low-temperature fraction* can also be explained along the lines previously suggested. The four most strongly depleted elements, Pb to In, indeed are the last to condense. The equilibrium sequence clearly gives the better match. The nonequilibrium curves slope too steeply and would cause Pb and Bi to condense quantitatively before any Tl had condensed. The accretion temperature of ordinary chondrites may thus be bracketed between rather close limits. It must have been greater than 520°K to prevent substantial condensation of $PbCl_2$ and less than 680°K to allow formation of FeS.

We can try to refine our estimate by plotting actual abundances in Figure 5. Data on bulk meteorites from Figure 4 were multiplied by $1/0.28$ to convert them to abundances in the low-temperature fraction. The abundances of Pb, Bi, and Tl, recalculated in this manner, are 7×10^{-2}, 2×10^{-2}, and 6×10^{-3} (circles in Figure 5). As expected, they decrease with increasing volatility. Corresponding accretion temperatures are 560, 550, and 490°K. The last value can be brought into accord with the other two by assuming a higher solubility of Tl in nickel–iron. In any case, it seems that the mean accretion temperature of ordinary chondrites was in the neighborhood of 550°K. Judging from the abundance variation in Figure 4 (factors of 6, 14, and 40 for Pb, Bi, and Tl), the dispersion in accretion temperatures was small, $\pm 30°$.

A few other observations must be accounted for. The strongly depleted elements show a remarkable degree of covariance: if a given meteorite is low in one element, it tends to be low in all others as well. One striking example is the correlation between In and Xe (or Ar), discovered by Tandon and Wasson[30] (Figure 6). These obviously dissimilar elements correlate over more than two orders of magnitude. Indeed, such interelement correlations seem to extend to all strongly depleted elements. Larimer and I have plotted abundances of depleted elements in the three most widely studied meteorites.[11] Surprisingly, the strongly depleted elements Tl to C show a consistent abundance trend in the order Beardsley > Richardton > Allegan, with a tenfold spread over-all. It seems that Beardsley was uniformly more successful in picking up volatiles than were Richardton or Allegan.

This difference can be explained by equilibrium factors alone. Beardsley may have accreted at a lower temperature, where condensation of the strongly depleted elements was more complete. A temperature drop of 40° would suffice to raise abundances tenfold. Alternatively, kinetic factors may be invoked. Beardsley may have had a finer grain size, or a longer contact time with the gas phase. Either of these would favor

(29) K. O. Bennington, *J. Geol.*, **64**, 558 (1956).

(30) (a) S. N. Tandon and J. T. Wasson, *Science*, **158**, 259 (1967); (b) *Geochim. Cosmochim. Acta*, in press.
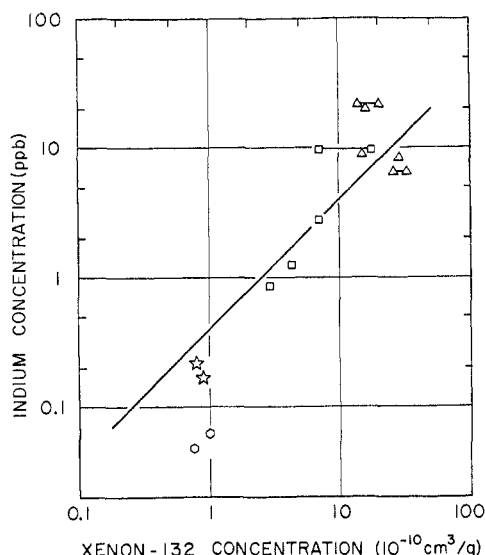
Figure 6. Correlation between In and ^{132}Xe in L-group chondrites (after Tandon and Wasson[30b]). These two elements correlate strongly, in spite of their markedly different volatilities. Horizontal bars connect measurements on two specimens of the same meteorite. Point symbols were chosen so that the number of corners corresponds to "petrologic grade" number,[31] the degree of recrystallization increasing from grades 3 to 6.

more complete equilibration, and hence condensation. It is not clear, however, that the In–Xe correlation in Figure 6 can be explained along these lines. This correlation apparently requires that trapping of a noble gas and condensation of a metal both have similar temperature dependence. More data are obviously needed on the solubility of noble gases in meteoritic minerals.

Origin of the High-Temperature Fraction. Most of our concern thus far has been with the low-temperature fraction. It appears that it precipitated from the gas at high temperatures, collected a succession of volatiles on cooling, and finally became separated from the gas by accretion into larger bodies. Clues to the history of the high-temperature fraction are not very specific, and thus its origin is explained largely by *ad hoc* postulates.

One possibility, first suggested by Wood,[32,33] is that the high-temperature fraction represents that portion of the condensate which passed through the liquid field of the phase diagram. Droplets of silicate and metal would grow by coalescence into millimeter-sized chondrules and metal particles, while material condensing from vapor directly to solid would remain in the form of a micron-sized smoke (=matrix). On cooling, the matrix material with its large surface-to-volume ratio would continue to equilibrate with the gas, unlike the coarse chondrules-plus-metal fraction. Thus the formation of an undepleted and a depleted fraction can be understood.

Wood's model requires pressures of $\geq 10^2$ atm, hardly

attainable in a solar nebula except during transient shocks. However, Blander and Katz[34] have pointed out that supercooling can change the situation radically, condensation to liquids being possible at pressures as low as 10^{-4} atm.

Another possibility has been suggested by Whipple[35] and was later elaborated by Cameron.[36] Whipple notes that considerable charge separation can occur in dust-laden, nonconducting gases; hence the solar nebula should have passed through a stage of intense lightning activity. Such lightning discharges would melt any dust agglomerates in the vicinity, changing them into chondrules and metal grains. Even though the time scale of remelting would be very short, volatiles would be largely lost. Thus a depleted, high-temperature fraction would result. Inasmuch as its formation on this model is a purely local event, its amount and formation temperature may be expected to vary from place to place. The alkali depletion in carbonaceous chondrites may well imply an origin at greater distances from the sun, where pressures and volatilization temperatures were lower.

Other Models. One must consider the possibility that the fractionation happened in the solar nebula, as outlined here, but at higher or lower pressure or at a different composition. It turns out that there is not much latitude in these parameters. Pressures outside the range 10^{-2}–10^{-6} atm would shift the condensation curves by a prohibitive amount, leading to various inconsistencies. *Major* deviations from solar composition are also unlikely, although minor fractionations of gas and dust actually seem necessary to account for the highly reduced state of carbonaceous and enstatite chondrites.[37,38] A further alternative is that the fractionation happened *after* accretion, in the meteorite parent bodies. Chondrites have undergone recrystallization to a variable degree: one finds a continuous transition from meteorites with a fine-grained opaque matrix and sharply delineated chondrules to highly recrystallized ones in which the chondrules are barely resolvable from the coarse-grained matrix.[32,39,40] It is striking that the trace element depletion tends to parallel the degree of recrystallization (Figure 6). This suggests a causal relationship. Wood[41] has proposed that trace element depletion is caused by reheating in the parent body ("metamorphism"), while Ringwood[12,42] has suggested volatilization at an earlier, igneous stage. Either model implies that the meteorite parent bodies were open systems, free to lose volatiles.

(31) W. R. Van Schmus and J. A. Wood, *Science*, 31, 747 (1967).
(32) (a) J. A. Wood, Technical Report No. 10, Smithsonian Institute of Astrophysics Observatory (ASTIA Document No. AD 158364), 1958; (b) J. A. Wood, *Nature*, 194, 127 (1962).
(33) J. A. Wood, *Icarus*, 2, 152 (1963).

(34) M. Blander and J. L. Katz, *Geochim. Cosmochim. Acta*, 31, 1025 (1967).
(35) F. L. Whipple, *Science*, 153, 54 (1966).
(36) A. G. W. Cameron, *Earth Planetary Sci. Letters*, 1, 93 (1966).
(37) J. A. Wood, *Geochim. Cosmochim. Acta*, 31, 2095 (1967).
(38) J. W. Larimer, *ibid.*, 32, 965 (1968).
(39) J. A. Wood in "The Moon, Meteorites, and Comets," B. M. Middlehurst and G. P. Kuiper, Ed., University of Chicago Press, Chicago, Ill., 1963, Chapter 12, p 337.
(40) (a) R. T. Dodd, Jr., and R. Van Schmus, *J. Geophys. Res.*, 70, 3801 (1965); (b) R. T. Dodd, Jr., W. R. Van Schmus, and D. M. Koffman, *Geochim. Cosmochim. Acta*, 31, 921 (1967).
(41) J. A. Wood, *Icarus*, 6, 1 (1967).
(42) A. E. Ringwood, *Geochim. Cosmochim. Acta*, 30, 41 (1966).

The same correlation between trace element content and recrystallization would be expected for the condensation model. Meteorites last to accrete would be richest in volatiles, especially if temperatures declined during accretion. Being situated in the outermost layers of the asteroid, these meteorites would be least reheated during metamorphism. Here we are assuming that the body was a closed system during metamorphism, with negligible loss or transport of volatiles.

The available evidence seems to favor the condensation model. Reheating during metamorphism cannot account for the uniform depletion of the "normally depleted" elements, whose volatilities span a wide range. Other objections exist as well.[11]

Discussion

The evidence presented here suggests that most meteorites accreted at a temperature of 520–680°K. This is more than three times the present black-body temperature in the asteroid belt, 170°K. Apparently a powerful, transient heat source was present in the early solar system. One possibility is the primitive sun itself.[11] Hayashi[43] showed several years ago that the sun must have passed through a brief high-luminosity stage before settling down to its present state on the main sequence. Recent work by Cameron[28,44] on the evolution of the solar nebula shows, however, that the sun would be a rather late phenomenon, forming at the expense of the solar nebula during the final stages of its existence. Part of the nebular material would be absorbed by the growing sun, the remainder being expelled from the solar system. Only rather sizable bodies would survive this process, and they must therefore have accreted prior to the sun's formation. High temperatures during accretion hence must have been maintained by some mechanism other than solar heating.

The nebula itself would be heated by the release of gravitational potential energy during contraction. For the asteroid belt, Cameron predicts a temperature of ~500°K, in close agreement with our estimate of 520–680°K.

Earth. What bearing does this conclusion have on the inner planets, especially the Earth? If temperatures were high in the asteroid belt, they must have been high elsewhere in the inner solar system, and this, in turn, should have led to important chemical fractionations during accretion of the planets. Such fractionations may be hard to recognize in the Earth, where large-scale redistribution of elements has occurred and only a thin outer crust is accessible to chemical analysis. There is a possibility, however, that at least the most volatile elements are quantitatively concentrated in the crust, atmosphere, or oceans.[45] Let us therefore calculate nominal "whole-earth" abundances for a number of volatile elements on the assumption that the amount
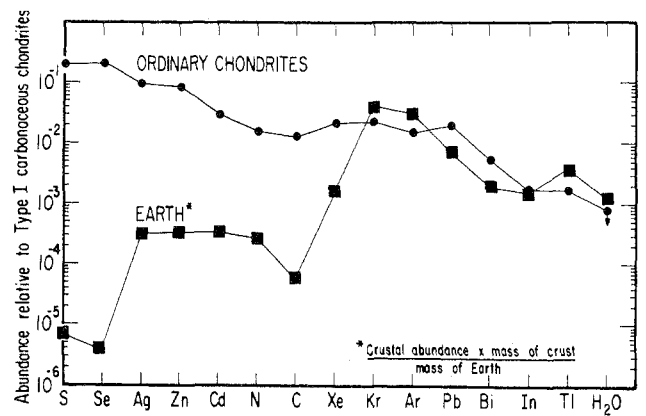

Figure 7. Abundance of volatile elements on Earth and in ordinary chondrites. Terrestrial abundances were computed from Taylor's crustal abundances on the assumption that the amount in the crust represents Earth's entire inventory of a given element (S. R. Taylor, *Geochim. Cosmochim. Acta*, **28**, 1273 (1964)). This assumption is realistic only for highly volatile elements that were largely outgassed from Earth's interior; the values for all others will be too low. It is interesting that the last seven values, Kr to H_2O, are high, and coincide with the values in ordinary chondrites. Apparently Earth, too, accreted near 600°K.

in the crust represents the Earth's entire inventory of this element.

It is instructive to compare these "terrestrial" abundances with the meteoritic ones (Figure 7). For the first eight elements the terrestrial curve is systematically low by several orders of magnitude. This may imply that these elements are largely concentrated in the earth's interior. The remainder of the curve, from Kr to H_2O, virtually coincides with the chondritic curve. These elements are the most volatile ones, for which the postulate of surface concentration is most likely to be correct. It is remarkable that the curves match so well in both slope and position. This suggests that Earth and ordinary chondrites accreted at about the same temperature, around 600°K.

One cannot rule out an alternative possibility: that the bulk of Earth accreted at still higher temperatures, with a small amount of volatiles being brought in at a late stage *via* carbonaceous chondrite-like material. About 3% of such material would be required to account for Earth's Kr and Ar. The whole-earth abundances of the remaining elements in Figure 7 should then also be at the 3% level; the fact that they are lower must be ascribed to retention in Earth's interior. A slight disadvantage of this model is its failure to account for the resemblance of the two curves in the $Kr–H_2O$ region, but whichever model is correct, the bulk of Earth apparently accreted at a rather high temperature, at least ~600°K.

This temperature is much higher than Urey's original estimate, ~300°K. The reason is not hard to find. The abundance data available in 1952–1954, though incomplete, showed no clear-cut depletion of volatile metals. This ruled out high-temperature condensation in its simplest form (without formation of solid solutions) and seemed to suggest low-temperature condensation instead. A decade later the picture had changed.

(43) C. Hayashi, *Publ. Astron. Soc. Japan*, **13**, 450 (1961).
(44) A. G. W. Cameron, paper presented at International Symposium on Meteorites, Vienna, Aug 7–13, 1968. To be published by Reidel, Dordrecht, Netherlands.
(45) H. C. Urey, *Proc. Roy. Soc.* (London), **A219**, 281 (1953).

Most of the volatile elements turned out to be depleted, but by small and frequently constant factors. Thus a more complicated, two-fraction model became necessary, involving solid-solution formation. Let us see how well this high-temperature condensation model accounts for the chemical differences among the remaining inner planets.

Inner Planets. It has been known for some time that the inner planets differ markedly in density, from 5.5 g/cm³ for Mercury to 4.0 g/cm³ for Mars (both corrected to zero pressure). Noddack[7] and Urey[16] attributed these differences to variations in metal–silicate ratio. Such variations are hard to explain in terms of the low-temperature model, which assumes that the planets accreted from highly oxidized material, containing Fe_3O_4 rather than Fe. The high-temperature model,[32] on the other hand, produces metal and silicate particles from the nebula. Given their differences in density, brittleness, and magnetic susceptibility, it is not hard to imagine how they might be fractionated from each other.[32b]

The situation is similar in regard to the volatile content of inner planets. According to the low-temperature model, only slight differences might be expected, corresponding to the $r^{-1/2}$ variation of temperature with distance from the sun. The high-temperature model provides two additional degrees of freedom. First, temperatures probably varied with time as well as distance. This difference might be enhanced by variations in the effective cutoff times for accretion. Mars, a small planet sweeping out a large volume of space, may have been much less effective than Earth or Venus in collecting the late, volatile-rich condensate prior to its dissipation. Second, the proportion of high- to low-temperature fraction may have varied from planet to planet, just as it seems to have varied from one class of meteorites to the next.

One interesting case in point is Venus. It seems to have less than 10^{-3} Earth's water content, although both planets contain similar amounts of C and N. Their sizes are nearly identical, and there is no obvious way in which Venus could have lost large amounts of water. Libby[46] has recently suggested that most of the water is present in the form of giant ice caps. An alternative possibility is that temperatures in the neighborhood of Venus did not fall below 400°K (the estimated formation temperature for hydrated silicates at 0.7 astronomical unit) until very late, when little accretable material remained in the nebula. Earth would have passed this point several hundred thousand years earlier.[11]

Of course it is a risky undertaking to deduce the formation conditions of a planet from the volatiles in the accessible portions: crust and atmosphere. One must know what fraction of the planet's initial endowment these surface volatiles represent. A major part may still be trapped in the interior or may have escaped from the planet altogether; hence the surface

volatiles merely provide a lower limit. Nonetheless, even a lower limit can be quite informative, particularly if an upper limit can be obtained from other evidence. Mueller[47] and Lippincott, et al.,[48] have studied this problem in detail, using the present atmospheric composition of Venus to deduce the surface mineralogy and the history of the atmosphere.

Organic Compounds. Finally, this model seems to provide the proper setting for production of organic compounds in meteorites.[49] Studier, et al.,[50] have recently shown that all organic compounds reliably identified in meteorites can be made from CO, H_2, and NH_3 by a Fischer–Tropsch type reaction if iron meteorite particles are present to act as catalysts. This reaction produces a number of compounds, including some biologically important ones: normal alkanes and isoalkanes, isoprenoid alkanes, adenine, guanine, polynuclear aromatics, alkylbenzenes, etc. The starting materials for this reaction, CO, H_2, NH_3, and metal particles, would certainly be present in a cooling solar nebula. On cooling, methane should form as the equilibrium product, but laboratory experiments show that high-molecular weight organic compounds form instead as metastable products.[50] Indeed, the existence of fairly nonvolatile carbon compounds in the inner solar system must be postulated on independent grounds: methane, with a condensation temperature of 48°K at 10^{-3} atm, is too volatile to condense in the region of the inner planets.[16,18] The suggestion that carbon was incorporated in Earth and meteorites as organic compounds was first made by Urey in 1953.[18] He showed that carbides and graphite were unlikely to form in a gas of solar composition and suggested that "complex tarry organic compounds" might have formed as metastable intermediates in the reaction of CO or C_2H_2 with H_2. Dayhoff, et al.,[51] have shown by thermodynamic calculations that complex aromatic hydrocarbons can indeed form metastably under such conditions, and Studier, et al.,[50] have observed such compounds, along with alkanes, in their experiments.

Some Remaining Problems. The two-component model seems to account for all the available evidence. However, quite a few details remain to be filled in. Estimates and guesses must be replaced by accurate measurements. It is possible that such new data may prove incompatible with the model, forcing its revision or abandonment.

Not enough is known about the chemistry involved

(46) W. F. Libby, *Science*, **159**, 1097 (1968).

(47) (a) R. F. Mueller, *ibid.*, **141**, 1046 (1963); (b) *Nature*, **203**, 625 (1964); (c) *Icarus*, **3**, 83 (1964); (d) *ibid.*, **3**, 285 (1964); (e) *ibid.*, **4**, 506 (1965); (f) *J. Chem. Educ.*, **42**, 294 (1965).

(48) E. R. Lippincott, R. V. Eck, M. O. Dayhoff, and C. Sagan, *Astrophys. J.*, **147**, 753 (1967).

(49) A recent review by J. M. Hayes, *Giochim. Cosmochim. Acta*, **31**, 1395 (1967), provides an excellent introduction to this controversial subject.

(50) (a) M. H. Studier, R. Hayatsu, and E. Anders, *ibid.*, **32**, 151 (1968); (b) R. Hayatsu, M. H. Studier, A. Oda, K. Fuse, and E. Anders, *ibid.*, **32**, 175 (1968); (c) M. H. Studier, R. Hayatsu, and E. Anders, Enrico Fermi Institute preprint, EFINS 65-115, 1965.

(51) (a) M. O. Dayhoff, E. R. Lippincott, and R. V. Eck, *Science*, **146**, 1461 (1964); (b) R. V. Eck, E. R. Lippincott, M. O. Dayhoff, and Y. T. Pratt, *ibid.*, **153**, 628 (1966).

in trapping strongly depleted elements. Noble gases were probably dissolved in the crystal lattices of major phases (silicates, FeS, and Fe_3O_4). Solubilities in these phases are unknown, at least in the temperature range of interest. Small amounts of water would be trapped in similar manner. Again, data are lacking.

The problem of carbon condensation has not yet been completely solved. True, aliphatic and aromatic hydrocarbons of 30 or more carbon atoms can be produced by Fischer–Tropsch reactions or pyrolysis of methane,[50a,c,52] but nobody has yet duplicated the aromatic polymer which accounts for the bulk of the carbon in carbonaceous and ordinary chondrites.[49,53] Similarly, the chemical state of condensed nitrogen has not been settled. Carbonaceous chondrites contain about 0.3% N,[54] mostly as heterocyclics and other organic nitrogen compounds,[50b,55] not as NH_4^+.[25] Ordinary chondrites contain a few parts per million of N of unknown chemical state (iron nitride, titanium nitride, organic polymers?). The inner planets presumably acquired their N in the same form, and for this reason alone it would be interesting to learn more about the chemistry involved.

The condensation behavior of several other partially condensed trace elements cannot be accurately determined for lack of pertinent data. Thermodynamic data are lacking for FeSe and FeTe. Solubilities are largely unknown for solid solutions of Pb, Bi, In, Tl, Cd, Zn, Se, and Te in Fe, Fe–Ni alloys, and FeS. The problem is not an easy one from an experimental point of view, diffusion rates near 600°K being rather slow. Moreover, the situation is complicated by the existence of intermetallic compounds, but these systems can certainly be studied with the tools of modern physical chemistry and metallurgy. Perhaps the great cosmochemical interest of these systems will provide the needed incentive.

Conclusions

If our analysis is valid, the chemical composition of the chondrites was established in the solar nebula and has changed but little in subsequent eons. As first noted by Wood, this has opened up the exciting prospect of having at our disposal samples of the legendary "primordial dust" from which the planets formed. Some of the properties of meteorites were undoubtedly established in the meteorite parent bodies, but these late alterations have not obscured the record of the earlier, far more interesting stage. The meteorites falling on earth represent a fairly wide range of environments, from high to low temperatures and strongly reducing to oxidizing conditions. One of the great remaining challenges to meteoriticists is to determine the place of origin of each kind of meteorite. With this information, it should be possible to derive a fairly detailed picture of chemical and physical conditions in the early solar system and their variation with time.

(52) J. Oró and J. Han, *Science*, **153**, 1393 (1966).
(53) M. C. Bitz and B. Nagy, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1383 (1966).
(54) B. Mason, *Space Sci. Rev.*, **1**, 621 (1963).
(55) R. Hayatsu, *Science*, **146**, 1291 (1964).