

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

COO-382-118

CONDITIONS IN THE EARLY SOLAR SYSTEM, AS INFERRED FROM METEORITES

Edward Anders

Enrico Fermi Institute and Department of Chemistry
University of Chicago, Chicago, Illinois 60637

Presented at

Nobel Symposium # 21

"From Plasma to Planet"

Saltsjöbaden, Sweden

September 6-10, 1971



NASA Grant NGL 14-001-010

AEC Contract AT(11-1)-382

FACILITY FORM 602

N71-38570
(ACCESSION NUMBER)
39
(PAGES)
CR-123180
(NASA CR OR TMX OR AD NUMBER)

Q3 ~~AN~~
(THRU)
(CODE)
30
(CATEGORY)

EFI-71-40

CONDITIONS IN THE EARLY SOLAR SYSTEM, AS INFERRED FROM METEORITES

Edward Anders

Enrico Fermi Institute and Department of Chemistry

University of Chicago, Chicago, Illinois 60637

ABSTRACT

Many properties of meteorites suggest that they formed in a cooling gas of solar composition (solar nebula?). Chemical differences among chondrites, encompassing nearly all known elements, can be accounted for by only 4 processes: loss of an early condensate ($\geq 1300^\circ\text{K}$), loss of nickel-iron (1050 to 700°K), partial remelting of the condensate (600°K), and accretion (560 to 350°K). Reasonably concordant temperatures are obtained by various cosmothermometers: abundance of volatile metals (Pb, Bi, Tl, In), planetary noble gases, $\text{O}^{18}/\text{O}^{16}$ fractionations, and low-temperature minerals (Fe_3O_4 , FeS, hydrated silicates). The accretion temperatures are 3 times higher than present black-body temperatures in the asteroid belt, suggesting the presence of a transient heat source such as the sun in its Hayashi stage. Pressures seem to have been about 10^{-4} to 10^{-6} atm in the region of the ordinary chondrites; 5×10^{-6} atm in the region of carbonaceous chondrites. Laboratory experiments show that Fischer-Tropsch-type reactions of CO, H_2 , and NH_3 in the nebula, catalyzed by iron or silicate grains, can also account for the organic compounds in

meteorites (n-alkanes, purines, pyrimidines, amino acids, porphyrin-like pigments), carbon-isotope fractionations, and for interstellar molecules. Although this model has not yet accounted for every detail, its general success in explaining a large and diverse body of evidence tends to support its premise: existence of a hot solar nebula of about $0.1-1 M_{\odot}$.

I. INTRODUCTION

Traditionally one has assumed that meteorites and planets originated from a solar nebula of about 0.1 to $1 M_{\odot}$. Solid grains condensed on cooling and accreted into larger bodies, leaving the gas behind. Condensation proceeded largely under conditions of thermodynamic equilibrium (Urey 1952a,b, 1954; Lord 1965; Larimer 1967; Larimer and Anders 1967, 1970; Grossman 1971).

This view has been challenged by Arrhenius and Alfvén (1971) in a very stimulating paper. They propose that condensation took place from a plasma, not a neutral gas. A major fractionation mechanism was separation of ions from neutral atoms, preceding the separation of solids from gas. Pressures in the inner solar system were orders of magnitude lower than those assumed in the equilibrium model ($10^{-4 \pm 2}$ atm), and temperatures were much higher (4000 to 10000°K vs. 350 to 2000°K).

The ultimate test of any such model is its ability to account for the empirical evidence, principally meteorite data. It has become apparent during the last decade that most properties of

chondrites were established prior to accretion of their (asteroidal?) parent bodies. Thus the chondrites contain a detailed record of the pre-accretionary stage of the solar system. The problem is to decipher this record; to translate structure, composition, and mineralogy into temperature, pressure, time, and chemical environment.

I have discussed the meteoritic evidence in terms of the equilibrium model in several recent reviews (Anders 1968, 1971a) and papers (Larimer and Anders 1967, 1970; Keays Ganapathy and Anders 1971). I shall therefore limit myself to a fairly brief summary, omitting many qualifications and details, but stressing quantitative predictions and inferences. These inferences, about pressures, temperatures, and time scales in the early solar system, themselves constitute a test of the model. They must be internally and externally consistent, not only with each other but also with independent evidence from other sources.

The paper begins with a brief glossary, followed by a discussion of the condensation sequence of a cosmic gas. §IV to VI review chemical evidence from meteorites, while §VII discusses the chronology of the early solar system. §VIII attempts a critical comparison of the two models in the light of the evidence presented.

II. GLOSSARY

Chondrites are stony meteorites containig chondrules, mm-sized silicate spherules that appear to be frozen droplets of a melt. They consist largely of olivine $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$, pyroxene $[(\text{Mg},\text{Fe})\text{SiO}_3]$,

and plagioclase feldspar [solid solution of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{NaAlSi}_3\text{O}_8$]. In the more primitive chondrites, glass is often found in place of crystalline feldspar.

Chondrules are embedded in a ground-mass or matrix. In the less primitive chondrites, the matrix is somewhat more fine-grained than the chondrules, but otherwise has the same mineralogy and composition. Millimeter-sized particles of metal (nickel-iron with 5-60% Ni) and troilite (FeS) are also present. In the more primitive chondrites, the matrix is very fine grained (to $\sim 10^{-6}$ cm) and richer in Fe^{2+} than the chondrules.

Five chondrite classes are recognized, differing in the proportions of oxidized to reduced iron. Enstatite (=E) chondrites are highly reduced, containing iron only as metal and FeS . Carbonaceous (=C) chondrites are highly oxidized, containing mainly Fe^{2+} , Fe^{3+} , and little or no Fe^0 . The middle ground is occupied by 3 classes of intermediate oxidation state and total iron content: H, L, and LL chondrites. Collectively, they are often called ordinary (=O) chondrites.

Each of these classes is further subdivided into "petrologic types" numbered from 1 to 6 (Van Schmus and Wood 1967). These types were originally designed to reflect increasing chondrule-to-matrix intergrowth (probably due to metamorphic recrystallization in the meteorite parent bodies), but have turned out to correlate well with compositional trends, e.g. volatile content.

III. CONDENSATION SEQUENCE OF A COSMIC GAS

Two condensation diagrams based on the work of Larimer (1967 and unpublished) are shown in Fig. 1. They were calculated for a total pressure of 10^{-4} atm and Cameron's (1968) cosmic abundances. This pressure is thought to be representative of the asteroid belt. At higher pressures (or lower H/metal ratios) the curves shift to the right, by varying amounts.

The upper diagram applies to conditions of rapid cooling, where substances condense in successive layers without interdiffusion or alloy formation. The lower diagram, on the other hand, assumes complete diffusional equilibration, with formation of alloys and solid solutions to the limit of solubility. The effect of such alloy formation is to raise the condensation temperatures of minor elements, and to widen their condensation intervals. Of course, all intermediate situations are possible.

A cooling gas of cosmic composition should thus condense in the following order. Below 2000°K , some highly refractory compounds of Ca, Al, Mg, and Ti appear, followed by magnesium silicates and nickel-iron at ~ 1350 to $\sim 1200^{\circ}\text{K}$ and alkali silicates at 1100 to 1000°K . Up to this point, some 90% of chondritic matter has condensed. Only H, C, N, O, S, and some volatile trace elements still remain in the gas phase. At 680°K sulfur begins to condense on solid Fe grains by the reaction $\text{Fe} + \text{H}_2\text{S} \rightleftharpoons \text{FeS} + \text{H}_2$, followed by Pb, Bi, Tl, and In. Any remaining Fe reacts with H_2O at 400°K to give Fe_3O_4 . Finally, water is bound as hydrated silicates at some temperature between 250 and 400°K .

IV. CHEMICAL FRACTIONATIONS IN CHONDRITES

a) Refractory Elements

The elements heading the condensation sequence (Ca, Ti, Al, Mg) all are fractionated among the major chondrite classes, by small but definite factors. Analogous fractionations are found for some 20-odd refractory elements (Fig. 2). Their abundances increase in the order $E < O < C$, in the average ratio 0.56:0.73:1.00. All these elements are quite non-volatile, and would be expected to concentrate in an early condensate or a volatilization residue at $\geq 1300^\circ\text{K}$.

Larimer and Anders (1970) have suggested that the trend from C to E chondrites reflects progressively greater loss of an early condensate (MgAl_2O_4 , CaTiO_3 , Mg_2SiO_4 , etc.), comprising 15-30% of the total condensable matter. Inclusions of such composition are in fact found in C3 chondrites but not in E or O chondrites. Apparently only the C chondrites retained their early condensate.

Arrhenius and Alfvén state that the refractory inclusions in C3's are "entirely unexpected and the extreme opposite of what would be expected on the basis of condensation in thermal equilibrium". This is not the case; the existence of such compounds was predicted by Lord in 1965 and Larimer in 1967, before they were actually discovered in meteorites. That such minerals occur in carbonaceous chondrites is not at all surprising. These meteorites have nearly cosmic composition (Anders 1971b), and must, ipso facto, have collected their proportionate share of every successive

condensate, high-, medium-, or low-temperature. The mineralogy of the refractory inclusions likewise poses no paradoxes, as shown in detail by Grossman (1971).

Herbig (1970a) has noted that the interstellar gas is deficient in these same elements (Ca, Ti, Al) and suggested that this might be due to partial condensation of refractories. Such condensation cannot have taken place at the low densities of interstellar space. Herbig therefore suggests that a major part of interstellar matter has once passed through solar nebulae. It would seem that partial condensation of refractories is a fairly universal feature, not limited to our own solar system.

Some of the least volatile transition metals (Ir, Os, Re, Pt) may have been involved in the same fractionation. Their abundances in iron meteorites vary by 3 orders of magnitude and are anti-correlated with those of equally reducible but more volatile elements, e.g. Pd and Ni. Similar though much smaller variations have been observed in chondrites. Arrhenius and Alfvén attribute this fractionation to differences in ionization potential, but it can equally well be explained by differences in volatility (Anders 1971a).

b) Metal-Silicate Fractionation

The elements marked siderophile in Fig. 2 correlate with iron in each chondrite class. Total variation is again small (less than a factor of 2) but definite (Urey and Craig, 1953). Density

differences among the inner planets also imply a difference in metal/silicate ratio (Urey 1952a). Apparently a metal-silicate fractionation took place in the early solar system. A likely mechanism is preferential loss of metal grains in the nebula.

Two attempts have been made to estimate the temperature during metal-silicate fractionation (Larimer and Anders 1970). Upper limits of $\leq 1050^\circ\text{K}$ and $\leq 985 \pm 50^\circ\text{K}$ for O and E chondrites were based on the observation that elements less volatile than Ge correlated with metal content and hence apparently were already condensed at the time of fractionation, while more volatile elements (Ga, S) were not. Lower limits of $\geq 650^\circ$ and $\geq 680^\circ\text{K}$ were derived from the Fe^{2+} content of silicates and absence of FeS during fractionation, as inferred from regressions of Ni/Mg and Fe/Mg ratios in chondrites. The former value may be too high, however, because the inferred Fe^{2+} content of O chondrites may not represent a true equilibrium value (see § IV f).

Interestingly, the upper limits are close to the ferromagnetic Curie points of the metal in E and O chondrites, 940 and 900°K . Perhaps this is a coincidence, but then it is hard to understand why the temperature had to fall 400° after the refractory-element fractionation, before the metal-silicate fractionation began. More probably, the relationship is causal, the fractionation being triggered by the appearance of ferromagnetism in the metal grains (Wood, 1962).

c) Volatile Elements; Formation of Chondrules and Matrix

Some 37 volatile elements are fractionated in chondrites

(Fig. 2). C chondrites show the simplest pattern: abundances decrease uniformly from C1's to C3's, by mean ratios of 1:0.55:0.33. This has been explained by a two component model (Wood 1963; Anders 1964, 1971a; Larimer and Anders 1967). Chondrites are a mixture of a volatile-rich, low-temperature component (= matrix) and volatile-free, high-temperature component (= chondrules + metal grains), both formed in the solar nebula. The decline in volatile content from C1 to C3 is attributed to increasing chondrule content which goes from ~0 in C1's to ~70-80% in C3's.

Matrix is thought to be the original condensate, whose small grain size ($\sim 10^{-6}$ cm) enabled it to equilibrate with the gas down to quite low temperatures. Chondrules probably represent remelted matrix, the remelting and outgassing having taken place in brief local heating events, such as electric discharges (Whipple 1966; Cameron 1966). With $\sim 10^5$ times the size of matrix grains, they would be far less efficient collectors of volatiles, having 10^{-10} the specific surface area and 10^{10} the diffusional equilibration time. Thus Fig. 1a is pertinent to chondrules, and Fig. 1b, to matrix.

Ordinary chondrites show a more variable pattern (Larimer and Anders 1967; Anders 1971a). Elements fairly high in the condensation sequence (Cu, Ge, Sn, Ga, S) again are depleted by nearly constant factors, averaging 0.24. This suggests a matrix content of 24%. But the last 4 metals in the condensation sequence (Pb, Bi, Tl, In) are depleted by much more variable factors, down to $\sim 10^{-3}$. Several other volatile elements whose condensation behavior

is less well understood (Cl, Br, I, Hg, Cs, Cd, etc.) show variations of similar magnitude. The depletion generally increases with petrologic type. Apparently these meteorites accreted at so high a temperature that not even the matrix acquired its full complement of volatile metals. And each meteorite seems to have its own individual kind of matrix, reflecting its P,T history up to the time of accretion.

d) Accretion Temperatures

One can use volatile metals as "cosmothermometers", as first attempted by Urey (1952a, 1954). The temperature corresponding to a given metal content can be read off the condensation curve (Fig. 1b). Keays et al. (1971) have reported values for 11 L-chondrites, based on Bi, Tl, and In contents. Results ranged from 460°K for L3's to 560°K for L6's (all at an assumed P of 10^{-4} atm) and were reasonably concordant for the 3 thermometers. The event recorded by these thermometers is the chemical isolation of the dust grains from the gas, when they ceased to take up volatile metals. However, this probably coincided with their physical isolation from the gas (= accretion). Estimates of diffusion rates show that grains of $\leq 10^{-5}$ cm will remain in equilibrium with Pb, Bi, Tl vapor in the gas down to 500°K, at cooling times as short as a few years (Larimer 1967). Thus the temperatures calculated can in fact be interpreted as accretion temperatures.

Similar temperature estimates have been attempted for the Earth, Moon, and several classes of achondritic meteorites (Anders Ganapathy Keays Laul and Morgan 1971; Laul Morgan Ganapathy Anders

1971a). The procedure is less straightforward because the effects of planetary differentiation are superimposed on the original nebular fractionation and must be separated from it. Moreover, for a differentiated planet one can at best obtain only a planet-wide average abundance of a volatile element. This does not give the true average temperature during accretion, but a value biased toward lower temperatures, because abundance is a logarithmic, not a linear function of temperature (Fig. 1). The error thus introduced seems to be of the order of 30°K (Anders et al. 1971).

The mean values obtained are shown in Table 1. These values apply to an assumed total pressure of 10^{-4} atm for the Earth and Moon. The results are moderately sensitive to pressure: at 10^{-4} atm, the values for Earth and Moon become 456 and 502°K. For the L chondrites at least, P can be bracketed between 10^{-2} and 10^{-6} atm by chemical arguments. At pressures of 10^{-2} or 10^{-6} atm, calculated Bi-Tl correlation curves fit the data noticeably less well than at 10^{-4} atm. Moreover, all chondrites contain FeS, whose formation temperature (680°K) is pressure independent. At a pressure of 10^{-2} atm, the condensation curves of Bi and Tl are shifted upward sufficiently to imply accretion temperatures greater than 680°K for the more strongly depleted type 6's. Such meteorites then should contain no FeS, contrary to observation. Similarly, a lower limit of 10^{-6} to 10^{-7} atm can be inferred from the absence of Fe_3O_4 (formation temperature, 400°K) from all but the least recrystallized and least depleted type 3's. Thus the pressure in the region of

the L chondrites apparently was $10^{-4\pm 2}$ atm. Somewhat more restrictive limits will be given in § VIII.

It is remarkable that temperatures as high as 500°K prevailed during accretion of the meteorite parent bodies, because the present black body temperature at 2.8 AU is only 170°K . Thus a powerful, transient heat source must have been present. One possibility is the Hayashi stage of the Sun; another is the collapse stage of the nebula which would release vast amounts of gravitational potential energy over a short span of time (Cameron 1962, 1963, 1969). Indeed, the temperatures inferred for the dust shells or disks surrounding protostars are of the right order: ≤ 1850 to 350°K for VY Canis Majoris and $\sim 850^\circ\text{K}$ for R Monocerotis and other infrared stars (see Anders 1971a for references). Perhaps it will soon be possible to compare time, temperature, and pressure estimates from meteorites with observational and theoretical data for protostars.

There is some indication that the bulk of the accretion in the inner solar system took place between 500 and 700°K . Only 5-10% of the ordinary chondrites are type 3's which accreted below 500°K , and no known meteorites have the FeS-free, but otherwise chondritic composition expected for material accreted above 680°K . The Earth, too, seems to contain substantial amounts of FeS (Anderson Sammis and Jordan 1971), and resembles 04-06 chondrites in the abundance of volatile elements (Anders 1968;

Larimer 1971). There are two limiting interpretations for this pattern: accretion at a constant temperature of $\sim 540^\circ\text{K}$ (at 10^{-2} atm) or at falling temperatures from >700 to $\sim 350^\circ\text{K}$. In the latter case, a large part of the volatiles may have been brought in as a thin veneer of carbonaceous-chondrite-like material, swept up by the Earth in the final stage of accretion (Turekian and Clark 1969).

The Moon seems to be depleted in volatiles by another 2 orders of magnitude relative to the Earth (Ganapathy Keays Laul and Anders 1970; Anders 1970; Anders et al. 1971). In terms of the preceding 2 models, this may imply either accretion at a higher temperature (610°K at 10^{-2} atm) or a much lower accretion efficiency in the final stages of formation, when volatile-rich material was being swept up.

e) Material Balance

The fate of the lost volatiles remains largely undetermined. A few of the most volatile elements (In, Bi, Tl, Cs, and Br) are occasionally enriched in O3 chondrites beyond cosmic levels. Such enrichment might be expected in the final stages of accretion when the gas phase had become enriched in volatiles left behind by the previously accreted O4's-O6's. An even more striking enrichment is shown by Hg, thought to be the most volatile of all metals (Urey 1952a, 1954). It is enriched in C chondrites by 1-2 orders of magnitude above cosmic levels and is only slightly depleted in

O chondrites (see Anders 1971a for references). Larimer and Anders (1967) have tried to explain the "mercury paradox" by postulating the existence of a relatively involatile Hg compound, but Arrhenius and Alfvén (1971) have proposed an attractive alternative. If condensation took place from a partially ionized plasma, Hg, because of its high ionization potential, would be neutralized ahead of most other elements, thus becoming available for condensation at an earlier stage.

Some part of the volatiles may have been lost with the gases during dissipation of the solar nebula. Hence it seems unlikely that the average composition of all meteorites is close to cosmic. Meteorites apparently did not evolve in a closed system.

f) Other Cosmothermometers: Fe^{2+} and O^{18}

If the dust remains in equilibrium with the gas on cooling, metallic Fe will be oxidized to Fe^{2+} which enters magnesium silicates and forms the solid solutions $(\text{Mg},\text{Fe})_2\text{SiO}_4$ (= olivine) and $(\text{Mg},\text{Fe})\text{SiO}_3$ (= orthopyroxene). The Fe^{2+} content of olivine in O chondrites, ranging from 16 mol percent in H's to 31 mol percent in LL's, corresponds to equilibrium at 650-580°K (Larimer, 1968). These temperatures are independent of pressure, but depend on $\text{H}_2/\text{H}_2\text{O}$ ratio. The above values apply to a gas of solar composition, $\text{H}_2/\text{H}_2\text{O} = 500$.

The simplest interpretation in terms of the two-component model is that this was the temperature range of the dust when

O chondrites (see Anders 1971a for references). Larimer and Anders (1967) have tried to explain the "mercury paradox" by postulating the existence of a relatively involatile Hg compound, but Arrhenius and Alfvén (1971) have proposed an attractive alternative. If condensation took place from a partially ionized plasma, Hg, because of its high ionization potential, would be neutralized ahead of most other elements, thus becoming available for condensation at an earlier stage.

Some part of the volatiles may have been lost with the gases during dissipation of the solar nebula. Hence it seems unlikely that the average composition of all meteorites is close to cosmic. Meteorites apparently did not evolve in a closed system.

f) Other Cosmothermometers: Fe^{2+} and O^{18}

If the dust remains in equilibrium with the gas on cooling, metallic Fe will be oxidized to Fe^{2+} which enters magnesium silicates and forms the solid solutions $(\text{Mg,Fe})_2\text{SiO}_4$ (= olivine) and $(\text{Mg,Fe})\text{SiO}_3$ (= orthopyroxene). The Fe^{2+} content of olivine in O chondrites, ranging from 16 mol percent in H's to 31 mol percent in LL's, corresponds to equilibrium at 650-580°K (Larimer, 1968). These temperatures are independent of pressure, but depend on $\text{H}_2/\text{H}_2\text{O}$ ratio. The above values apply to a gas of solar composition, $\text{H}_2/\text{H}_2\text{O} = 500$.

The simplest interpretation in terms of the two-component model is that this was the temperature range of the dust when

chondrule formation began. This is probably an oversimplification, as it implies no reduction of Fe^{2+} to Fe^0 during remelting. The equilibrium $\text{FeO} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{O}$ shifts to the right on heating, and thus some reduction is expected even at the short time scales (~ 1 min) implied by the textures of chondrules. This is confirmed by the relatively unmetamorphosed chondrites of petrologic type 3, whose chondrules are appreciably poorer in Fe^{2+} than their matrices. Presumably such differences were also present in types 4 to 6, but were averaged out during metamorphism. Since chondrules predominate over matrix in 3:1 ratio, the original Fe^{2+} content of the matrix may have been appreciably higher than the present content. Accordingly the dust temperature may have been less than the 580-650°K estimated from the present Fe^{2+} content, perhaps close to the accretion temperatures of 460-560°K estimated from volatile metals. Chondrule formation and accretion may in fact have proceeded simultaneously (Larimer and Anders 1970).

Very similar temperatures have been estimated by Onuma Clayton and Mayeda (1971) from the O^{18} content of chondrites. They note that most of the oxygen in a solar nebula will be contained in gaseous species: CO and H_2O at high temperature; H_2O alone at low temperature. If the dust maintains isotopic equilibrium with the gas, its O^{18} content will vary with temperature. The temperature dependence can be predicted from the relevant chemical and isotopic-exchange equilibria.

For the O chondrites, Onuma et al. obtain chondrule formation temperatures of 450 to 470°K. These temperatures again refer to the temperature of the dust at the onset of chondrule formation. They are independent of pressure above 10^{-6} atm, but depend on O^{18}/O^{16} ratio in the nebula and isotopic fractionation factors for the relevant minerals. The combined uncertainty is probably a few tens of degrees.

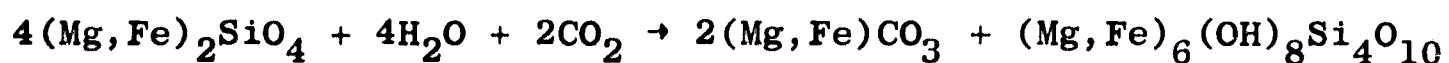
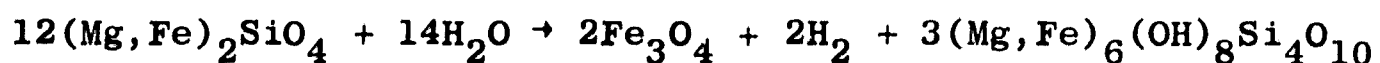
The O^{18} temperatures are lower than the accretion temperatures based on volatile metals, 460 to 560°K. The latter are pressure dependent, however, and can be brought into approximate concordancy with the O^{18} temperatures by lowering the pressure to 10^{-5} to 10^{-6} atm, well within the quoted limits of $10^{-4\pm2}$ atm (§ VIII). The O^{18} temperatures also disagree rather markedly with the chondrule formation temperatures estimated from Fe^{2+} (580-650°K). As noted above, the latter temperatures probably are too high because of Fe^{2+} -reduction during chondrule formation. The O^{18} temperatures are less susceptible to error, because O^{18} exchange between molten silicates and gas is apt to be slower than Fe^{2+} -reduction by H_2 .

For carbonaceous chondrites, higher chondrule formation temperatures were found, 530 to 620°K at 10^{-4} atm (Onuma et al. 1971). The higher of these values are pressure dependent, because they fall in a range where the O reservoir in the nebula changes from CO to H_2O , by the pressure dependent CO/ CH_4 equilibrium. At

pressures of 10^{-5} to 10^{-6} atm, these temperatures would be lowered by ≤ 50 and $\leq 100^\circ\text{K}$.

The higher temperatures (or lower pressures) for C chondrites are consistent with the fact that these meteorites are depleted in Na, K, and Mn, elements of only moderate volatility which are not depleted in O chondrites (Fig. 1).

Onuma et al. also obtained formation temperatures for 2 of the low-temperature minerals in C1, C2 chondrites: hydrated silicates (probably serpentine and montmorillonite, Bass 1971) and dolomite $[(\text{Ca}, \text{Mg})\text{CO}_3]$. The temperatures for C1's were 360 ± 15 and $360 \pm 5^\circ\text{K}$; for C2's (silicate only): $380 \pm 15^\circ\text{K}$. These minerals probably formed from anhydrous silicates in the primary condensate, by reactions such as:



Roughly similar temperatures had previously been estimated from the presence of Fe_3O_4 ($\leq 400^\circ\text{K}$) and hydrated silicates (300 to 350°K ; Larimer and Anders 1967; Anders 1968).

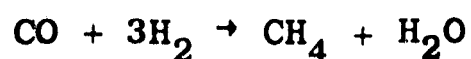
V. ORGANIC MATTER

Carbonaceous chondrites contain up to 4% carbon. Most of it is in the form of an insoluble, aromatic polymer with -OH and -COOH groups, somewhat similar to coal or to humic acids in soils.

The remainder consists of Mg, Fe, and Ca carbonates and a variety of organic compounds. O chondrites contain smaller amounts of C (0.01 to 2%) in an ill-defined chemical form, presumably again an aromatic polymer. The literature up to late 1966 has been reviewed by Hayes (1967) and Vdovykin (1967).

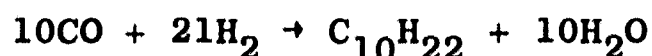
a) Origin of Organic Compounds

The existence of organic compounds in meteorites is a paradox under the equilibrium condensation model. At equilibrium in a solar gas of 10^{-4} atm, C should be present as small molecules of high volatility: CO at high temperatures ($>600^{\circ}\text{K}$), CH_4 at low temperatures. Two alternatives may be considered. One view, widely held but never developed in detail, is that organic compounds were produced from $\text{CH}_4 + \text{NH}_3 + \text{H}_2\text{O}$ by Miller-Urey reactions. In these reactions energy is supplied from an external source (UV, charged particles, electric discharges) to produce free radicals which combine to more complex compounds lying thermodynamically "uphill" from the reactants. The other alternative is that the organic compounds formed spontaneously as metastable products, during hydrogenation of CO on cooling of the nebula. Under equilibrium conditions, methane should result by a hydrogenation reaction:



But hydrogenation of CO proceeds rapidly only on solid catalyst

surfaces, in which case partially hydrogenated hydrocarbons with $H/C < 4$ are formed in preference to CH_4 , e.g.



This reaction, the Fischer-Tropsch synthesis, is used industrially for the production of gasoline.

Some of the minerals of meteorites (Fe-Ni, silicates, and especially Fe_3O_4) are good catalysts for this reaction. One may thus expect it to have taken place on the surfaces of dust grains in the solar nebula. Indeed, meteoritic hydrocarbons show a striking resemblance to Fischer-Tropsch hydrocarbons (Studier Hayatsu and Anders 1968). Normal (= straight chain) molecules predominate, followed by 4-5 slightly branched (mono- and di-methyl) isomers. This resemblance is highly significant if one considers that some 10^3 to 10^5 structural isomers exist for hydrocarbons with 15 to 20 C atoms. The Miller-Urey reaction shows no such selectivity, producing all possible isomers in comparable abundance.

A systematic study of the Fischer-Tropsch reaction, as applied to meteorites, was begun by M. H. Studier, R. Hayatsu, and the writer 6 years ago. It appears that all compound classes reliably identified in meteorites are produced by the Fischer-Tropsch reaction, or some variant thereof (Table 2). In the presence of NH_3 , even compounds of biological interest are produced:

amino acids, including heterocyclic or aromatic ones such as histidine and tyrosine; nucleotide bases such as adenine and guanine; porphyrins, etc. Contamination was precluded by use of deuterium in the synthesis. The Miller-Urey reaction is able to account for some of these compounds, but not for others. A few compound classes, including the polymer, yet remain to be investigated, and it is conceivable that other processes will have to be invoked. At present, however, the Fischer-Tropsch reaction adequately accounts for the evidence.

b) Carbon-Isotope Fractionations

A further argument for the Fischer-Tropsch reaction comes from the isotopic differences between carbonate C (= bonded to O, e.g. MgCO_3) and organic C (= bonded to H, e.g. C_xH_y) in carbonaceous chondrites. Clayton (1963) showed that the carbonate C was some 7-8% richer in C^{13} than the organic C (see Anders 1971a for references). Although fractionations of this magnitude are theoretically possible under equilibrium conditions at very low temperatures ($\leq 0^\circ\text{C}$), they are not observed in nature. Urey (1967) therefore proposed that the 2 types of C came from 2 unrelated reservoirs while Arrhenius and Alfvén suggested fractionation during carbonate growth from the gas phase, involving multiple desorption or metastable molecules.

It turns out, however, that the Fischer-Tropsch reaction gives an isotopic fractionation of just the right sign and magni-

tude, owing to a kinetic isotopic effect (Lancet and Anders 1970). From the temperature dependence of the fractionation between 375 and 550°K, the observed fractionations in C1 and C2 chondrites correspond to 350-358 and 392-418°K. These values agree rather well with the O^{18} -based formation temperatures of carbonates and silicates, 360°K for C1's and 380°K for C2's (Onuma et al. 1971). The Miller-Urey reaction gives a fractionation of only $-0.04 \pm 0.02\%$ (Lancet and Anders, to be published).

It seems likely that the Fischer-Tropsch reaction is also responsible for interstellar molecules (Herbig 1970a,b). Even C1 chondrites contain only ~6% their cosmic complement of C; for other meteorites and the inner planets, the amount is even smaller. The missing C was probably lost to interstellar space along with H_2 , He, H_2O , and other volatiles. Its chemical state may never be known with certainty, but since the retained C appears to show the imprint of the Fischer-Tropsch reaction, it seems likely that the lost C, too, had been involved in this process. Many of the interstellar molecules identified thus far have also been seen in meteorites or in variants of the Fischer-Tropsch synthesis: $HCHO$, CH_3OH , $HCOOH$, HCN , $HNCO$, CH_3CN , COS .

VI. PRIMORDIAL NOBLE GASES

Two types of "primordial" gas are found in meteorites, termed "solar" and "planetary" (Signer and Suess 1963). We are not concerned with the former which is sporadically distributed and

apparently represents solar wind trapped on the surface of the meteorite parent body after accretion (Wänke 1965). Our interest is confined to the planetary component which seems to date from a pre-accretional stage. Three properties need to be explained: amounts, elemental ratios, and isotopic ratios.

The amounts of planetary gas show a most remarkable correlation with petrologic type, among both the ordinary and carbonaceous chondrites (see Anders 1971a for references). Absolute abundances of Ar, Kr, Xe rise by 3 orders of magnitude from O6 to C1 chondrites or ureilites. (He and Ne show a different behavior: they are found only in C1,2's and a few O3's.) Elemental ratios of the heavier gases (Ar/Kr, Ar/Xe) remain constant within a factor of ≤ 6 over the entire range.

A rather common view is that planetary gases reflect some kind of solubility equilibrium between nebula and solid phase, perhaps modified by adsorption effects. The equilibrium solubility of these gases may be expected to follow Henry's law, the amount of dissolved gas at a given temperature being proportional to its partial pressure. Experimental measurements at the temperatures of interest ($\sim 500^\circ\text{K}$) are difficult, because diffusion rates are too slow to permit equilibration in times comparable to the human lifespan. The problem has been circumvented by growing a mineral directly in a noble-gas atmosphere (Lancet and Anders 1971). Solubility data were obtained for all 5 noble gases in magnetite,

between 450 and 700°K. Values were highly reproducible and gave reasonable heats of solution. Henry's law was obeyed below partial pressures of 10^{-2} atm. This suggests that true equilibrium solubilities were being measured.

Data from these experiments may be compared with the noble-gas content of magnetite from the Orgueil C1 chondrite (Jeffery and Anders 1970). Extrapolating the laboratory data to 357°K, the mean formation temperature of Orgueil minerals from O^{18}/O^{16} and C^{12}/C^{13} data (Onuma et al. 1971), one finds that the following partial and total pressures are required to account for the observed gas contents:

	Ar	Kr	Xe
Partial P (atm)	6.8×10^{-11}	9.4×10^{-12}	5.5×10^{-12}
Total P (atm)	4.5×10^{-6}	2.2×10^{-3}	1.16×10^{-2}

The Ar value should be given greatest weight, because the Kr, Xe contents of meteoritic magnetite may be systematically too high owing to retention of a small amount (<2%) of silicate. The total pressure found here, 5×10^{-6} atm, is consistent with previous estimates for the solar nebula. It is much higher, however, than the pressure expected for the Arrhenius-Alfvén model.

The elemental ratios are not yet fully accounted for. He and Ne have almost equal solubilities in Fe_3O_4 and will therefore appear in nearly cosmic ratio, as observed in meteorites. But solubilities of Ar, Kr, Xe in Fe_3O_4 are nearly equal, in contrast to the decreasing depletion of the heavier gases in meteorites.

Perhaps this is beside the point, because more than 99% of the Kr, Xe in Orgueil resides in hydrated silicates, not magnetite (Jeffery and Anders 1970). Thus the meteoritic pattern must be governed by the solubilities in silicate, not magnetite. Measurements on silicates will be needed to settle the matter conclusively, but since hydrated silicates, unlike magnetite, are not close-packed, it seems reasonable to expect higher solubilities, especially for the heavier gases.

The isotopic differences between solar and planetary gas have not yet been satisfactorily accounted for. Neither mass-dependent fractionations (gravitational escape, volume diffusion) nor nuclear reactions give comprehensive, quantitatively self-consistent explanations (Herzog 1971). This is a common shortcoming of all models of the early solar system and hence cannot be held against any one of them.

VII. CHRONOLOGY

This subject has been discussed in my recent review (Anders 1971a). In the present context, the most important point is the time scale of the evolution of the solar system. Previous age determinations had shown that all chondrites began to retain Xe^{129} (from extinct I^{129} ; $t_{1/2} = 16.4$ Myr) within 15 Myr of each other (Podosek 1970). However, all these meteorites had experienced at least 2 heating events. Chondrule formation and metamorphism in the following schematic history.

Initial		Chondrule			End of
Condensation	Δt_1	Formation	Δt_2	Accretion	Δt_3 Metamorphism

Both of these heating events were capable of expelling Xe, I and thus resetting the $\text{Xe}^{129}\text{-I}^{129}$ clock. The dispersion in I-Xe dates thus gave only the differences in $\Delta t_1 + \Delta t_2 + \Delta t_3$ from meteorite to meteorite, not the absolute value of $\Delta t_1 + \Delta t_2 + \Delta t_3$. Though the total range of 15 Myr suggested that the time scale was on the order of 10^7 years, a longer time scale, as favored by Arrhenius and Alfvén, could not be ruled out.

Meanwhile some new data have become available which provide an absolute value for $\Delta t_1 + \Delta t_2 + \Delta t_3$. Alexander et al. (1971) measured Fe_3O_4 from an unmetamorphosed meteorite, the C1 chondrite Orgueil, and found it to be 2.1 Myr older than the metamorphosed C4 chondrite Karoonda (Podosek 1970). Both meteorites are genetically related by various chemical criteria, and so it is probably safe to assume that Karoonda originally had the same $\text{I}^{129}/\text{I}^{127}$ ratio as Orgueil. The above age of 2.1 Myr thus represents $\Delta t_1 + \Delta t_2 + \Delta t_3$ for Karoonda. A sizable part of the total interval must have been taken up by Δt_3 , because cooling times even for small asteroids are on the order of 10^6 to 10^7 yr. Thus the entire interval between condensation and accretion must have been less than 2.1 Myr, perhaps much less.

VIII. CONDITIONS IN THE EARLY SOLAR SYSTEM

Figure 3 illustrates temperature and pressure estimates for two localities in the early solar system: the source regions for the Cl and ordinary chondrites. Temperatures for the Cl chondrites are very well determined by three isotopic thermometers, all nominally independent of pressure. The pressure, as given by the intercept of the Ar solubility line with the temperature lines, is probably good to within a factor of 2, because Ar contents of meteorites and Ar solubilities are accurately known.

For ordinary chondrites, two pressure-independent thermometers are available, O^{18}/O^{16} and Fe^{2+} . The former, giving temperatures of 450-470°K, is probably more reliable, as discussed in the text. Substituting the O^{18} temperatures in the condensation equation for Bi, we can solve for the pressure corresponding to the observed Bi contents.

$$\log P_t = 9.25 + \log [\alpha/(1-\alpha)] - 6100/T$$

Here $9.25 = b - \log (2 \text{ Bi}/H)$, where Bi and H are the atomic abundances of Bi and H, while b is the integration constant of the Clausius-Clapeyron equation, plus the standard entropy of solution. The fraction condensed is α , while $6100 = (\Delta H_v - \Delta H_s)/2.303 R$, where ΔH_v is the heat of vaporization of Bi, ΔH_s is its heat of solution in nickel-iron, and R is the gas constant (Keays et al. 1971).

Results are plotted in Fig. 3 for 9 meteorites for which both O^{18} and Bi data are available. The points scatter somewhat, but at least some of the scatter may reflect genuine differences among classes. The LL chondrites are highest, while the H chondrites are lowest. Error bars (having the slope of the Bi condensation curve) correspond to a nominal uncertainty of $\pm 10^\circ$ in the O^{18} temperatures.

On the face of it, the agreement of the points is not bad. Temperature errors less than 10° would be required to give concordant pressures of $10^{-5} - 10^{-6}$ atm for each chondrite class. However, the actual uncertainty is somewhat greater than that. Neither the vapor pressure equation of Bi nor its heat of solution in nickel-iron are known very accurately. The magnitude of the uncertainty is indicated by the fact that pressures estimated analogously from Tl data are about an order of magnitude higher than those based on Bi data. Thus the pressures in the source region of the ordinary chondrites can only be bracketed between 10^{-4} and 10^{-6} atm. More accurate estimates will be possible when better thermodynamic data become available. But even the present data agree rather well with previous estimates for the solar nebula, and are orders of magnitude higher than those expected for a plasma.

It seems rather significant that the various cosmothermometers and barometers give largely concordant answers. They are based

on quite diverse processes: gross chemical transformations, solubilities of trace metals or gases in solids, equilibrium isotope fractionations, kinetic isotope fractionations, etc. One can never be completely sure that this agreement is not fortuitous. Perhaps plasma reactions at much lower pressures can mimic the exact combination of isotopic and elemental ratios corresponding to P,T concordancy at higher pressures. But until such a series of coincidences is actually demonstrated, it seems justified to accept the P,T data in Table 3 at face value.

The obvious conclusion thus seems to be that the meteorites and planets formed from a hot solar nebula of $\sim 0.1-1 M_{\odot}$. Most or all of their properties can be quantitatively accounted for by condensation processes, largely under equilibrium conditions.

Acknowledgments. This work was supported in part by NASA Grant NGL 14-001-010 and AEC Contract AT(11-1)-382.

References

- Alexander, C., et al. 1971, manuscript in preparation.
- Anders, E. 1964, Space Sci. Rev., 3, 583-714.
- 1968, Acc. Chem. Res., 1, 289-298.
- 1970, Science, 169, 1309-1310.
- 1971a, Ann. Rev. Astron. Astrophys., 9, 1-34.
- 1971b, Geochim. Cosmochim. Acta, 35, 516-5221
- Anders, E., Ganapathy, R., Keays, R. R., Laul, J. C., and Morgan, J. W. 1971, Proc. Second Lunar Sci. Conf., 2, Geochim. Cosmochim. Acta, Suppl. 2, 1021-1036.
- Anderson, D. L., Sammis, C., and Jordan, T. 1971, Science, 171, 1103-1112.
- Arrhenius, G., and Alfvén, H. 1971, Earth Planet. Sci. Lett., 10, 253-267.
- Bass, M. N. 1971, Geochim. Cosmochim. Acta, 35, 139-147.
- Cameron, A. G. W. 1962, Icarus, 1, 13-69.
- 1963, Icarus, 1, 339-342.
- 1966, Earth Planet. Sci. Lett., 1, 93-96.
- 1968, in Origin and Distribution of the Elements, ed. L. H. Ahrens (Pergamon: Oxford), pp. 125-143.
- 1969, in Meteorite Research, ed. P. M. Millman (Dordrecht: D. Reidel), pp. 7-15.
- Clayton, R. N. 1963, Science, 140, 192-193.
- Ganapathy, R., Keays, R. R., Laul, J. C., and Anders, E. 1970, Proc. Apollo 11 Lunar Sci. Conf., 2, Geochim. Cosmochim. Acta, Suppl. 1, 1117-1142.
- Grossman, L. 1971, Ph.D. dissertation, Yale University.
- Hayes, J. M. 1967, Geochim. Cosmochim. Acta, 31, 1395-1440.

- Herbig, G. H. 1970a, paper presented at American Astronomical Society meeting, Boulder, Colorado.
- 1970b, Mém. Soc. Sci. Liège [8°], 5th sér., 19, 13-26.
- Herzog, G. F. 1971, submitted to J. Geophys. Res.
- Jeffery, P. M., and Anders, E. 1970, Geochim. Cosmochim. Acta, 34, 1175-1198.
- Keays, R. R., Ganapathy, R., and Anders, E. 1971, Geochim. Cosmochim. Acta, 35, 337-363.
- Lancet, M. S., and Anders, E. 1970, Science, 170, 980-982.
- 1971, paper presented at Meteoritical Society meeting, Tübingen, Germany.
- Larimer, J. W. 1967, Geochim. Cosmochim. Acta, 31, 1215-1238.
- 1968, Geochim. Cosmochim. Acta, 32, 1187-1207.
- 1971, Geochim. Cosmochim. Acta, 35, in press.
- Larimer, J. W., and Anders, E. 1967, Geochim. Cosmochim. Acta, 31, 1239-1270.
- 1970, Geochim. Cosmochim. Acta, 34, 367-388.
- Laul, J. C., Morgan, J. W., Ganapathy, R., and Anders, E. 1971, Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2, in press.
- Lord, H. C. III 1965, Icarus, 4, 279-288.
- Onuma, N., Clayton, R. N., and Mayeda, T. K. 1971, submitted to Geochim. Cosmochim. Acta.
- Podosek, F. A. 1970, Geochim. Cosmochim. Acta, 34, 341-365.
- Reuter, J. H., Epstein, S., and Taylor, H. P., Jr. 1965, Geochim. Cosmochim. Acta, 29, 481-488.

- Signer, P., and Suess, H. E. 1963, in Earth Science and Meteoritics, ed. J. Geiss and E. D. Goldberg (Amsterdam: North Holland), pp. 241-272.
- Studier, M. H., Hayatsu, R., and Anders, E. 1968, Geochim. Cosmochim. Acta, 32, 151-174.
- 1971, submitted to Geochim. Cosmochim. Acta.
- Turekian, K. K., and Clark, S. P., Jr. 1969, Earth Planet. Sci. Lett., 6, 346-348.
- Urey, H. C. 1952a, The Planets (New Haven: Yale University Press).
- 1952b, Geochim. Cosmochim. Acta, 2, 269-282.
- 1954, Astrophys. J., Suppl. 1, [6], 147-173.
- 1967, Quart. J. Roy. Astron. Soc., 8, 23-47.
- Urey, H. C., and Craig, H. 1953, Geochim. Cosmochim. Acta, 4, 36-82.
- Van Schmus, W. R., and Wood, J. A. 1967, Geochim. Cosmochim. Acta, 31, 747-765.
- Vdovykin, G. P. 1967, Carbon Matter of Meteorites (Organic Compounds, Diamonds, Graphite), (Moscow: Nauka Publishing Office).
- Wanke, H. 1965, Z. Naturforsch., 20a, 946-949.
- Whipple, F. L. 1966, Science, 153, 54-56.
- Wood, J. A. 1962, Nature, 194, 127-130.
- 1963, Icarus, 2, 152-180.

Table 1. Accretion Temperatures from Volatile Metal Content

Object	Low-T fraction	Accretion T	P	Ref. [†]
	%	°K	atm	
L Chondrites	24	513*	10 ⁻⁴	1
Eucrites	0.8	460	10 ⁻⁴	2
Shergottites	28	471	10 ⁻⁴	2
Nakhlites	38	478	10 ⁻⁴	2
Earth	11	544	10 ⁻²	3
Moon	2.4	610	10 ⁻²	3

*This is an average value, weighted in such a manner as to make it consistent with the temperatures of the remaining, chemical differentiated objects in this table (Anders et al. 1971). The actual range for L chondrites is 460 to 560°K.

- †1. Keays et al. (1971)
 2. Laul et al. (1971)
 3. Anders et al. (1971)

Table 2. Organic Compounds in Meteorites*

Compound Class	Fischer-Tropsch-Type Reactions [†]
Alkanes (normal, 2-Me, 3-Me, 4,5-DiMe)	+
Alkenes	+
Isoprenoids (<C ₁₅)	+
Aromatic Hydrocarbons (benzene, alkylbenzenes, polycyclics)	+
Fatty Acids (mainly normal)	?
Nitrogen Bases (adenine, guanine, etc.)	+
Amino Acids (protein and non-protein)	+
Porphyrin-like Compounds	+
Cl- and S-compounds (Ø-Cl, thiophenes)	?
Polymer (aromatic, with -OH and -COOH group)	?

* For references see Hayes (1967); Anders (1971a); Studier et al. (1971).

[†] + accounts reasonably well for meteoritic feature

? not yet investigated

Figure Captions

Figure 1. Condensation sequence of a gas of cosmic composition (Larimer 1967; Anders 1968, with minor revisions). Slow-cooling sequence assumes diffusional equilibrium between grain surfaces and interiors, with formation of solid solutions, while fast cooling sequence corresponds to deposition of pure elements and compounds, without interdiffusion. Shaded areas represent condensation or chemical transformation of major constituents. The formation range of hydrated silicates is poorly known.

Figure 2. Elements fall into 3 groups, based on their fractionation behavior in meteorites. In terms of the condensation model, these reflect 4 main cosmochemical fractionation processes: loss of refractories, loss of metal, loss of volatiles during remelting, and loss of volatiles during accretion. Refractories and siderophiles each tend to vary in unison, and by rather small factors (less than 2). Volatiles show greater and more variable depletions (to 10^{-3}) and at least the more strongly depleted elements do not vary in unison.

Figure 3. Temperatures and pressures in the source regions of Cl and O chondrites. Sloping lines represent P,T-dependent equilibria; their intercept with pressure-independent temperature estimates (vertical lines or points) gives both P and T. For Cl chondrites $T = 357^{\circ}\text{K}$ and $P = 5 \times 10^{-6}$ atm is indicated. For the O chondrites, conditions are less well-determined: $T = 450\text{--}470^{\circ}\text{K}$, $P = 10^{-4}$ to 10^{-6} atm. $\text{O}^{18}/\text{O}^{16}$ data from Onuma et al. (1971) and Reuter et al. (1965); $\text{C}^{13}/\text{C}^{12}$ and Ar from Lancet and Anders (1971 and unpublished); Bi from Keays et al. (1971) and Laul et al. (unpublished).

Figure 3. Temperatures and pressures in the source regions of Cl and O chondrites. Sloping lines represent P,T-dependent equilibria; their intercept with pressure-independent temperature estimates (vertical lines or points) gives both P and T. For Cl chondrites $T = 357^\circ\text{K}$ and $P = 5 \times 10^{-6}$ atm is indicated. For the O chondrites, conditions are less well-determined: $T = 450\text{--}470^\circ\text{K}$, $P = 10^{-4}$ to 10^{-6} atm. $\text{O}^{18}/\text{O}^{16}$ data from Onuma et al. (1971) and Reuter et al. (1965); $\text{C}^{13}/\text{C}^{12}$ and Ar from Lancet and Anders (1971 and unpublished); Bi from Keays et al. (1971) and Laul et al. (unpublished).

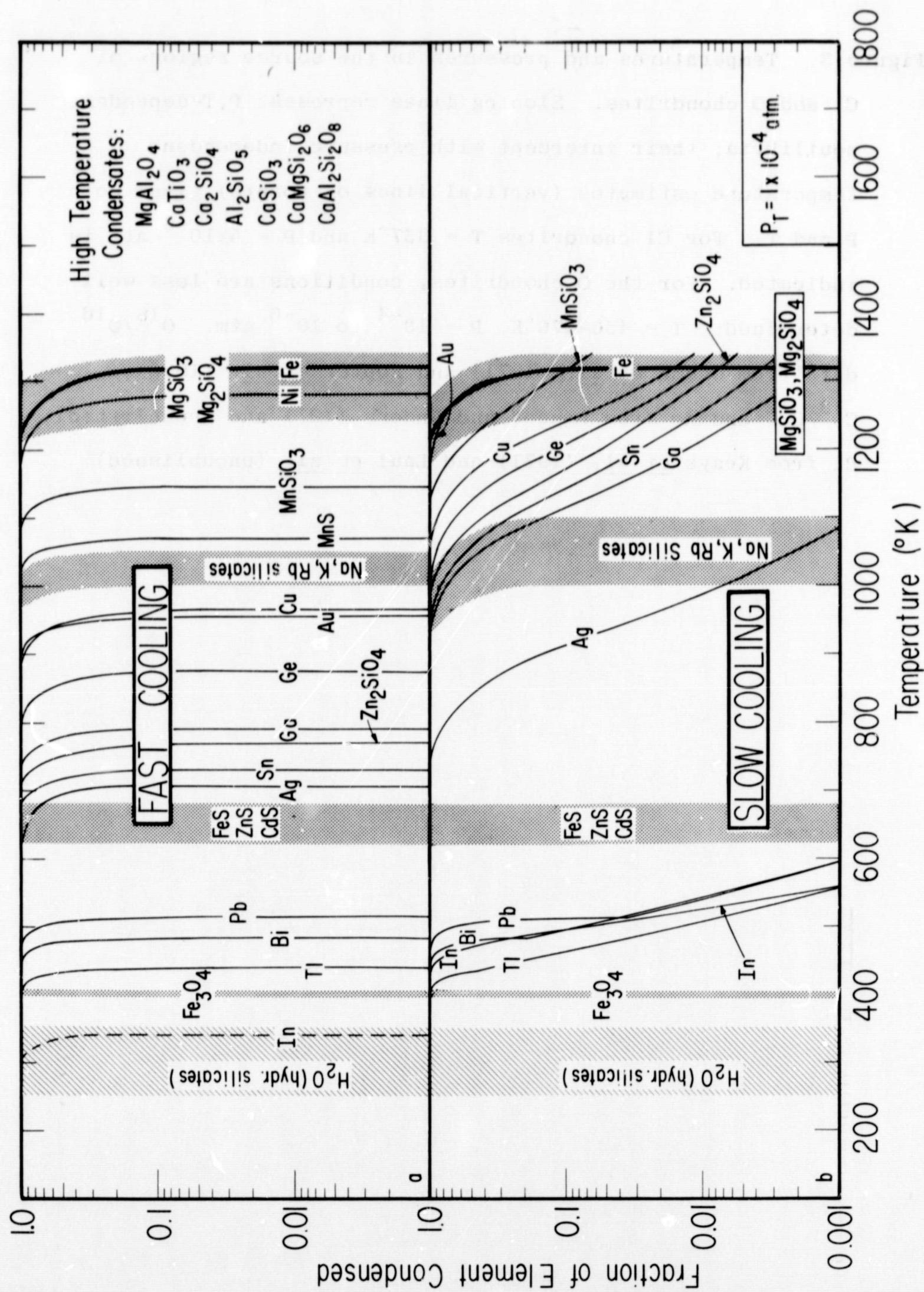


Fig. 1

Chemical Fractionations in Chondrites

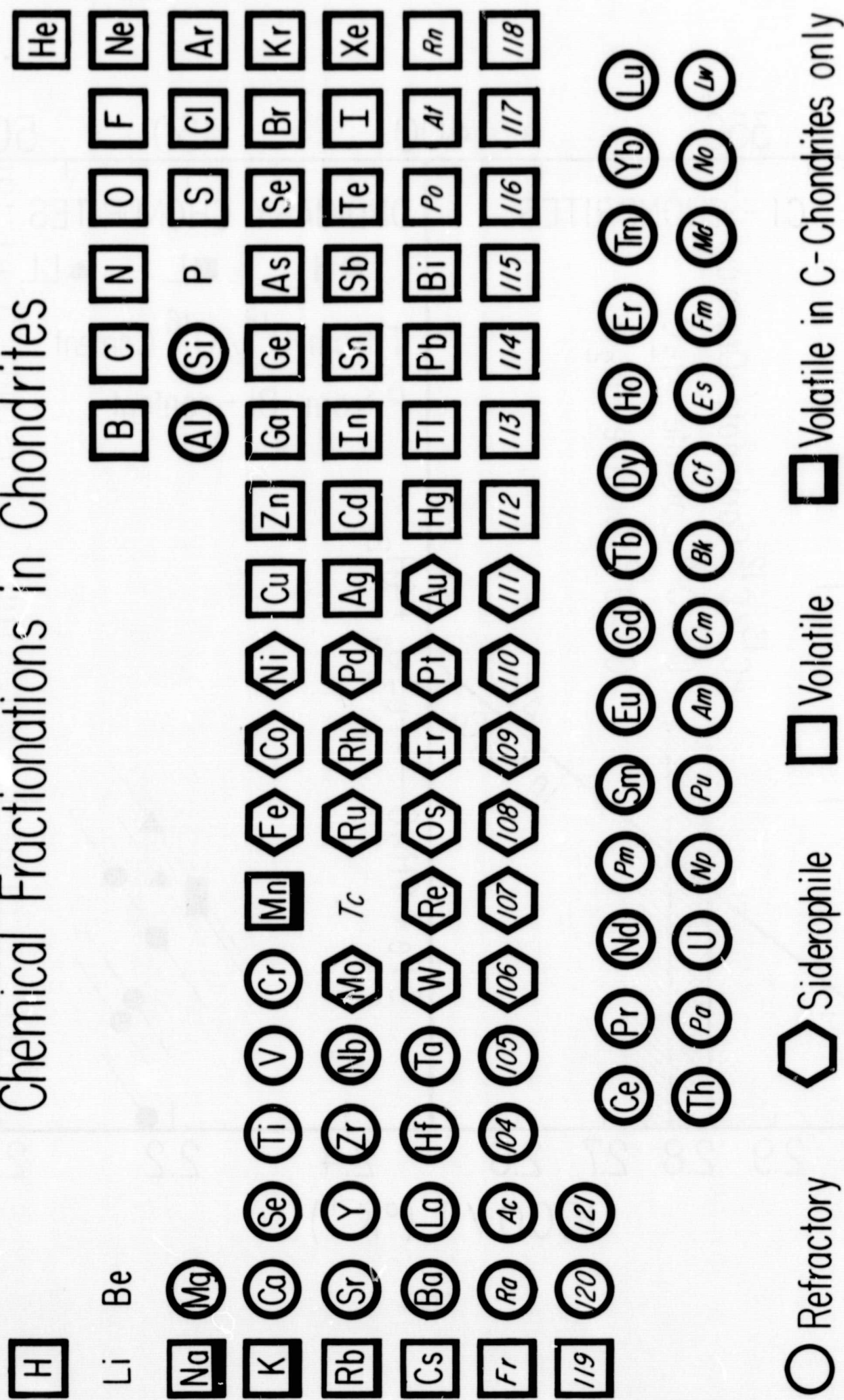


Fig. 2

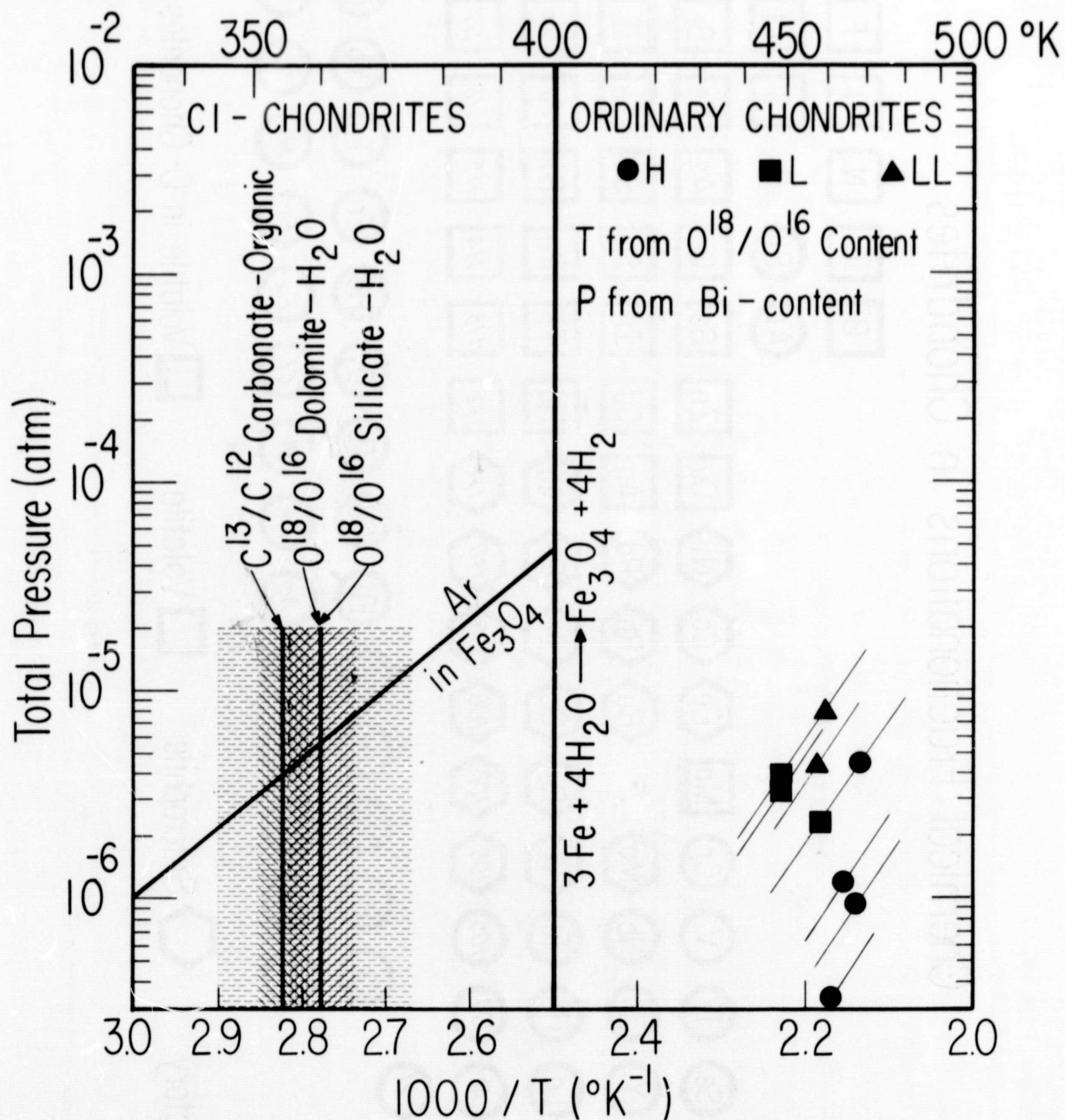


Fig.3