# FROM FeO REDUCTION TO PERCOLATION AND OUTFLOW OF IRON: THERMAL EVOLUTION OF CHONDRITE PARENT BODIES

Sz. Bérczi[1,2], B. Lukács[3], A. Holba[3], A. Kiss[2] & É. Papp[4]

[1] Dean's Office, R. Eötvös Univ., Fac. Sci., H-1088 Budapest, Rákóczi út 5., Hungary
[2] Dept. of Petrology, R. Eötvös University, H-1088 Budapest, Múzeum krt. 4/a., Hungary
[3] Central Research Institute for Physics RMKI, H-1525 Bp. 114. Pf. 49., Budapest, Hungary
[4] Dept. of Geology, Univ. of Western Australia, Nedlands, WA 6009, Australia

## ABSTRACT

Some high petrologic class (6 & 7) members of the NIPR Antarctic Meteorite collection show signals indicating iron outflow. Meteorites are endpoints of heat-driven evolutions at various temperatures, and probably higher petrologic class corresponds to higher heat impact. At high enough temperature one expects liquidification of iron, resulting in iron loss from the texture. Compositional data suggest that the iron loss starts at petrologic class 6; at classes 6 and 7 of any chondrite type metallic iron (and maybe FeS) is less than for 1-5.

So petrologic class 6 exhibit a stage just before iron loss by flowing out: a stage of starting percolation of Fe. Percolation is a stage of phase transitions, when all the domains of the growing new phase have become interconnected but still the old phase exists. In this phase molten iron can form interconnected patches. This is the last stage before iron loss: if the percolated domain reaches a fault line, then Fe can start to flow out. This stage of thermal evolution is the link between chondrites and some achondrites, because at this stage the temperature is already high enough, so diffusion is so strong that chondrules start to be obliterated.

In order to see if this scheme is viable, it is necessary to give an overview of heat-induced evolution; afterwards we give measurements for the differences of iron grain distribution throughout the type LL, according to PC's.

## INTRODUCTION

Thermal metamorphism is an important and well known process in terrestrial geology, which is there mainly surface process. In contrast, for meteorites this metamorphism mostly went inside the *original* parent body, so it can be used for tracing back the thermal history of that body. With as many meteorites, samples of the parent bodies, now available from Antarctic searches, it starts to be possible to distinguish different mechanisms and evolutionary stages among them. Textural evidences of such processes were recognised and studied as early as in the 60's (DODD & al., 1967; van SCHMUS & WOOD, 1967; KEIL & FREDRIKSSON, 1964; HUSS & al., 1981; LUX & al., 1981; SCOTT & al., 1984). In the 80's the center of gravity of the studies had shifted to transformations in the primordial solar nebula before condensation (KRONACKY & WOOD 1984; METZLER & al. 1992; WOOD & HASHIMOTO 1993; SCOTT & al. 1996). However now, when a large amount of chemical composition data have been accumulated (YANAI, KOJIMA & HARAMURA, 1995), it is again profitable to return to metamorphism in the accreted bodies.

Here we focus on thermal history on the basis of the NIPR thin section collections. The thermodynamic evolution of the condensed and accumulated material of the Solar System is studied, mainly for the small bodies which became cold early in the history of the Solar System. We guess that the original heat impact was generated by short-living radionuclides, so the heating and transformation of these bodies depended on their size and solar distance.

## THERMODYNAMICS OF THE PARENT BODIES

Meteorite parent bodies are matters of theoretical reconstructions. Eucrites probably come from Vesta, but this is an idea based on the similarity of reflection spectra, not a fact. By simple logic we can see 3 possibilities for the origin of meteorites:

1) They can be remainders of primordial condensation, i.e. rocks on individual orbits. Then the parent body was essentially the meteorite itself, except for the outer layers lost in the atmosphere.

2) They can be the stony components of an extinct comet.

3) They can be fragments of asteroidal or planetary bodies.

Most probably all 3 cases are represented among the meteorites. However all these possible parent bodies classify together from thermodynamic point of view. Namely they are all quasistationary open thermodynamic systems in vacuo with an approximately fixed volume.

Let us make this statement explicit. Consider a parent body orbiting around Sun. If it is a thermodynamic system at all (we shall see immediately this problem), then it is characterized by its extensive variables. Generally they are: the volume $V$, internal energy $E$, and quantities of some independent chemical components $N^i$. For *closed* systems these quantities totally characterize the final state of the system and the Second Law tells that the system is going towards this final state with growing entropy; generally via decreasing inhomogeneities.

However now the system is not closed: there are fluxes through its boundary. These fluxes can be classified into 3 groups:

1) Irradiation comes in with solar (high temperature) spectrum, heats up the body, and leaves the body in infrared.

2) The internal energy production (i.e. by radionuclides) goes through the body and leaves it at the boundary.

3) Volatiles evaporate from the body: that is an outward particle flux. There is no incoming particle flux being in vacuo.

Now, the formalism of the thermodynamics of open systems is still not complete, there is argumentation about the general governing principle substituting the Second Law. As far as we know, it may be the minimal production rate of some entropy-type quantity, if the fluxes are fixed. However not too far from equilibrium the evolution equations of the system are known: for each extensive there is a balance equation

$$dx^i/dt + div J^i = \sigma^i \tag{2.1}$$

where $x^i$ is the extensive density, $J^i$ is its flux, which, in the conductive regime and near equilibrium reads as

$$J^i = -L^{ir} grad Y_r \tag{2.2}$$

where $Y_i$ is the conjugate intensive and $L^{ik}$ is the conduction matrix (Einstein convention is used for summation), while $\sigma^i$ is the production rate in unit volume. Near

equilibrium $L^{ik}$ and $\sigma^i$ are some functions of the densities $x^i$. Upper and lower indices, due to the existence of a Riemannian structure in the thermodynamic state space (DIÓSI & LUKÁCS 1984), are connected by the metric tensor, which is the negative of the second derivative matrix of the entropy density or by its inverse.

By these equations one can calculate the evolution of the body from some initial stage forward. What is needed is the specification of the initial state, and the conditions just outside the boundary surface. The latter ones are well-defined: there is a constant energy flux from Sun, determined by the orbital radius r, and lack of any chemical components. As for the initial state one may try with a C1 or C2 composition.

There is a problem with thermodynamics for large bodies where self-gravitation is already essential. There is no well-founded thermodynamics for systems with self-gravitation, since it is a volume force and then there will be problems with the additivity of subsystems in equilibrium. However until no great mass movements appear, the gravity field is practically constant and then it can be substituted by a prescribed *external* field. In that case the gravity potential gives a correction to the internal energy, resulting in barometric formulae for the concentrations. However this approximation breaks down if the matter melts and starts to rearrange itself. Then convection appears and the barometric formula is no longer valid. That phase is rather hard to follow, but one expects that still the denser components will be more abundant in the neighbourhood of the center.

In this paper we give an approximate treatment. The simplified model cannot give exact results in the fine details, but the model is transparent and gives correct trends.

First, let us neglect cross effects between heat and particle fluxes. Then for a homogeneous body (correct at least for the initial state) the heat conduction equation can be integrated as

$$T(R';t) \sim T_S + (F(t)/6k)(R^2 - R'^2) \tag{2.3}$$
$$T_S(t) = T_E(t)(r_E/r) \tag{2.4}$$

where R' is distance from the center, F is radioactive heat production rate in volume unit, k is heat conduction coefficient, $T_E$ is equilibrium temperature at Earth's orbit; r is solar distance and R is radius (HOLBA & LUKÁCS 1994).

Now, there are two kinds of energy fluxes going through the body. The first flux belongs to this temperature field as

$$q_1 = FR'/3 \tag{2.5}$$

the second one is the incoming, converted and reradiated solar radiation. More or less the entropy loss in the second flux balances the entropy production in the irreversible processes converting the shortwave solar radiation into planetary infrared; the first flux can keep the entropy of the planetary interior low. Namely, in a stationary process, if the energy is lost at lower temperature than received, a negative term $dE(1/T_1 - 1/T_2)$ appears in the entropy balance, and this flux starts in the center with temperatures higher than on the surface. Until this internal heat production is substantial, the body may remain young, far from thermodynamic equilibrium, and with fast cooling unequilibrium features may freeze in.

## OBSERVATIONS AND CLASSIFICATIONS

The Antarctic meteorite collecting project is a great possibility to get a true cross section and statistics about the material composition of the (outer) solar system, because i) survival chances of fragile meteorites are somewhat better than in other terrestrial
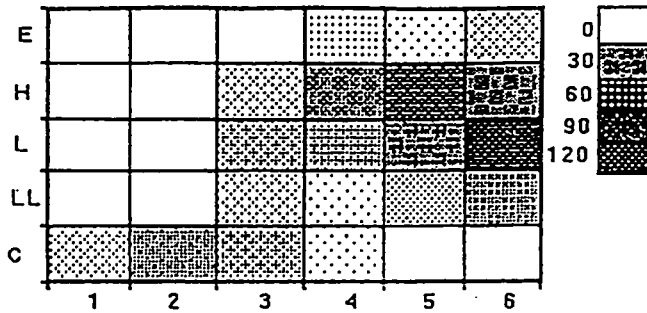
*Fig. 1.* Frequency of chondrite types according to the data of WASSON (1974), all types represented by a grade of gray color on their place in the Van Schmus - Wood table.
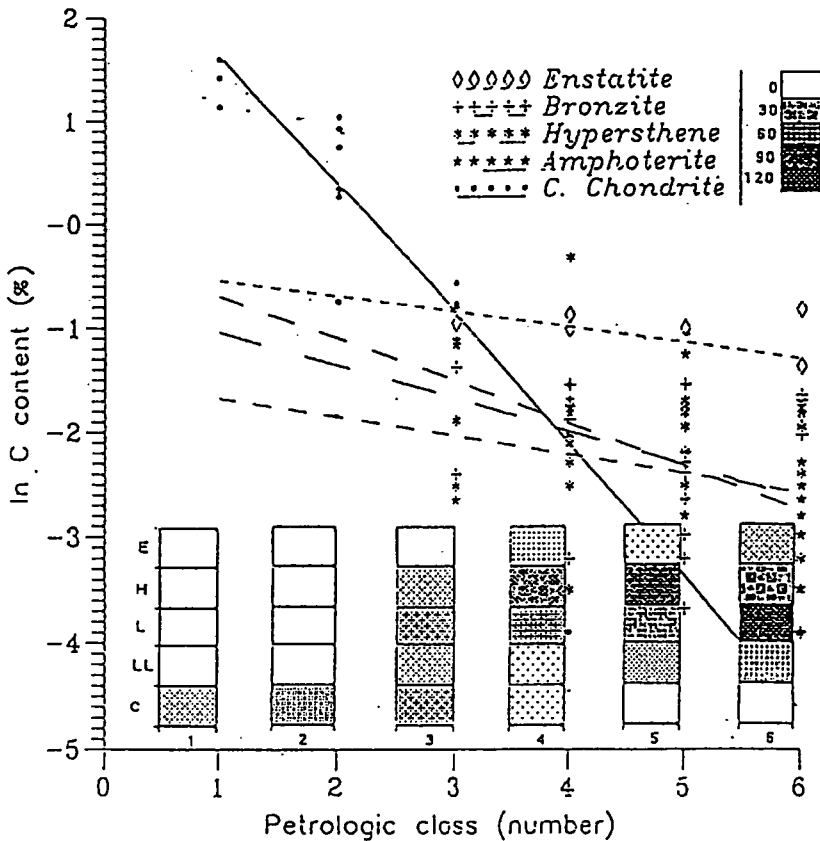


*Fig. 2.* Composite diagram about the carbon content of meteorite types and PC's. Columns are from *Fig. 1.* Van Schmus - Wood table with the corresponding frequencies of occurrences were added to each PC's. Therefore both carbon (from OTTING & ZÄHRINGER, 1967) and the total iron content are represented in this diagram. Lines have been fitted to the changing carbon content with PC at each meteorite types. The carbon slope corresponds to the intensity of carbon loss during thermal transformations.

localities; ii) any stony object is equally conspicious on an ice field. However even before this project it was known that not all logically possible classes are equally abundant; what is more, some classes are absent. This suggests genetic relations among some classes.

In this paper we concentrate on the connection between the VAN SCHMUS - WOOD (1967) classification of chondrites and the Fe-FeO-C contents. This classification uses a letter and a number. The letters refer chemical composition, mainly of pyroxenes and olivines, but also oxidized iron content: E (enstatite), H (bronzite), L (hypersthene), LL (amphoterite) and C (carbonaceous), (Type, here T), while the number shows the status of chondrules (correlated with carbon and water content): 1 (absent), 2 (sharp) to 6 (very obscure) (petrologic class, here PC). (For the different C types, see OTTING & ZÄHRINGER, 1967.) *Fig. 1.* is based on the statistics of Wasson (1974). The diagonal structure of the graph is obvious: e.g. very few high numbers are seen for C and no low ones for E, H, L and LL.

Now, it is advisable to make as few assumptions as possible. However it seems natural to see some thermodynamic process behind the obscuring of chondrules; e.g. diffusion. This is faster with higher temperatures, and may freeze in with cooling. So the higher PC suggests higher and/or longer heat impact; higher PC's should be thermodynamically, and specially chemically "more evolved". To see the paths of this evolution the chemical compositions should somehow be compared to chondrite types and PC's. One may expect volatiles negatively correlated with PC if the above guess is correct, and the evolution may be different for different types.

Let us see first the C content. We use a graph of OTTING & ZÄHRINGER (1967). The vertical axis is logarithmic, and we fitted exponentials in PC number for individual T's. That is *Fig. 2.* Indeed, in general the volatile C content decreases with PC.
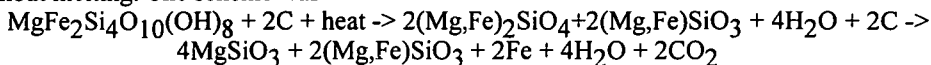
E2, H2, L2 and LL2 chondrites are unknown, but PC 2's may be visualized as startpoint of chondrule unsharpening via diffusion. The curves extrapolate back there. The E and H lines are clearly parallel, although mean deviation is substantial for H. The slope is smallest for E and H, then come LL, L and C. C leaves through the surface, so it is tempting to conclude that this was the size sequence from upward down for the parent bodies. Lines C and E meet at PC 3, and that is the lowest petrological class for E. This fact does not prove the C origin of E-s, but is compatible with such an idea. The original lower C content of H-s is surprising; we do not suggest any reason just now; an analogy is the difference in total Fe content between (E,H,C) and (L,LL) (WIIK, 1956).


## THE ORIGIN OF CHONDRULES

The origin of chondrules may have been a process on its own right albeit somewhat connected to that of the matrix (RADOMSKY & HEWINS, 1990; SCOTT & al., 1996). One fact supporting this is the roughly spherical, droplet-like form. This suggests original melting. If so, then there was a heat-flash around the very young, non-equilibrium Sun, and somehow chondrule-free "pre-chondrites" were bombarded with the solidified droplets. In this scheme C1 "chondrites" somehow avoided the bombardment. If so, then orderly thermal evolution started in PC 2. However that is not the only viable explanation. The thermodynamics of open systems knows an interesting effect when at sufficiently high fluxes and/or entropy production rates the homogeneity of the system breaks down and some internal structure appears (PRIGOGINE, 1969). So there is no fundamental argument against chondrules differentiating from a homogeneous pre-matrix, provided that high

thermodynamic fluxes were present, which is not impossible during condensation or in a large hot body. Of course this statement does not substitute an idea how the differentiation happened.

Long ago MASON (1962) suggested an evolutionary path, starting with C1. Then, with higher and higher heat effects first serpentine loses water (this process is perceptible at 400 C°), and some olivine chondrules crystallize, then the groundmass serpentine decomposes into olivine and pyroxene, finally C starts to reduce the iron oxide in olivine. Let us note that phase transitions starting from separate nucleation cores result in growing "bubbles" of the new phase, roughly spherical. If this process freezes in and the new phase cannot percolate, the general picture may be similar to matrix+chondrules in PC 2 even without melting. The scheme was

$$MgFe_2Si_4O_{10}(OH)_8 + 2C + heat \rightarrow 2(Mg,Fe)_2SiO_4 + 2(Mg,Fe)SiO_3 + 4H_2O + 2C \rightarrow$$
$$4MgSiO_3 + 2(Mg,Fe)SiO_3 + 2Fe + 4H_2O + 2CO_2$$

where water and $CO_2$ evaporate. In addition, C as volatile can be lost by diffusion.

One of such schemes may be proven true in the future; indeed it seems as if asteroid 3-filter colors were to suggest an evolution from something exotic in meteorites towards olivine and/or serpentine (BÉRCZI, HOLBA, & LUKÁCS 1995a). However now we want to use minimal theory. Still, no doubt, C can reduce FeO even well below melting point, and C can be lost by diffusion.

## FeO REDUCTION (AND C EVAPORATION): MODEL EQUATIONS

Consider a model meteorite class whose main chemical components, according to the above Mason scheme, are silicates with some FeO in the lattice, metallic Fe and C, all others negligible. In such a system there are strong correlations between chemical composition and PC. The higher heat impact means i) more diffusion, so higher PC; ii) more diffusion, so lower C content; iii) more reduction by C, so again lower C content, less FeO in the silicates and more Fe. Two quantities are constant: Si and total Fe. Since chondrites are roughly classified into a high-Fe group of 27 % total Fe content and a low-Fe one with 20 % (WIIK, 1956), the picture is simplified but not obviously absurd. Therefore let us be investigating this model system for a while.

Let us start from PC 2, so chondrules are already in the matrix. Consider mole concentrations of only 3 independent chemical components: Fe (z), FeO (x) and C (y); the other concentrations are taken constant. The environment is oxygenfree, so the main processes are reduction of FeO by C, formation of CO and $CO_2$, and evaporation of C, CO and $CO_2$ through the surface. In first approximation we neglect the internal inhomogeneities. Then, assuming that gases vanish rapidly,

$$dx/dt \sim -2A(T)xy \qquad (5.1)$$
$$dy/dt \sim -A(T)xy - R^{-1}B(T)y \qquad (5.2)$$
$$dz/dt \sim -dx/dt \qquad (5.3)$$

The 1/R term takes into account that C loss is through the surface. The temperature-dependent factors have the structure

$$A(T) \sim A_0 exp(-Q_A/T); B(T) \sim B_0 exp(-Q_B/T) \qquad (5.4)$$

Assume that we know $A_0$, $Q_A$, $B_0$ and $Q_B$ from solid-state experiments or metallurgy; for the actual temperatures take eqs. (2.3-4). Then in a parent body of radius R, at R' from the center and on an orbit of radius r one can integrate (5.1-3) from some initial conditions.

Note that for anything in asteroid range the early higher temperatures could not be maintained by anything else than the short-living radioisotopes. If we represent them mainly by $Al^{26}$, then F is high for times comparable to its half-life, 700000 y. The temperature dependence of A(T) and B(t) is serious, so in first approximation one can solve the equations until $t=t_c$, somewhere in the order of a million years, and then stop.

The solutions have the form

$$y_f = y_i - x_i + x_f + (B/2AR)\ln(x_f/x_i) \qquad (5.5)$$
$$z_f = z_i + x_i - x_f \qquad (5.6)$$

and $x_f$ is the solution of the implicit equation

$$2At_c = \int_{x_f}^{x_i} w^{-1}(y_i-x_i+w+(B/2AR)\ln(w/x_i))^{-1}dw \qquad (5.7)$$

Therefore the final concentrations depend on the initial ones, on the radius, and on the temperature (which again depends on radius if the heating is internal). Reduction and C loss together goes up with temperature, but C loss is sensitive on R too.

A(T) is fairly calculable from iron productive technics below melting point (mainly belonging to ancient ages, however cf. the Höganäs method), but for free iron oxides, not for silicates; and C diffusion coefficient B(T) is well known in iron (where it is remarkably high, see KITTEL (1961)), but not in all meteoritic matrices.


## DIFFUSION

Diffusion transforms the texture inside the parent body, not only the chondrules. Note that during heat impact various diffusion processes go on, each with its own diffusion coefficient D(t), and for order of magnitude the final diffusion length $a_f$ will be

$$a_f \sim (D(T)t_c)^{1/2}; \quad D(T) \sim D_0\exp(-Q_D/T) \qquad (6.1)$$

Concentrate first on chondrules. They are "sharpest" in PC 2 and "most obscure" in 6, while cannot be seen in 7. So, with chondrules of radius $a_0$ the PC is 2 if $a_f \ll a_0$, and 6 if $a_f \sim a_0$. Being $t_c$ fixed, this ratio depends on T, and if A(T), B(T) and D(T) are known, by inverting the formulae A and B will depend on $a_f/a_0$. So concentrations must (more or less) depend on the PC and size.

At even higher temperatures the diffusion length becomes macroscopic. Line C is where the C diffusiion during the hot million years becomes macroscopic, i.e. cca. 1 cm. Such diffusion may have produced e.g. ureilites. On the line

$$D_0\exp(-Q/T)*t_c \sim 1 \ cm^2 \qquad (6.2)$$

where Q is some characteristic activation energy. The corresponding diffusion coefficient is $D=3*10^{-14}$ cm$^2$/s. There are measurements for at least some volatile gases in augite, and for them 1000 C° would be needed for this value of D (FECHTIG, GENTNER & ZÄHRINGER, 1960).

As for the chondrule diffusion, matrices and chondrule compositions vary, and we do not have even olivine self-diffusion coefficient at reach. So here we try to guess only from the previous date. If volatiles can diffuse 1 cm in a million years in augite at 1000 C°, then maybe olivine could diffuse that distance at 1200 C°. Then the PC 7 is created in parent bodies above cca. line D.

Consider a stage of high enough temperature. This is the situation on orbits very near to Sun (e.g. at perihelia of Earth-crossers) or in parent bodies of substantial size when the short-living radioisotopes were still present.

The short-living radioisotopes, $Al^{26}$ and $Pu^{244}$, are extinct now. So their original concentration is unknown. Astronomers generally believe that $Al^{26}$ was the more important. Now, an estimation is possible for the initial radio-Al concentration, if we assume that F/k of the parent bodies did not differ too much. Consider eqs. (2.3-4) at the center R'=0. One gets:

$$T = T_E(r_E/r)^{\frac{1}{2}}(1-R/R_{cr})^2 + T_{cr}(R/R_{cr})^2 \qquad (7.1)$$

where $T_{cr}$ is some important temperature and $R_{cr}$ is the radius of the body in which $T=T_{cr}$ in the center. Now, global differentiation starts with melting of iron, because molten iron can flow out from the silicates. The corresponding temperature is cca. 1800 K for FeNi and ·1400 K for FeC.

The only free parameter is $R_{cr}$. Now, observations seem to suggest that the bigger asteroids are differentiated. The picture is not clear because it seems that 349 Dembowska is only partly differentiated, but 44 Nysa is completely so. A popular explanation is that 44 Nysa *was* a part of the mantle of an asteroid, whose iron core might have been 135 Hertha. If so, then differentiation started from $R_{cr} \sim 65$ km; this value may have to be revised in the future but now will do. By writing $T_{cr}$=1800 K one now gets the initial central temperatures in the function of R and r; and this initial temperature is declining with the extinction of radioisotopes. If they are dominantly $Al^{26}$, then the characteristic time is $t_c$~1 My. Then the initial central temperatures are shown in Fig. 3. We decline to discuss whence came the original $Al^{26}$ concentration; the differentiated asteroids must have been melted anyways.
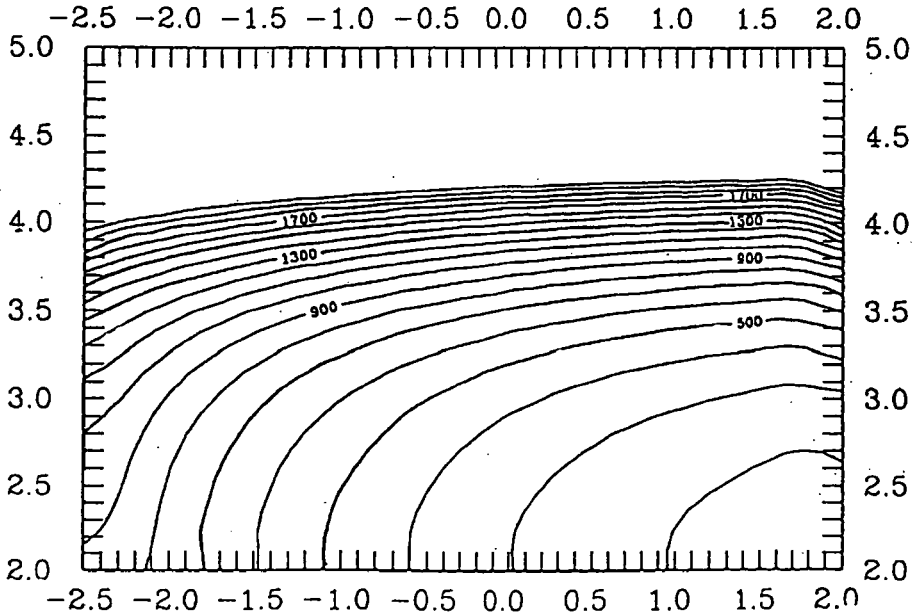


*Fig. 3.* Post-condensation central temperatures for bodies with different initial mass and solar distance

If iron could melt in the asteroid, then it began to accumulate in the central core of the body; during a million years even weak gravity can do it. The descending iron carries down alloying components (as C and Ni) and matter of similar density and melting point (as FeS). If partial melting in mantles of smaller bodies could produce basaltic type fluids, and they migrated to the surface, Vesta-like volcanic surfaces could develop on asteroids.

C diffuses in iron very easily in Fe; just below the melting point of carbonized iron D(T) seems to be 0.001-0.01 $cm^2/s$ (SHEWNON, 1963). Therefore C can diffuse out from the Fe core from km depths. Due to this process one expects only minor C content in iron meteorites or at the surface of iron asteroids (whence the mantle has been peeled off).

The picture seems to be coherent, but it is not necessarily true. Fortunately just recently it became possible to check it: the National Institute for Polar Research, Tokyo, Japan, has performed chemical analyses on several hundred meteorites of the NIPR collection, mainly Antarctic ones (YANAI, KOJIMA & HARAMURA, 1995). In the next Section we will see if our simplified thermodynamic model can describe chondrite evolution.


CHONDRITE EVOLUTION IN THE LIGHT OF THE RECENT NIPR ANALYSES

The NIPR collection contains cca. 8000 meteorites, mainly Antarctic ones. The most recent report from them is YANAI, KOJIMA & HARAMURA (1995). 3334 meteorites have been classified up to now, of which 3072 are chondrites. The recent report contains chemical analysis of 541 meteorites, the overwhelming majority performed by Dr. Haramura, with a homogeneous method. This huge database enables us to check evolutionary theories. Evolutionary positions of the 30 samples of the NIPR Educational Thin Section Set are shown on *Fig. 4.*; a detailed discussion will come in Sect. 11.

First let us see if the sample is representative. Fig. 1 gave a two-variable distribution of *falls* (numbers vs. type and PC). Now, the corresponding distribution for classified NIPR chondrites is *Fig. 5*. Obviously the two distributions differ. The most striking difference is the high representation of H4's in the NIPR collection. The ratio of the earlier and 1995 distributions is shown on *Fig. 6*. However for the average properties of chondrite classes these differences are irrelevant.

*Fig. 7.* shows the selection in analyses. It can be seen that the analyst generally tried to select relatively more samples from the rarer classes.

Let us remember that WIIK (1956) found two strips on a plot (Fe not in oxides vs. Fe in oxides): with cca. 20 % (LL & L) and 27 % (C, H, E) total Fe contents. Of course, Fe weight ratio changes with volatile loss, so the data should be somehow normalised. We normalised the composition data to Si. Namely, we practically do not know processes extracting Si. Si generally remains in the silicates, except for minor reduction in E6 (Wasson, 1974), and silicates are not volatile. Now, Fig. 8 is oxidised Fe/Si vs. other Fe/Si. Chondritic types modestly separate, but we do not see definite straight lines. Rather, two curved strips are seen, meeting at the lower part of the H region. It seems *as if* LL's and C's were the startpoints of two parallel evolutions towards H's, but, as we shall see, it cannot be so.

Since the number of the relevant chemical components is at least 3 (Fe°, FeO, C), we need a *tripolar* representation, e.g. colours, to describe the chemical evolution. Let 30 % metallic + sulphide Fe content be represented by pure red, 30 % FeO by pure green and 5 % C by pure blue. Then, going from low petrologic classes to high and finally to achondrites, E's start from brick red through strawberry red until cherry red; the E
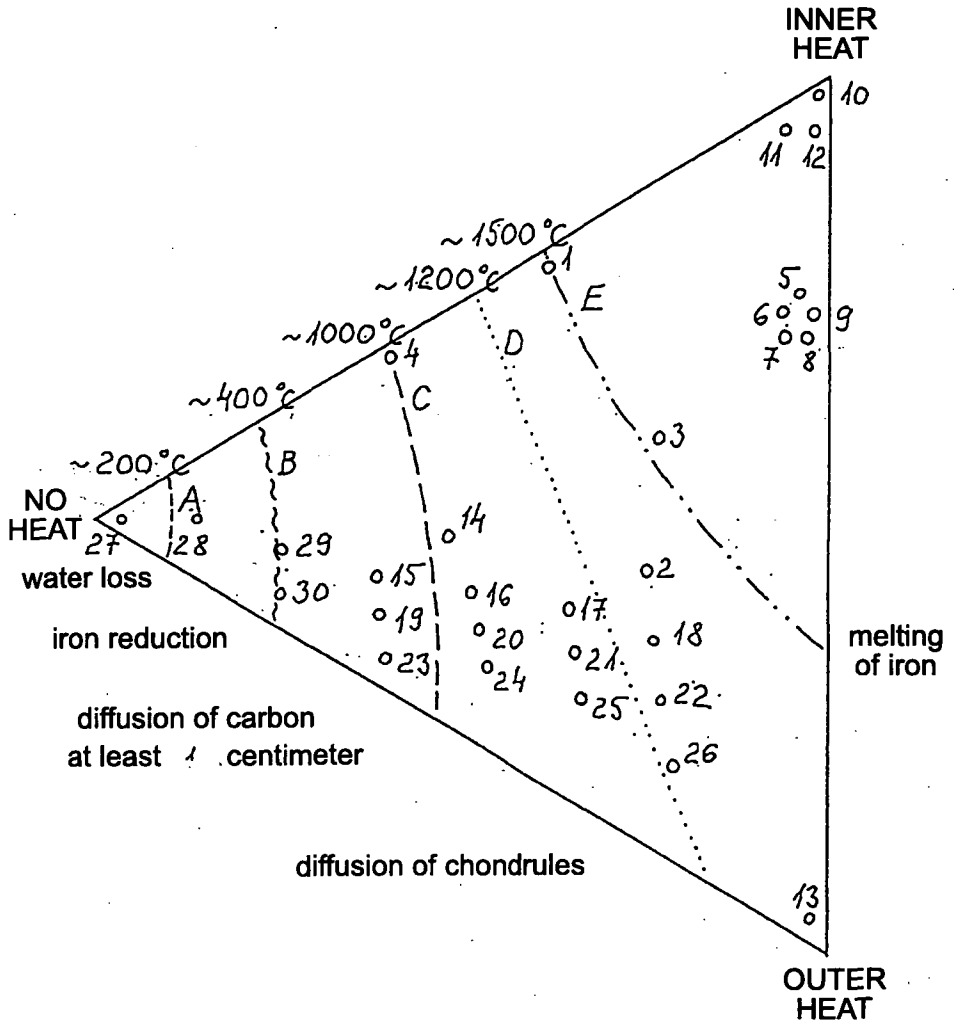
INNER
HEAT

~1500 °C
~1200 °C
~1000 °C
~400 °C
~200 °C

NO
HEAT
water loss

iron reduction

diffusion of carbon
at least 1 centimeter

diffusion of chondrules

OUTER
HEAT

melting
of iron

A B C D E

*Fig. 4.* The arrangement of the samples of the Japanese Antarctic Meteorite Thin Section Set in our tentative NO HEAT - INNER HEAT - OUTER HEAT triangle diagram. Detailed explanations in the text. Lines A, B, C, D, and E represent characteristical transformations in meteorites. Numbers represent meteorite types in the NIPR Thin Section Set.

achondrite is practically black. H3 is ochre yellow, H3-4 is exceptionally reddish, H4 and H5 are brownish, but H6 is greenish yellow. The H achondrite is not known. L's are oscillating between grayish green and greenish brown; the achondrite is rather green. LL's are all green, oscillating between grass green and olive green; the achondrite is deep green. Finally, C1's are bluish, C2's are grayish green, but then the colour becomes more and more green and C6 is deep green; the C achondrites are not identified, but ureilites are bluish.
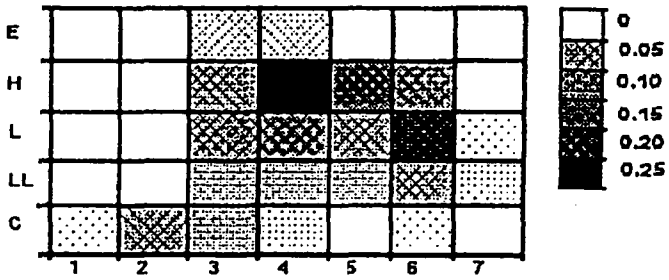
*Fig. 5.* Frequency of occurrence of meteorite types in that part of the NIPR Japanese Meteorite Collection where it was determined. Frequency data are transformed into a gray color grade, like as on *Fig. 1.* The two most frequent types are H4 and L6 in the NIPR Antarctic Meteorite Collection
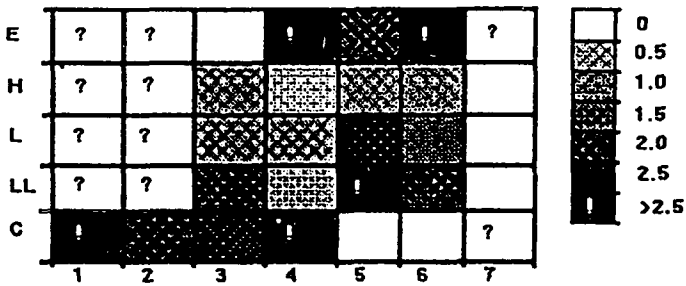


*Fig. 6.* Ratios of the occurrence frequencies for meteorites on *Fig. 1.* (Wasson) and *Fig. 6.* (NIPR). The "Wasson"/"NIPR" ratios show that there are considerable differences in occurence of chondritic meteorites of fall (Wasson) and found (NIPR) origin.
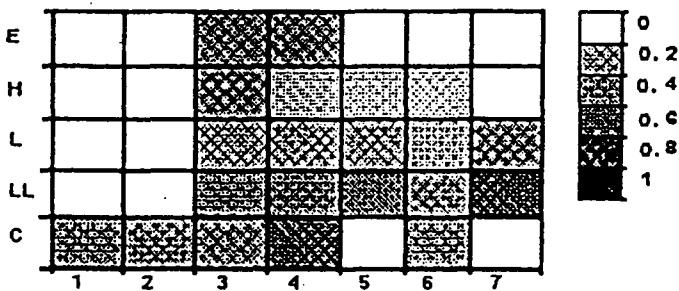


*Fig. 7.* This diagram shows how does the Japanese chemical analysis (Catalog of Antarctic Meteorites, NIPR, 1995 by YANAI, KOJIMA & HARAMURA) represent the various Van Schmus - Wood types.

97
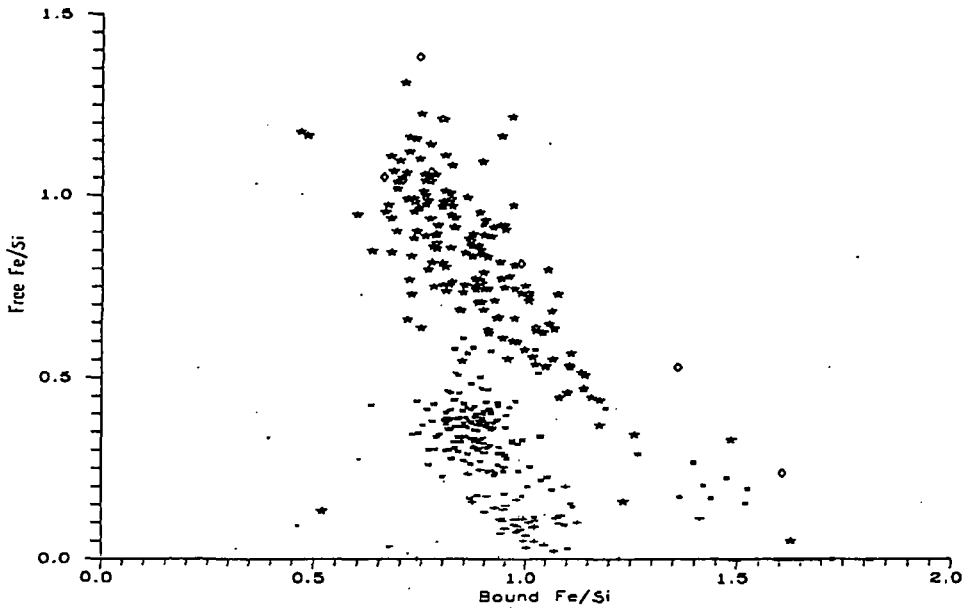
Fig. 8: NIPR Catalog Data for chondrites, arranged in the classical oxidized Fe/non-oxidised Fe diagram. The data were normalized to the Si content of the meteorites. For astronomers this diagram resembles the Hertzsprung-Russel diagram where two characteristical data of stars with different initial conditions and evolutionary paths are represented.

There are some oscillations in reduction/oxidation. *Fig. 9.* shows the five chondritic types on the Fe+FeS vs. Fe oxides map; the PC's are indicated as labels. Clearly "cycles" or "loops" are seen. This is incompatible with the evolution equations of Sect. 5. At the ends of the LL, L and E lines total Fe loss is seen; maybe there the temperature reached the melting point of carbonised Fe, so global differentiation started.

Of course the chondrites did *not* evolve through the present types, but represent final states after evolutions with the same lengths $t_c$ but different heat impact. However, although this distinction is important, it cannot explain the oscillation if the only possible reaction is reduction.

Let us note here something from the thermodynamics of open systems. The Second Law does not imply irreversible changes in an *open* system; if the fluxes through the system are strong enough, then the system may remain stationary, may go in cycles, &c. Still, if the only possible reaction is reduction, then the process cannot go backwards. So the oscillation between reduction and oxidation needs an oxidizing agent too.

We do not have direct information about the conditions in the parent bodies of meteorites in the very youth of the Solar System. However there is a quite common material, present in meteorites, which oxidizes iron on higher temperatures. That is water. Since Fe is of more positive nature than H, Fe can take O from $H_2O$, liberating H. This process is seen in laboratory, but only at high temperature (cca. from 600 C°). However this temperature is quite reasonable during the early meteorite evolution, and of course the reaction goes also at lower temperatures, only imperceptibly slowly, which on million years
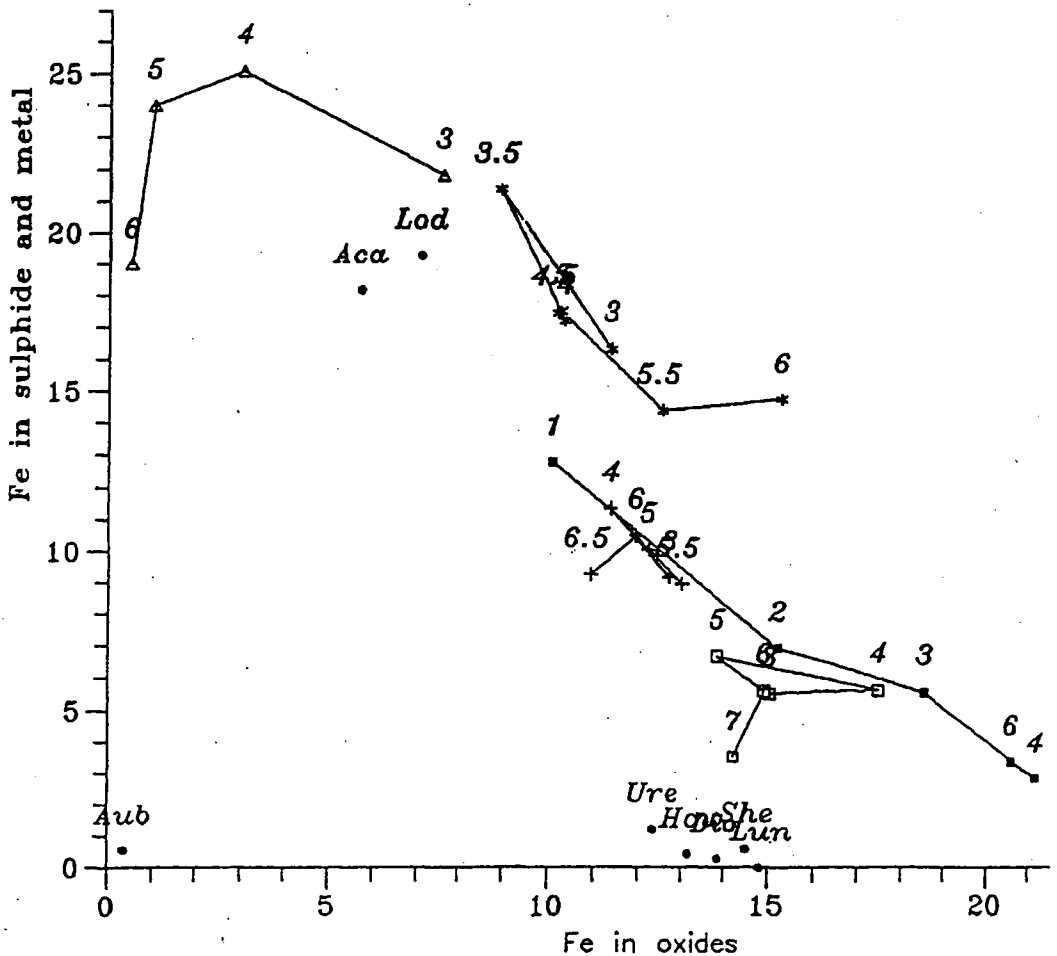
*Fig. 9.* Fe+FeS vs. Fe oxides data averaged from data of NIPR Catalog, connected by lines for individual T's. To and fro motions are seen. The early reduction and later oxidation can be seen for H, L, and LL groups, while the E group moves toward reduction.

scales still can be relevant. Water is a minor, but common component in LL's, L's and H's of moderate PC's, in 1 % order of magnitude (YANAI, KOJIMA & HARAMURA, 1995).

Then one could complete the system (5.1-3) by incorporating $H_2O$ (w), as

$$dx/dt \sim -2A(T)xy + C(T)wz \qquad (9.1)$$
$$dy/dt \sim -A(T)xy - R^{-1}B(T)y - Q(T)yw \qquad (9.2)$$
$$dz/dt \sim -dx/dt \qquad (9.3)$$
$$dw/dt \sim -2Q(T)yw - C(T)wz - R^{-1}W(T) \qquad (9.4)$$

where, as far as the new terms are considered, W is a coefficient of water diffusion, C is the coefficient in the reaction rate of $Fe+H_2O->FeO+2H$, and Q is that of $C+2H_2O->CO_2+2H$. Then again the equations have to be integrated up to $t_c \sim 1$ Ma, obtaining the final composition.

99

Unfortunately the rate coefficients $C(T)$ and $Q(T)$ are not available for us, although the latter could be taken from the experiences of the now practically defunct industry producing artificial cooking gas ("water gas") from coal. However it is easy to see that eqs. (9.1-4) will contain oscillatory solutions if $C(T)$ starts to rise later but more steeply in T than $A(T)$ does. And this may be so, since a part of the water is originally bound in the silicate lattice, so it will be effective only at higher temperatures. As for quantities, characteristic values are 0.2 weight % for C and 1 weight % for $H_2O$. Now 1 % C can reduce 9.5 % Fe from FeO, while 1 % $H_2O$ can oxidize 3.1 % Fe. Therefore the presence of water could explain an oscillation of amplitude about 3 %, and something similar is seen. As for the $H_2O/Si$ ratio, it is shown on *Fig. 10.*

In order to check the genetic relations among chondrite classes, *Fig. 11.* shows the average (total Fe)/Si mass ratio vs. PC separately for E, H, L, LL and C. Since neither Fe compounds, nor Si are volatile, this ratio cannot change in evolutionary processes except for melting and global differentiation, not expected for moderate PC's. Indeed, the curves are roughly horizontal, except for the ends where the obvious explanation is partial loss of molten Fe and FeS. Now, the 5 types clearly separate to a high Fe group (E, H, C) and a low Fe one (L and LL), quite conformally with the old results of WIIK (1956) on a much less sample; but, in addition, the differences between L and LL seem significant too. This means that L's and LL's cannot be in close genetic connection with the others (as seen earlier on *Fig. 8.*).

*Fig. 11.* makes a problem explicit. LL2 and L2 chondrites (i.e. ones with very sharp chondrules *and* high volatile content) are unknown. They are unknown for H and E as well, but the conserved Fe/Si ratio does not rule out the common origin of the C3, H3 and E3 chondrites from a C2-like precursor. But this seems impossible for LL3 and L3. Then either the high-volatile precursors did not survive the evolution, or they never existed. The second solution is possible if LL's and L's originate from the inner System, where neither water, nor hydrated silicates condensated; but then it is difficult to understand the low iron content. We cannot solve this problem at the present stage; however *Fig. 11.* clearly shows that the so called H3-4's are well out of the H line. They cannot seem H's at all; at least for iron content they could be rather E's. So no surprise if H3-4's do not fit between H3's and H4's also for FeO, FeS and $H_2O$.


EVOLUTION OF IRON GRAINS: PERCOLATION AND OUTFLOWING


If the above scheme is real, then one must see some signal of thermal evolution also in the texture of chondritic meteorites, e.g. in the number and grain size distribution of iron grains. This change is the result of the oxidation-reduction chemical reactions in the system. New iron grains appear, grow or older ones shrink or disappear. We checked this on grain size distributions of LL chondrites. It seems that the statistics of the present, first, investigation should be doubled or trebled; but even now some evolutionary effects are seen.

For determining the size distribution of iron grains we used two groups of Antarctic Meteorite Samples on loan from NIPR, Tokyo. One was a sequence of LL3, LL5 and LL7 petrologic types (ALH-77304, 83-4, Y-74022, 92-2, and Y-791067, 73-1), the other one was taken from the Antarctic Meteorite Thin Section Set of NIPR, the samples of 24, 25 and 26, LL4, LL5 and LL6, (Y-74442, 83-6, ALH-78109, 88-1, and Y-75258, 97-8), respectively. Number of grains were counted in petrographic microscope (Nicon-type)
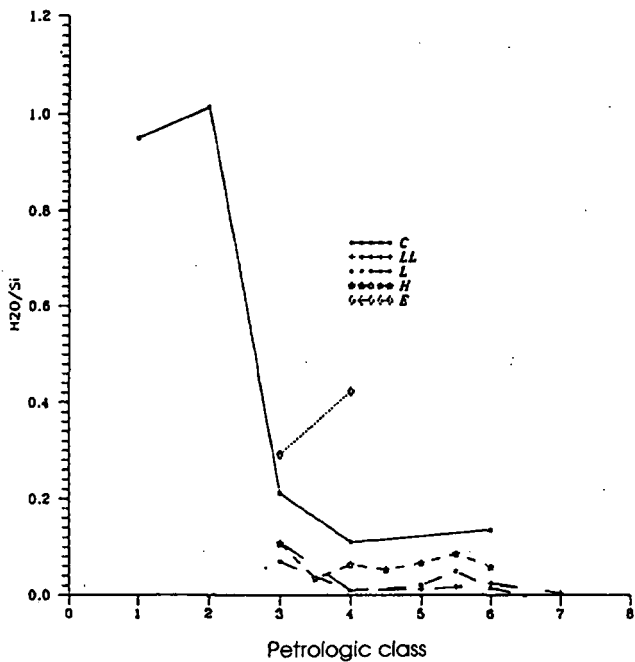
*Fig. 10.* H$_2$O data normalised to Si for chondrite types show the water loss trend for all meteorite types during thermal evolution of parent bodies.
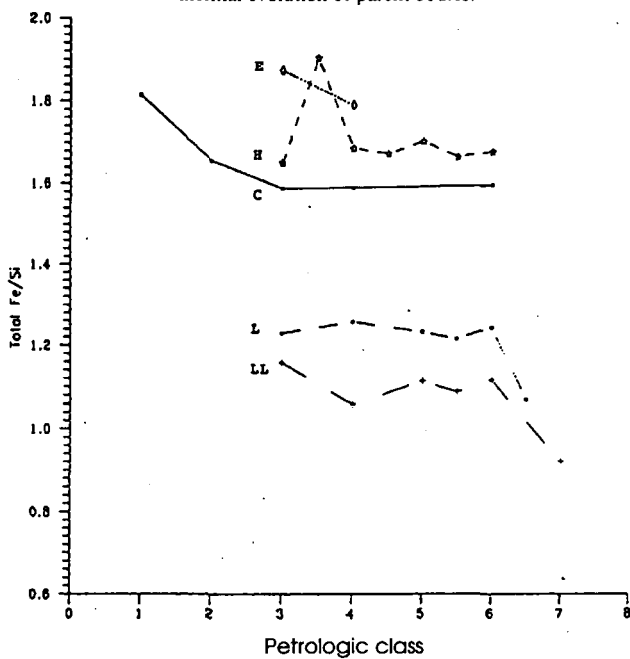


*Fig. 11.* Total Fe/Si versus PC for NIPR Catalog data. In first approximation we can see the two "lines" of Wiik (1956) in total Fe content.

101

belonging to 1: 0-25 μm, 2: 25-50 μm, ... up to 8: >175 μm size ranges. (In order to receive a more smooth averages, all 25 μm ranges were subdivided into three smaller intervals and counts were carried out for these shorter diameter ranges, then three of them were summed up.)

The measurements resulted in 6 iron grain size distributions: one for PC's LL3, LL4, LL6 and LL7 and two for LL5. The normalized distributions are shown in Figs. 12a-f. LL4 and both LL5's have "tails" at large grain sizes. It seems consistent with our observation that in the LL group at the final stage of their evolutionary path some iron loss is suspected; maybe at high temperature the substantial iron grains percolate and Fe flows out. Indeed, the "tail" is missing at LL6 and LL7.

Then we checked if there are statistically significant differences between the Fe grain distributions. In the lack of any serious theory for the shape of the distribution we used a $\chi^2$-type test. Our first null hypothesis is that all distributions are the same, and differences come purely from statistical fluctuations. This null hypothesis is disproven on a quite satisfactory significance level.

If in size range $i$ the actual grain size is $n_i$, then its statistical mean deviation is $\sim n_i^{1/2}$. Then

$$\chi^2_{12} = \Sigma_i (n_{1i}/N_1 - n_{2i}/N_2)^2/(n_{1i}/N_1^2 + n_{2i}/N_2^2) \tag{10.1}$$

N being the total grain number. We measured at 8 points, so the degree of freedom is 7. The $\chi^2$ values for various pairs are:

$$(34) = 18.5; (35) = 23.8; (36) = 31.5; (37) = 51.3$$
$$(45) = 23.2; (46) = 20.2; (47) = 47.8$$
$$(56) = 21.8; (57) = 21.2; (67) = 16.6$$

Here 5 stands for the united distribution of 2 LL5's. None of these values are conform with a uniform distribution considering that the expectation value is 7, and the mean deviation is $\sqrt{14}$. For more details of the test see JANOSSY (1965).

There may be moderate differences within the same van Schmus-Wood class too. We checked this possibility on the 2 LL5 samples, with the result

$$\chi^2_{55} = 12.2$$

compatible with no difference at all at slightly more than $1\sigma$ level.

Taking the numbers in face value, we can conclude that the two LL5's are undistinguishable at any fair significance level while any two samples of different classes can be; the differences are the smallest for neighbours. Our guess is that no more than 3 different thin sections for each class would suffice for settle the question if the classes are distinguishable for grain size distributions. Possibly LL5 is an exception; earlier we saw that oxidation takes over at LL5, so trends change there and the diversity may be higher.
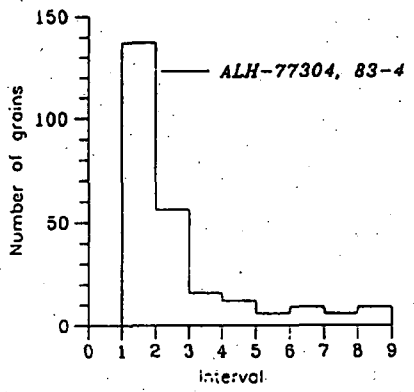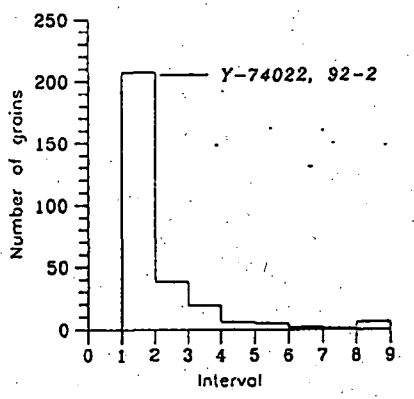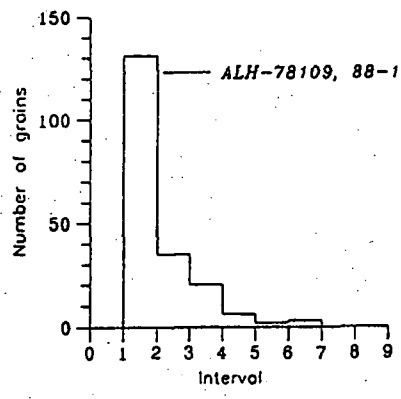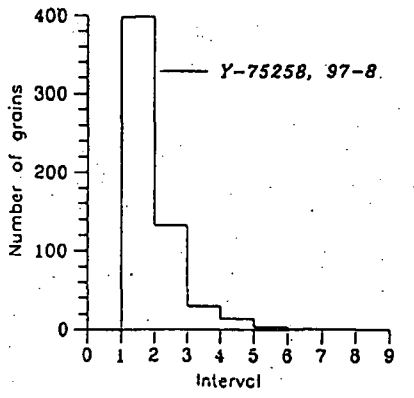
a. *Iron grain distribution in LL3*
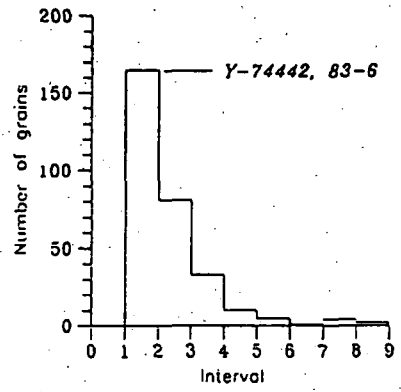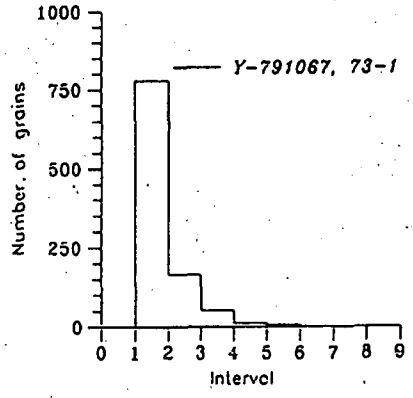
b. *Iron grain distribution in LL4*

c. *Iron grain distribution in LL5*

d. *Iron grain distribution in LL5*

e. *Iron grain distribution in LL6*

f. *Iron grain distribution in LL7*

*Fig. 12.* Grain size statistics for NIPR LL chondrites. a: LL3, b: LL4, c & d: LL5, e: LL6, f: LL7.

Now we can return to *Fig. 4*, the thermal evolution pattern for chondrites (and closely related achondrites). Although we have found no startpoint for LL's and L's, otherwise the general structure of Fig. 4 remained unchanged. Although the samples are products of a thermal history of 4.5 billion years, this thermal history depended on size and solar distance. We sketched the main processes of the thermal history of different sized parent bodies.

Our tentative guess for genetic connections can be formulated by 5 "chains", along which the sequences fron "primitive" to "evolved" is as follows. A startpoint may be *27* or *28*. After *28* there may seem to be a trifurcation. The "C" line goes through *29 & 30* -> C4 -> C5 -> C6 (absent in the NIPR Set) -> (maybe) *4*. The "H" line goes via *15* -> *16* -> *17* -> *18*, and may or may not end in *13*, whose chemical analysis is not available. The "E" line goes through *14*, continues with higher E's absent in the Set, and may end in one or more of *1*, *2* and *3*. The "LL" and "L" lines do *not* start from *28*; the traceable part of "LL" is *23* -> *24* -> *25* -> *26*, then an LL7 (absent) and it may end in pigeonite achondrites (absent), while that of the "L" seems to be *19* -> *20* -> *21* -> *22* -> L7 (absent), and it also may or may not end in *13*. Samples *5-12* differentiated inside of large bodies, so their original ancestry is doubtful and they are partially out of the scope of the present paper.

The picture is transparent (and oversimplified), and the detailed numerical model calculations are impossible until the temperature-dependence of the reaction rates will be known for water dissolution by Fe and C. But this needs only simple laboratory experiments (preferably with hydrated silicates). Now come here some serious problems.

We do not see the startpoints of LL's and L's.

Although no Figure has been given here for individual Fe *compounds* (for that see BÉRCZI, HOLBA & LUKÁCS, 1995b), according to the averaged NIPR data FeS content does not depend too much on PC, except for C's, although one would expect reduction by C here too, and $CS_2$ is a gas at higher temperatures, similarly to $CO_2$. But obviously we do not know enough about the behaviour of $CS_2$ without free O but together with Fe and FeO. Anyway, FeS concentration seriously changes in early C's. (Sulphide Fe)/Si~0.2 for LL, L and H, but ~0.5 for E. This is again a feature connecting E's intimately to C's of low PC's (others are the C and $H_2O$ data). A good explanation of the origin of the (rather rare) E chondrites should explain the high FeS concentration too.

Ureilites are similar to C2 for C and $H_2O$ content (cf. *Fig. 11.*), but in the same time they are achondrites with a substantial heating. A large body could stop evaporation of C *or* $H_2O$, but can it completely retain CO, $CO_2$ and $H_2$ appearing in chemical reactions as well?

If we imagine that C2 resembles the common precursor of C3, H3 and E3 (which is at least not impossible according to *Figs. 10 & 11.*), then an explanation would be needed for the trifurcation. A natural idea would be the size of the body (larger ones could retain more volatiles), but PC's 3 and 6 both exist in all the 3 groups, suggesting small and large bodies as well.

And finally: what has prohibited the formation of proto-meteorites with intermediate initial Fe/Si ratio? The gap on Fig. 11 is not decisive, being a gap in averages; but *Fig. 8.* clearly shows "forbideen regions". Does this dichotomy show something about the primordial condensation, or did bodies of "intermediate" Fe/Si ratios evolved so differently that they now are not considered chondrites?

# ACKNOWLEDGEMENTS

# REFERENCES

BARSHAY S. S., & LEWIS J. S. 1975: In : The Dusty Universe, eds. Field G. B. & Cameron A. G. W., Neale Watson Acad. Publ., New York

BÉRCZI SZ., HOLBA AGNES, & LUKÁCS B. 1995a: KFKI-1995-10

BÉRCZI SZ., HOLBA AGNES & LUKÁCS B. 1995b: Acta Miner. Petrog. Szeged, **XXXI**, 53

BÉRCZI SZ. & LUKÁCS B. 1994: KFKI-1994-11

DIÓSI L. & LUKÁCS B., 1984: Phys. Rev. **A29**, 3343

DODD JR. R., T., VAN SCHMUS W. R. & KOFFMAN D. N., 1967: Geochim. Cosmochim. Acta, **31**, 921

FECHTIG H., GENTNER W. & ZÄHRINGER J. 1960: Geochim. Cosmochim. Acta **19**, 70

HOLBA AGNES & LUKÁCS B. 1994: In Lukács B. & al., KFKI-1994-22, p. 81

HUSS G. R., KEIL K. & TAYLOR G. J., 1981: Geochim. Cosmochim. Acta **45**, 33

JANOSSY L. 1965: Theory and Practice of Evaluation of Measurements. Oxford University Press, Oxford

KEIL K. & FREDRIKSSON K., 1964: J. Geophys. Res. **69**, 3487

KITTEL CH. 1961: Introduction to Solid State Physics. J. Wiley, New York

KORNACKI A. S. & WOOD J. A., 1984: Geochim. Cosmochim. Acta **48**, 1663

KUBOVICS I. & al. 1994: In Lukács B. & al. KFKI-1994-22, p. 29

LUX G., KEIL K. & TAYLOR G. J., 1980: Geochim. Cosmochim. Acta **44**, 841

MASON B. 1962: Meteorites. J. Wiley & Sons, New York

METZLER K., BISCHOFF A. & STÖFFLER D., 1992: Geochim. Cosmochim. Acta **56**, 2873

OTTING W. & ZÄHRINGER J. 1967: Geochim. Cosmochim. Acta **31**, 1949

PRIGOGINE I: in: Theoretical Physics and Biology, ed. M. Marois, North-Holland, Amsterdam

RADOMSKY P. M. & HEWINS R. H., 1990: Geochim. Cosmochim. Acta **54**, 3475

SCOTT E. R. D., KROT A. N & BROWNING L. B., 1969: LPS **XXVII**, 1161

SCOTT E. R. D., RUBIN A. E., TAYLOR G. J. & KEIL K., 1984: Geochim. Cosmochim. Acta **48**, 1741

SHEWNON P. G. 1963: Diffusion in Solids, McGraw-Hill, Toronto

VAN SCHMUS W. R. & WOOD J. A. 1967: Geochim. Cosmochim. Acta **31**, 747

WASSON J. T. 1974: Meteorites. Springer, Berlin

WIIK H. B. 1956: Geochim. Cosmochim. Acta **9**, 279

WOOD J. A. & Hashimoto Akihiko, 1993: Geochim. Cosmochim. Acta **57**, 2377

YANAI K. & KOJIMA H. 1987: Photographic Catalog of the Antarctic Meteorites. NIPR, Tokyo

YANAI K. KOJIMA H. & Haramura H., 1995: Catalog of the Antarctic Meteorites. NIPR, Tokyo

YU Y. & HEWINS R. H., 1996: Geochim. Cosmochim. Acta **60**, in press

*Manuscript received 10 September, 1998.*