

Mössbauer study of redox processes in the evolution of chondrites

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Abstract

The evolution of Fe-containing phases of carbonaceous chondrites heated under various oxidation–reduction conditions was investigated by means of Mössbauer spectroscopy. Heating of the lower petrological types of chondrites (CM2) released gases which initially produced oxidizing conditions ($\sim 450^\circ\text{C}$) and then reducing conditions ($> 700^\circ\text{C}$). Phase transformation occurred rapidly (during 1–5 minutes) at all temperatures. During heating the Fe-bearing phyllosilicate phases in CM2-chondrite converted to Fe-bearing olivine, metallic iron and troilite (pentlandite). These phases resemble those of CO3, CV3 and EH-chondrites. Iron distribution resembling that of ordinary chondrites (some additional Fe^{2+} in pyroxene) was obtained only by heating a mixture of oxidized matter (CM2) with reduced matter (EH).

A phase transition discovered at 1050°C is probably the temperature boundary between conditions of formation of the two main components of ordinary chondrites: matrix and chondrules. Chondrules of ordinary chondrites may be formed at temperatures $> 1050^\circ\text{C}$ while the matrix forms at temperatures $< 1050^\circ\text{C}$. For the carbonaceous chondrite Kainzas (CO3) these temperatures are approximately 1000°C and $< 900^\circ\text{C}$. The experimental conditions determined for the evolution of chondrites do not contradict the theoretical two-component model of Wood-Anders-Ringwood and may further its development.

KEYWORDS: chondrites, Mössbauer study, iron-bearing minerals, redox processes.

Introduction

OF the many types of meteorites — iron, stony and stony-iron — only chondrites (stony meteorites that contain chondrules) did not undergo considerable alteration after their formation: their chemical composition is similar to the solar abundances of non-volatile elements (Mason, 1971). Therefore, these meteorites can provide much information about the early history of the solar system.

One peculiarity of chondrites is the sharp variation in the oxidation states in response to comparatively small changes in their chemical composition. It is well known that chondrites are divided into three large classes: the most oxidized — carbonaceous; the intermediate degree of oxidation — ordinary; and the highly reduced — enstatite chondrites.

The multivalent element Fe is an indicator of the oxidation state of matter. The degree of its oxidation state determines the phase composition of the various chondrite classes. Therefore, in the first instance it is necessary to explain the various forms of Fe in chondrites: in the metal phase, in silicates and in sulphides. The principle role of Fe in the determination of the genetic relationships and classification of meteorites was first shown by Prior (1916, 1920) in his well-known law that establishes an inverse relationship between the amount of silicate and metallic iron in ordinary chondrites. This is represented graphically as the plot of $(\text{Fe}^0 + \text{FeS})$ against Fe^{2+} in silicate (Urey and Craig, 1953).

The question is one of how the various oxidation–reduction conditions, that existed during the formation of chondrites, arose.

Latimer (1950) and Urey (1952) have shown that in a cold protoplanetary cloud in equilibrium between gas and solid matter, the primary nonvolatile elements, in particular Fe, Mg and Si, must be completely oxidized. In contrast, at high temperatures the oxidized forms of Fe are not stable. Thus the condensate from a cold protoplanetary cloud will be in the form of oxidized matter that is close in composition to carbonaceous chondrite CI (Mason, 1971). The other chondrites may be obtained from this oxidized matter by means of carbon reduction followed by heating (Ringwood, 1961, 1966). In early models it was proposed that this occurred in planetary-sized bodies by means of radioactive heating (Ringwood, 1961) or as a result of adiabatic compression (Urey, 1952). However, these models made it difficult to explain the formation of chondrules, whose texture and form suggest that they originated in low gravity, and to provide a mechanism for the loss of volatile elements. With time the size of the supposed bodies was gradually reduced to asteroid-size (Mason, 1960; Levin, 1965; Urey, 1964), to planetesimals (Ringwood, 1966), bodies < 10 km (Alfvén and Arrhenius, 1976) for which shock heating was proposed, or even to dust (Wood, 1963, 1967) where the reducing conditions occurred in the vapour state by means of hydrogen.

Wasson (1974, 1977) suggested that the oxidation state of the nebula may be a function of the distance from the Sun: enstatite chondrites formed in the Mercury region, carbonaceous near Jupiter and ordinary chondrites in the steroidal belt. For an explanation of the various oxidation states of chondritic matter Wood (1967) offered a two-component model in which chondrites are formed by the mixture of a high-temperature (reduced) and a low-temperature (oxidized) component. It is proposed that the first component is either a high-temperature condensate of the nebula (Larimer and Anders, 1970) or is derived from the low-temperature component by heating, for example by means of shock waves (Wood, 1971).

The purpose of this work is to review Mössbauer investigations of the Fe phases in carbonaceous chondrites and the evolution of these phases by heating in various redox conditions.

Method of investigation

The basic experimental method of the reviewed investigations consists of Mössbauer spectroscopy on the nucleus of ^{57}Fe . This method is background-free relative to Fe, and gives the distribu-

tion of Fe among the oxidation states, the mineralogy of Fe-containing phases and the relative ratio of these phases (Malysheva, 1975). Due to the exceptional sensitivity of spectral parameters to the neighbouring and distant order in the structure, each Fe-bearing mineral has an active spectrum that permits the identification of individual minerals in the whole sample without preliminary separation. The intensity of the resonance lines is a measure of the quantity of a given mineral in the chondrites. The sample is measured in powder form in quantities of 50–100 mg, distributed evenly over an area of $\sim 4 \text{ cm}^2$ (the optimum surface density is $\sim 20 \text{ mg/cm}^2$) that provide representative measurements. It is possible to identify fine-grained matter with grain sizes of around 20 Å. Consequently, growth of new phases can easily be determined in the course of heating experiments.

Despite several groups of scientists having used this method to study meteorites, investigation of carbonaceous chondrites was undertaken only in the work of Herr and Skerra (1969), Virgo (1972) and Roy-Poulsen *et al.* (1981). Heating experiments were carried out only in the reviewed papers.

The heating experiments were carried out in helium flow, in evacuated and fused quartz ampoules in the temperature range 200–1400°C for periods of 1 min. to several days with subsequent air quenching. The oxidation reaction of Ti to TiO_2 was used as a buffer to maintain a low oxygen partial pressure ($f_{\text{O}_2} = 10^{-22}$ – 10^{-24} atm). Mössbauer spectroscopy was combined with X-ray phase- and micro-probe analysis.

Iron phases in unequilibrium chondrites

The Table gives the results of computer evaluation of the Mössbauer data of natural samples by means of the least squares method, assuming a Lorentzian form of the resonance lines. The main conclusions are as follows:

- (1) In the Orgueil (CI) chondrite, approximately half the total Fe occurs as magnetite. The rest, mainly in the Fe^{3+} state, is present in phyllosilicates (montmorillonite). Olivine and pyroxene do not contain Fe. These results agree with those of Herr and Skerra (1969) and Virgo (1972).
- (2) In CM2 chondrites the distribution of iron among the mineral phases differs from the 'classical' data of Anders (1964) and the Mössbauer data of Herr and Skerra (1969) and Roy-Poulsen (1981): olivine and pyroxene also do not contain Fe. All Fe, within the limits of accuracy of the measurements, enters phyllosilicates (chlorites or prochlorites) in the ratio

$\text{Fe}^{2+}/\text{Fe}^{3+} \sim 1$. This fact is established by heating CM2 chondrite to 250°C in air: the Fe^{2+} doublet line decreased sharply owing to oxidation (Vdovykin *et al.*, 1975).

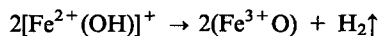
(3) The main result of measurements on CV3 and CO3 chondrites is that Fe is absent from pyroxenes. Iron enters mainly olivine, some is in the Fe^{3+} state in oxides, probably due to atmospheric weathering and some is in the metallic state and sulphides (CO3). In the (CV3) chondrite Allende besides olivine, approximately 15% of the Fe enters pentlandite.

(4) The Indarch (EH) chondrite contains Fe in the sulphide and in the metallic state. In ordinary chondrites there is Fe in olivine, pyroxenes, metal and sulphides according to other Mössbauer investigations, e.g. (Sprenkel-Segel and Hanna, 1964).

Thermal treatment of carbonaceous chondrites

The heating of CI and CM chondrites was conducted in various oxidation-reduction conditions in gases evaporated by heating in open and closed systems. Open systems produced more reducing conditions than did closed systems. The results are shown in Fig. 1, which also shows the results of Hashimoto *et al.* (1979). They investigated the nature of the evaporated gases

by heating the CM chondrite Murchison. By heating from 200 to 700°C in a stream of helium, degradation and oxidation of phyllosilicates occurs. The peak amount of H_2O evaporation from a CM chondrite at 450°C coincides with that of Fe^{3+} increasing in phyllosilicates according to the reaction:



Thus it can be concluded that the oxidation of chondritic matter is caused by bound water release from phyllosilicates during heating. The charge compensation occurs in Fe, and Mg cations leave the layered silicate structure. Iron separates out in the form of magnetite, and Mg does so in forsterite (Malysheva *et al.*, 1982). We think that Fe oxidation will be more pronounced in a closed system and the resultant material will tend towards a CI mineral assemblage.

Above 700°C dehydration ceases and decomposition of organic matter commences. Carbon now enters the gas phase and oxidizing conditions change to reducing ones. A sharp transition in the oxidation state of Fe occurs: the Fe^{3+} state disappears and Fe^{2+} grows rapidly. The main Fe-bearing phase now becomes olivine. In a closed system there forms a mineral assemblage containing Fe-phases similar to those in CV3-chondrites: olivine and pentlandite. The crystal lattice of olivine cannot contain as much Ca and

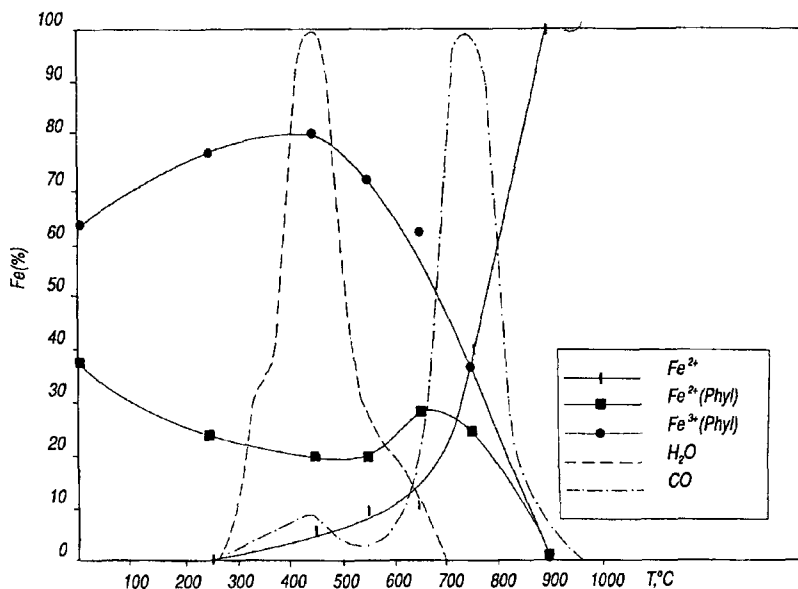


Fig. 1. Iron phase vs. heating temperature for chondrite Murray (CM) (40 min., He flow); dotted lines — data of Hashimoto *et al.* (1979).

Al as the phyllosilicates so these elements produce inclusions (Malysheva *et al.*, 1980). We have obtained Fe-phases similar to those in the Kainzas CO3-chondrite, as an intermediate product of heating a sample of carbonaceous chondrite under low P_{O_2} : Fe in olivine, troilite and metallic iron (Malysheva, 1977). Some Ca and Al can enter enstatite.

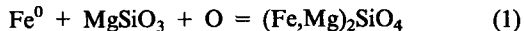
Reduction experiments with carbonaceous chondrites have shown that the isomorphous exchange of Fe^{2+} and Mg between Fe-bearing olivine and nascent enstatite does not occur at all: iron does not enter the pyroxenes. This is because the isomorphous exchange between Fe^{3+} and Mg in the silicate lattices is much slower than the rate of reduction. At the end-point of the reduction process there exists an assembly of minerals resembling those in enstatite chondrites: Fe as metal and FeS. For the Fe to be reduced to the point at which the full amount of troilite is not lost, high temperatures (1300°C) during a short period of time (5 min) are necessary (Malysheva *et al.*, 1979). Nevertheless, it is well known that the ratios Mg/Si, Al/Si and Ca/Si in enstatite chondrites are reduced relative to those in ordinary and especially carbonaceous chondrites. In order to explain this phenomenon we have evaporated CM2 chondrites in the highly reducing conditions of the carbon arc (Malysheva *et al.*, 1988). These experiments have shown that for both the chondrites investigated (Murray, Boriskino), Ca, Mg and Al according to the boiling points of these elements are evaporated

more quickly than Fe and Si. The reducing conditions of these experiments can be compared with those of the origin of enstatite chondrite.

The origin of ordinary chondrites

As a result of their investigation of sulphides in ordinary chondrites, Kurat *et al.* (1984) concluded that they were formed from highly reducing precursors, resembling enstatite chondrites. Ringwood (1981) proposed the origin of ordinary chondrites to be mixture of a highly reduced component (approximately 75%) and an oxidized one (approximately 25%) resembling the composition of CI chondrites.

We have conducted experiments with mixtures of enstatite (EH) chondrites and carbonaceous chondrites (CM2) by heating them in evacuated (to approximately 1 Torr) fused ampoules under various conditions (Malysheva *et al.*, 1984). The results of these experiments are shown in Fig. 2 where the heating time was 5 min. and the mixture used was 75 wt.% of EH and 25 wt.% CM chondrite. The oxidation of enstatite chondrite occurred very quickly, even at temperatures of 700°C and Fe-bearing olivine was produced according to reaction:



At temperatures up to 1050°C the only Fe-bearing phases are olivine and sulphide, and pyroxene does not contain any Fe. As the

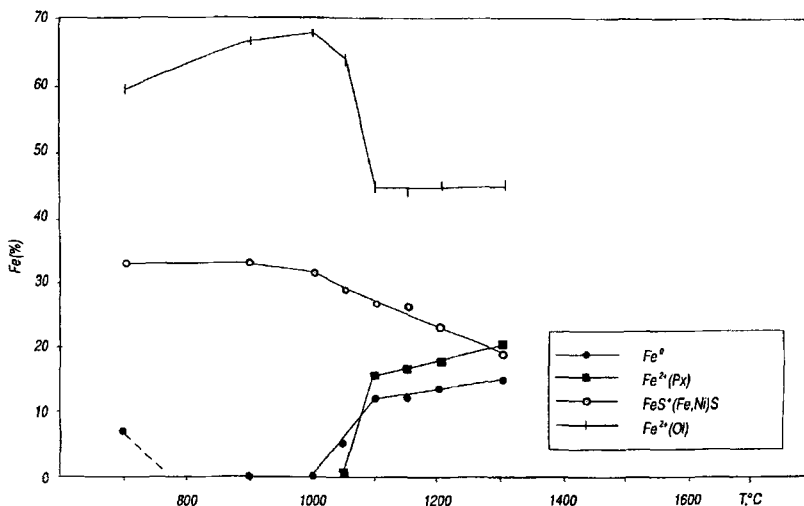


FIG. 2. Iron phases vs. heating temperature for the heating of a mixture of 75 wt.% Indarch (EH) and 25 wt.% Murchison (CM) for 5 min.

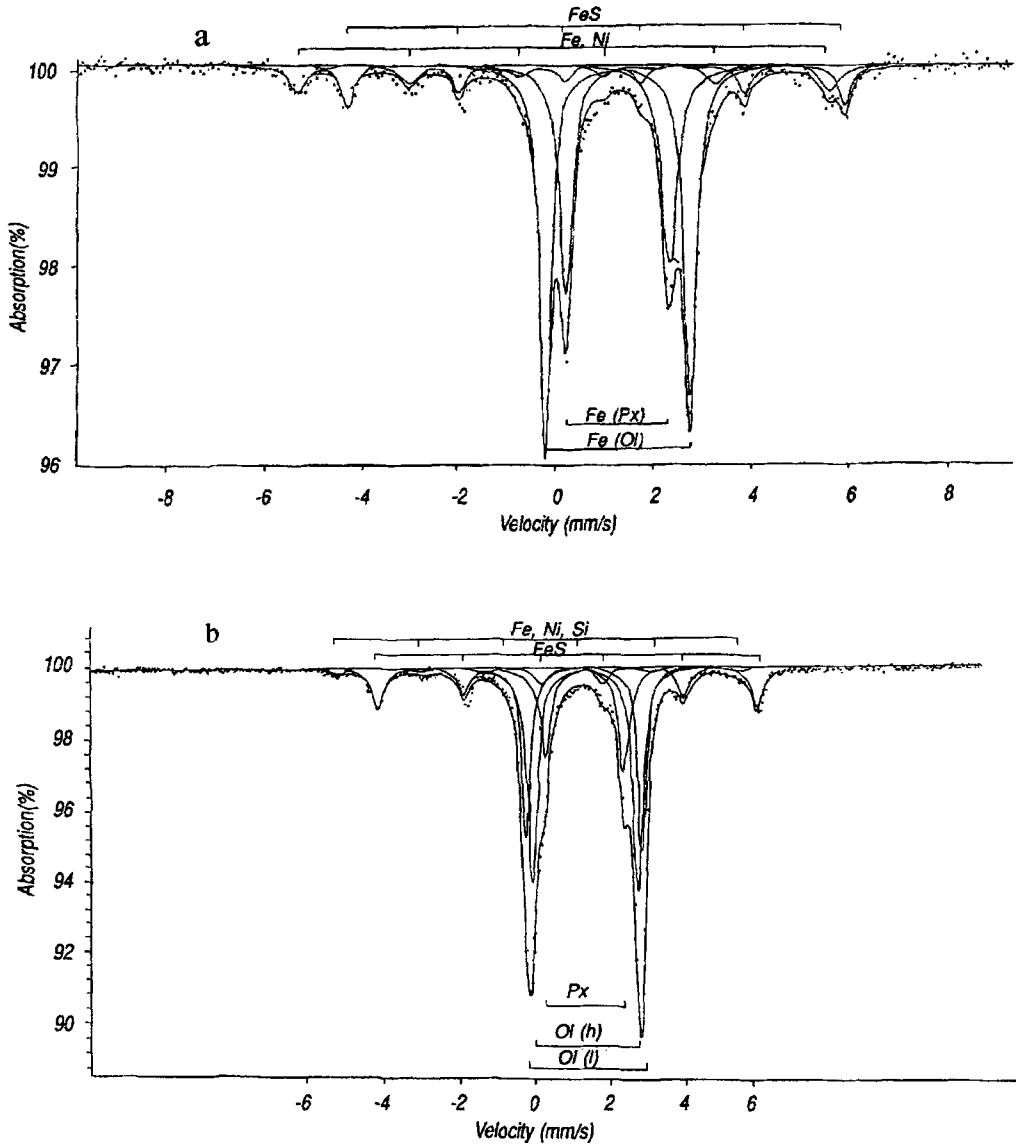
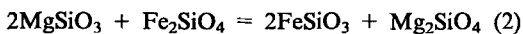
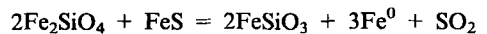


FIG. 3. (a) Mössbauer spectra of chondrules of ordinary chondrite Chainpur (LL3.4). (b) Mössbauer spectra of matrix (non-magnetic fraction) of ordinary chondrite Chainpur (LL3.4).

temperature rises above 1050°C there is a sharp change in the Fe distribution: the amount of Fe in olivine decreases and Fe appears in pyroxene and in metals. At this threshold temperature there is a sharp increase in the diffusion of Fe in pyroxene (Blander, 1979; Huebner and Nord, 1981) and the following reaction takes place:



Reaction (1) occurs very rapidly but reaction (2) is kinetically forbidden (Kerridge and MacDougall, 1976) and at low temperatures proceeds very slowly. Apart from this, at around 1000°C, decomposition of sulphides takes place (Hashimoto *et al.*, 1979; Gooding and Muenow, 1977) in accordance with the reduction reaction:



However, the amount of FeS does not decrease sharply (Fig. 2). This suggests that there is not direct dependence between the decomposition of FeS and the formation of Fe⁰. To explain the Fe reduction it appears necessary to take account of the other sulphides present in abundance in enstatite chondrites, e.g. MgS. This mineral disintegrates below 1000°C and can react with silicon-containing minerals:



Figure 2 shows that at the point of phase transition (1050°C) the amount of Fe in olivine decreases by about 25% with a corresponding increase of Fe in the metallic state and in pyroxene. Iron reduction in silicates due to sulphur from sulphides by heating is pointed out by Hashimoto *et al.* (1979). Unfortunately, thermodynamic data for many of these sulphides are not available.

Chondrule and matrix investigations

To establish the conditions for the origin of chondrules and matrix of some unequilibrated chondrites, we have investigated the distribution

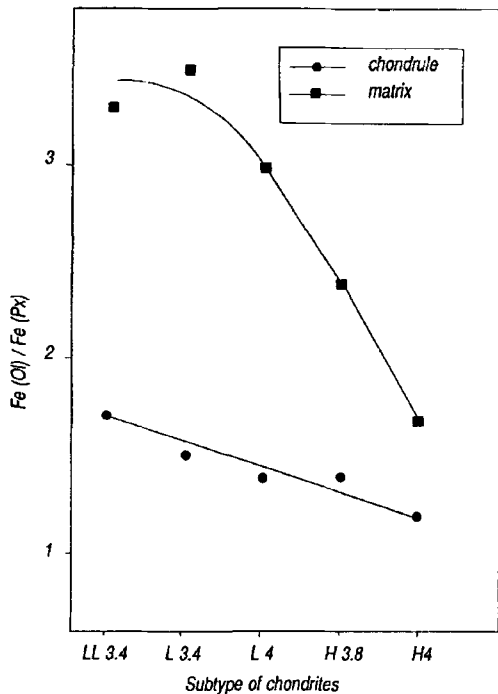


FIG. 4. The ratio Fe(Ol)/Fe(Px) for chondrules and matrix of ordinary chondrites.

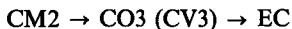
of iron among mineral phases, separately for chondrules and matrix (whole samples depleted of chondrules) (Malysheva *et al.*, 1986, 1989). The Mössbauer spectra of Chainpur (LL3.4) are shown in Fig. 3. The Fe distribution among chondrules and matrix (non-magnetic fraction) is different. In the matrix there is more iron in olivine than in the chondrules. This result agrees well with data of other investigators based on non-Mössbauer methods of measurement (Huss *et al.*, 1981; Nagahara, 1984). In the work of Alexander *et al.* (1989) it is pointed out that olivines both in matrix and rims are more Fe-rich than in chondrules.

The ratio of Fe(Ol) to Fe(Px) in the Chainpur chondrite is 3.0 for the matrix and 1.4 for the chondrules. This ratio decreases from LL to H chondrites in the chondritic matrix (Fig. 4). As a result, the temperature (or the time of heating) must increase in the region of matrix formation. However, this effect is much reduced in the case of chondrules.

The comparison of the above data with the results of heating experiments shown in Fig. 2, allows us to assess that chondrules of ordinary chondrites are formed at temperatures $\geq 1050^\circ\text{C}$, while the matrix is formed at temperatures $< 1050^\circ\text{C}$. For the carbonaceous chondrite Kainzas (CO3) these temperatures are approximately 1000°C and $< 900^\circ\text{C}$ respectively. In Fig. 3 it is also shown that two kinds of olivine are distinguished: low-Fe (l) — Fo ~ 90 , and high-Fe (h) — Fo ≤ 50 . This bimodal distribution presumably reflects the process of origin: high-Fe olivine as the result of oxidation ($< 1050^\circ\text{C}$) and low-iron olivine by reduction ($> 1050^\circ\text{C}$). Such temperatures during the formation of chondrules most probably arose during shock events in the turbulent nebula at the time of accretion (Ruzmajkina, 1990), under the influence of electric discharges (Wasson *et al.*, 1982) or by drag heating (Wood, 1985).

Discussion

We have outlined the heating measurements of carbonaceous chondrites, in which the evolution of the Fe-bearing phases was established by means of Mössbauer spectroscopy. As described above, various oxidation/reduction conditions occurred during heating of the primitive CM2 chondrites at various temperatures. Such processes were also observed by Ramensee and Wänke (1981) and other investigators. Heating in an open system indicates the following evolutionary sequence for the Fe-bearing phases:



The first part of this chain was obtained in the heating experiments by Hashimoto *et al.* (1979) and Matza and Lipschutz (1978), but an Fe-distribution like that in ordinary chondrites was obtained only by heating a mixture of oxidized (CM2) and reduced matter (EC). The origin of ordinary chondrites as a result of such a process does not conflict with the chemical composition of chondrites (Ahrens *et al.*, 1973): which have intermediate ratios of Mg/Si, Al/Si and Ca/Si.

The existence of the second part of the above chain, CO3 → EC, together with the origin of the 'two-component' ordinary chondrites are modelled here for the first time but the oxygen isotopic ratios must be considered. Doubts were cast on the idea of an homogeneous nebula during the seventies when Clayton *et al.* (1976, 1977) classified all meteorites into several groups on the basis of oxygen isotopes. According to the principles of this classification each group of meteorites cannot be obtained by simple mass-dependent fractionation processes. However, more recently it has become increasingly evident that some isotopic anomalies are not just of nuclear origin, but also due to physical-chemical mass-independent fractionation (Clayton, 1990; Allégre and Birek, 1985). We hope that these processes — nuclear-spin effect (Galimov, 1970), fractionation in plasma (Arrhenius and McCrumb, 1980), etc. — can help to confirm the genetic relationships among chondritic groups. For example, Carr *et al.* (1984) have shown that acid residues of the chondrite Indarch EH resemble carbonaceous chondrites in some aspects (Ne-Ar and Cc-Xe). Clayton and Mayeda (1981) postulate a common solid precursor (enriched in ¹⁶O) for ordinary and C3-chondrites. Investigation of the oxygen isotope evolution of chondrules shows that chondrules may be formed by mixing two solid precursors (Gooding *et al.*, 1983): one such component being dust enriched in ¹⁶O (CM-matrix ?) the other having a slope of ½ on the plot of oxygen isotopes. The isotope data for enstatite chondrites lie just on this fractionation line (Clayton *et al.*, 1984). One should also mention that the enrichment in ¹⁶O depends on the size of the dust grains (Clayton *et al.*, 1990) or on the dust's age (Clayton *et al.*, 1989). Unfortunately, the explanations given above are not unanimously accepted.

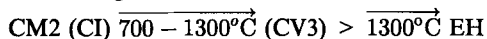
The possibility of the mixing of two components during the formation of ordinary chondrites in the nebula may take place according to the estimate of Ruzmajkina (1986). This is also confirmed by the existence of the Kaidun

chondrite breccia which consists of both enstatite and carbonaceous chondrite matter (Ivanov *et al.*, 1986).

Conclusions

The overall results of our investigations, using Mössbauer spectroscopy, into the evolution of the Fe-containing phases of carbonaceous chondrites heated in various oxidation-reduction conditions are:

- (1) Oxidation-reduction conditions required for the production of all the Fe-containing phases of carbonaceous chondrites may be produced by gases released by heating lower petrological types of chondrite;
- (2) Transformation of the phases occurs very rapidly — during 1–5 min. — at all temperatures.
- (3) Iron-containing phase analogous to those of the following chondrites were realized:



- (4) Iron phases analogous to those of the ordinary chondrites Fe(O), Fe(Px), FeS and Fe⁰ were obtained as the result of the heating of a mixture of carbonaceous CM2- and enstatite chondrites. The discovered phase transition at 1050°C is simply the temperature boundary for the production of chondrules (> 1050°C) and matrix (< 1050°C).

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