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Chondrules from Chainpur (LL-3): reduced parent rocks and vapor fractionation

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Nineteen chondrules from the Chainpur (LL-3) chondrite were analyzed for their bulk lithophile element contents and mineral chemistries. Chondrule compositions are highly fractionated. The following compositional groups can be distinguished: (1) refractory (depleted in Na and K); (2) K-depleted ($K \ll CI$, $Na > CI$); (3) approximately chondritic ($Na/K \sim CI$, $Na > CI$); and (4) K-enriched ($K \gg CI$, $Na > CI$).

The most refractory chondrules are depleted in K ($0.11 \times CI$ abundances normalized to Sc), Na (0.26), Mn (0.52), and Cr (0.71). Therefore we conclude that the refractory group was mainly produced by vapor fractionation during the chondrule forming event. The majority of chondrules is enriched in Na (1.37 – $1.40 \times CI$) but fractionated in K which ranges from $0.4 \times CI$ (K-depleted) to $2.84 \times CI$ (K-enriched). For the fractionation of K from Na we suggest a separation mechanism via alkali sulfides. Uncorrelated fractionations of Ca, Mn, Cr, Eu, Yb, Sm give supporting evidence for such a mechanism.

These findings imply that the pre-Chainpur matter went through highly reducing conditions (high H_2/O_2 and S_2/O_2 ratios) before it was sampled by the chondrule forming process. Most chondrules of our suite have similar fa contents in olivine (11–21) and are enriched in volatile elements. From this we conclude that these chondrules were formed under oxidizing conditions in a relatively dense atmosphere with high partial pressures of volatile elements (alkalis, halogens). A proto-planetary atmosphere could have provided these conditions.

The fractionation process proposed should also be applicable to fractionations on a large scale like the Na/K and Mg/Si fractionations among chondrites.

1. Introduction

Chondrules are important constituents of chondrites, the most primitive and most common meteorites. Their genesis is still subject of considerable debate and actually is largely unresolved (e.g. [1]). Chondrules, therefore, have been the subject of many studies ever since they have been recognized. Although a large amount of petrological and geochemical data already exists on chondrules [2] there is still no consensus on how to interpret these data. Just a few processes have been identified which were active during chondrule formation:

(1) There was a melting event which formed

molten droplets [3]—if we restrict the term “chondrule” to formerly molten droplets (for a discussion see Kurat [2]).

(2) Melting affected pre-existing solids which occasionally are partially preserved as relics [4–6].

(3) Metal-silicate fractionation affected most chondrules [7] probably during the melting event.

(4) Some chondrules suffered vapor fractionation [8] which led to depletions in alkali elements [8,9] and other effects (see Kurat [2]).

(5) Some chondrules show evidence for recondensation [10–12].

Chondrule bulk compositions are complex not only because of several processes having been active during chondrule formation but apparently

also because of fractionations among the precursor matter and subsequent by-chance mixing [5,9,13–15]. The nature of the precursor matter is not known but relics document that it was mainly rather coarse-grained matter [4–6,16,17].

In this paper we present a new attempt in interpreting bulk chemical data of chondrules from the Chainpur (LL-3) chondrite with respect to the unresolved question of the nature of chondrule precursor material and the processes having been operative during chondrule formation. We concentrate on the lithophile elements and present new data for 19 chondrules from Chainpur which have been carefully selected and petrologically characterized.

2. Analytical procedure and results

Ten perfectly round to oval objects with smooth surfaces have been selected for $^{39}\text{Ar}/^{40}\text{Ar}$ dating

[18–20]. Their weights ranged from 8 to 24 mg. It seemed essential to us to select only chondrules in the strict sense, which are “partially to fully crystalline, once-molten droplets” [2]. This cannot be verified by visual inspection of the surface alone. In addition it seemed desirable to save part of each chondrule for future work. Therefore the chondrules were broken in a stainless steel mortar. It was confirmed before by crushing spectroscopically pure quartz grains that no contamination resulted from this procedure. The broken chondrules were divided into three parts: one for neutron activation analysis and age determination, one for petrological investigations and one part was stored. For the age determination the chondrule sample and a “matrix” sample ($< 400\ \mu\text{m}$) were exposed to an epithermal and fast ($E > 0.1\ \text{MeV}$) neutron fluence of $1 \times 10^{19}\ \text{n cm}^{-2}$. Gamma rays of the long-lived radionuclides produced in this irradiation were used to determine the concentrations of Sc, Cr, Fe, Br, and Sm. Sodium and

TABLE 1

Bulk major, minor, and trace lithophile element contents of chondrules and matrix from the Chainpur (LL-3) chondrite

Chondrule	Na (mg/g)	K ($\mu\text{g/g}$)	Ca (mg/g)	Sc ($\mu\text{g/g}$)	Cr (mg/g)	Mn (mg/g)	Br ($\mu\text{g/g}$)	Rb ($\mu\text{g/g}$)	Cs (ng/g)	La (ng/g)	Sm (ng/g)	Eu (ng/g)	Yb (ng/g)	Lu (ng/g)
Ch-1	6.32	530	5.5	5.7	3.09	1.38	2.6	–	–	–	140	–	–	–
Ch-2	8.50	410	17.0	19.8	4.90	3.36	1.3	–	–	–	690	–	–	–
Ch-3	3.65	151	11.5	14.2	4.94	2.10	0.5	–	–	–	390	–	–	–
Ch-4	2.72	128	10.4	11.7	3.59	1.92	1.4	–	–	–	300	–	–	–
Ch-5	10.6	1816	10.6	8.5	3.40	4.33	0.6	–	–	–	210	–	–	–
Ch-6	13.1	370	10.2	11.1	4.2	2.38	1.4	–	–	–	250	–	–	–
Ch-7	9.48	1398	8.5	9.7	3.28	3.44	0.8	–	–	–	210	–	–	–
Ch-8	6.18	350	9.8	11.4	3.91	4.20	0.5	–	–	–	280	–	–	–
Ch-9	2.70	98	7.6	13.1	3.61	2.38	1.0	–	–	–	280	–	–	–
Ch-10	9.30	299	8.0	8.1	3.24	2.79	2.4	–	–	–	210	–	–	–
Ch-11	2.06	170	12	8.44	1.19	2.44	–	2.6	< 85	180	90	33	290	29
Ch-13	2.76	150	19	14.30	5.03	2.11	–	2.7	100	540	375	94	710	63
Ch-14	15.11	1250	9.5	10.91	3.96	3.74	–	< 2.3	110	280	250	76	590	60
Ch-15	15.49	2820	19	10.85	3.80	2.98	–	4.6	380	300	230	81	460	70
Ch-16	11.70	4000	9.0	11.16	4.58	3.95	–	11.2	210	300	240	46	380	63
Ch-17	8.86	1800	11	8.41	3.58	2.32	–	4.2	< 110	315	180	51	110	< 32
Ch-18	14.37	2400	14	12.15	3.96	3.46	–	12.9	210	510	220	107	400	65
Ch-19	12.80	1300	12	10.72	4.38	4.35	–	< 2.9	230	650	220	146	260	43
Ch-20	21.18	1700	7.0	18.12	2.41	0.25	–	10.8	220	1240	340	171	490	50
Ch-M	7.63	575	9.0	9.1	3.28	2.78	1.2	–	–	–	230	–	–	–
Precision	3	$< 5^a$	$< 5^b$	2	2	3	25	25	15	15	10	15	15	20

^a < 20 for Ch-16 to Ch-20.

^b < 20 for Ch-11 to Ch-20.

Mn were measured after a second irradiation for 10 minutes at a thermal neutron flux of $4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. Because of the interesting results obtained [9] a second set of ten round to oval objects was selected and subjected to the same sample preparation procedure. Although it is convenient to use the same irradiation for age determination and gamma spectroscopy, the disadvantage of the large background from ^{58}Co , ^{54}Mn (produced by n,p reactions from ^{58}Ni and ^{54}Fe , respectively), and ^{51}Cr outweighs the advantage that sample handling is reduced. Therefore the samples of the second set were irradiated twice with thermal neutrons (10 minutes at $4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for Na,

K, and Mn and 12 hours at $4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for the other elements) before the irradiation with fast neutrons. In addition to the elements analyzed in the first chondrule set concentrations of Rb and Cs and a few rare earth elements (REE) have been determined in the second sample set. All elements have been determined by INAA except for the concentrations of K and Ca in chondrules Ch-1 to Ch-10 which have been measured by mass spectrometry via ^{39}Ar and ^{37}Ar , respectively, and K in chondrules Ch-11 to Ch-15, which was measured after radiochemical separation. The results are given in Table 1.

Small splits of each chondrule were mounted in

TABLE 2

Summary of petrological data on chondrules from the Chainpur (LL-3) chondrite

Chondrule	Phases ^a	Mol. % fa(fs)		Fe/Mn ol or px	Texture
		range	average		
Ch-1	ol, gl	1.1–3.4	1.9	> 100	porphyritic to mosaic, metal globules in ol and gl, metal-sulfide-silicate rim
Ch-2	ol, px, mx	13.7–22.9	18.5(19.8)	30	porphyritic, prismatic px in mx, very minor metal and sulfides
Ch-3	ol, gl	15.0–20.0	16.5	41	barred, very minor gl, some chromites, thin rim with metal and sulfide
Ch-4	ol, mx	15.1–17.9	15.9	52	barred, very minor mx, little metal at surface
Ch-5	ol, mx	18.6–23.4	19.7	21	quench ol in gl, little metal + sulfide in gl
Ch-6	ol, mx	10.0–43.0	20.6	38	porphyritic, abundant mx, some metal + sulfide at surface
Ch-7	ol, mx	10.7–21.0	15.5	29	porphyritic, abundant mx, very few metal blebs in matrix
Ch-8	px, mx	(5.3–5.9)	(5.6)	8	radiating px with little mx, metal scarce
Ch-9	ol, mx	18.5–21.1	20.3	32	barred and mosaic, little mx, some chromites, no metal
Ch-10	ol, mx	10.3–18.0	14.1	28	porphyritic, abundant mx, little metal in matrix, rim rich in metal
Ch-11	ol, px, mx	24.2–25.4	25.2	72	radiating ol-px with little mx, small metal blebs common, concentrated close to surface
Ch-13	ol, mx	14.5–15.4	14.8	45	barred and mosaic ol, some mx, chromite, little metal in mx
Ch-14	ol, px, mx	11.4–20.8	15.3	35	porphyritic ol in ol + px + gl mx (abundant), few metal blebs in ol and mx
Ch-15	ol, mx	12.2–29.5	18.0	42	porphyritic ol in ol + px mx (abundant), some metal in ol + mx
Ch-16	px, ol, mx	9.8–12.5	11.1	13	quench px in abundant ol + px + gl mx, small metal blebs abundant, large metal at surface
Ch-17	ol, mx	11.6–24.9	15.6	31	porphyritic ol in microporphyritic ol + gl mx, large metal globules
Ch-18	ol, mx	12.6–22.0	16.7	23	porphyritic ol in abundant ol + px mx, some metal in mx
Ch-19	ol, mx	10.2–13.2	11.5	20	porphyritic ol in abundant ol + px mx, very few metal blebs
Ch-20	ol, gl	0.8–1.0	0.9	> 100	radiating ol in abundant gl, no metal

^a Phases: ol = olivine, px = pyroxene, mx = matrix, gl = glass.

epoxy resin, cut and polished and studied microscopically in reflected light. It turned out that sample Ch-12 was a fragment thickly coated with matrix ("snowball"). Consequently we exclude it from this report. Olivine, pyroxene, metal, sulfide, matrix, and glass compositions were determined using an ARL-SEMQ electron microprobe. Natural and synthetic minerals were used as standards and standard Bence-Albee correction procedures were applied. The petrological and mineral chemical data are summarized in Table 2. Although we cannot be sure that our sample comprises only chondrules, there is a good chance that it contains mostly chondrules *sensu strictu*, in contrast to samples investigated by others (e.g. [15,21-23]) who used different definitions of the term "chondrule".

3. Discussion

In principle three components contribute to the bulk chemical composition of chondrules: silicates and oxides, metal, and sulfides. The mixing proportions are highly variable and unknown. Therefore, chondrule bulk chemical data can only reveal rough estimates of the mixing proportions of the three principal constituents but cannot give direct insight into the geochemistry of the components themselves. For an understanding of the genesis of chondrules, however, the geochemical characteristics of each of the components have to be evaluated. This can be done by using concentration ratios of geochemically similar elements rather than the bulk contents. These ratios are practically independent of the mixing proportions of the principal components and conveniently compensate the dilution effects of the other components.

To study the silicate/oxide fraction of chondrules, concentrations of the lithophile elements (Na, K, Ca, Cr, Mn, Br, Rb, Cs, REE) were normalized to Sc, because Sc, a refractory element, is relatively insensitive to cosmochemical (gas-solid/liquid) and geochemical (solid-liquid) fractionation as compared to the other lithophile elements. Although normalization to Sm should be a comparable choice, we prefer Sc because of its higher abundance and because it can be measured with high precision by INAA.

TABLE 3

Averaged lithophile element/Sc ratios of chondrules from Chainpur arranged in order of increasing standard deviation (SD)

	Sm/Sc $\times 10^4$	Cr/Sc	Ca/Sc	Mn/Sc	Na/Sc	K/Sc
Average	229	342	1007	268	854	104.9
SD	47	95	313	115	452	102.3
n	19	19	19	19	19	19
CI ^a	261	453	1525	308	850	87.6

^a CI ratios from Orgueil (unpublished analysis, MPI Mainz).

The results are somewhat surprising. From Table 3 it is apparent that the average chondrule in Chainpur is depleted in the refractory elements Sm and Ca and the moderately volatile elements Cr and Mn but is not depleted in the volatile elements Na and K. Variance of the data is—as expected—highest for the volatile elements K and Na and lowest for the refractory Sm. Unexpected is the high variance of the refractory Ca, which is higher than that for the moderately volatile Cr (31% vs. 28%, respectively).

The extraordinary variability of some element/

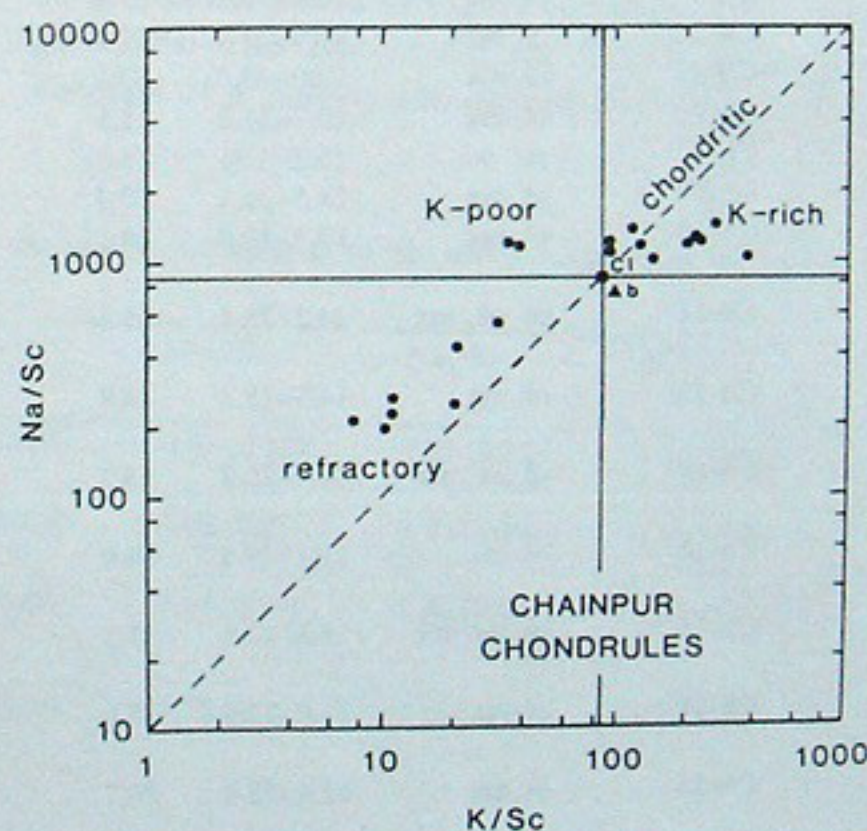


Fig. 1. Logarithmic plot of K/Sc vs. Na/Sc ratios of chondrule bulk compositions from Chainpur compared to Chainpur bulk (b) [15] and carbonaceous chondrite Orgueil (CI, unpublished data, MPI Mainz).

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Sc ratios is a strong indication of very effective fractionation processes having been active before or during chondrule formation. From averaged data (Table 3) there is an indication for volatility-dependent fractionation. The fact that the volatile elements on average are not depleted but the moderately volatile and refractory elements are depleted in Chainpur chondrules relative to CI could suggest chondrule formation via fractional condensation. A plot of Na/Sc vs. K/Sc, however, reveals a somewhat different and more complicated picture (Fig. 1):

(1) Most chondrules (12 out of 19) are approximately uniformly enriched in Na as compared to CI but are strongly fractionated in K.

(2) Seven of the 19 chondrules analyzed plot far below the CI Na/Sc and K/Sc ratios. They apparently form an alkali depletion sequence.

To simplify the discussion, we can group these compositions according to their points of projection in Fig. 1 into four groups: (1) refractory (depleted in Na and K), (2) K-depleted ($K \ll CI$, $Na > CI$), (3) approximately chondritic ($Na/K \sim CI$, $Na > CI$), and (4) K-enriched ($K \gg CI$, $Na > CI$).

Most of these groups established by the projection onto the Na-K plane comprise individuals which are quite similar to each other in all elements determined. Some, however, do not fit any

group. Chemical characteristics of similar chondrules, therefore, are given in Table 4 as group averages, the non-groupable ones are listed individually.

3.1. Vapor fractionation

The members of the refractory group apparently have experienced vapor fractionation. They project below the primitive (CI) Na/Sc ratio and tend to have increasing Na/K ratios with decreasing alkali contents. This is roughly in accordance with experimental volatility data [24] and apparently reflects increasing depletion by volatilization. The final products of this process apparently are the most refractory chondrules. This group consists of 4 members, all of which are barred olivine chondrules (Ch-3, Ch-4, Ch-9, Ch-13) (Table 2). They are depleted in all elements except Sm (Table 4). They form a rather homogeneous group. Variance of elemental contents is rather low except for Ca which is surprisingly high ($\pm 36\%$) for a refractory element. All members of that group are oxidized (fa 15–20) and have fractionated Fe/Mn ratios (35–52; Table 2).

The intermediate refractory chondrules cannot be grouped because of highly variable silicate compositions. This cluster (in the Na/K projection) consists of a porphyritic olivine chondrule (Ch-2).

TABLE 4

Averaged and selected lithophile element contents of Chainpur chondrules normalized to Sc and CI (standard deviation in parenthesis)

Chondrule group	Sm/Sc	Ca/Sc	Cr/Sc	Mn/Sc	Na/Sc	K/Sc
K-poor (Ch-6,10)	0.93 (0.09)	0.63 (0.03)	0.86 (0.03)	0.91 (0.30)	1.37 (0.02)	0.40 (0.03)
Chondritic (Ch-1,7,14,19)	0.86 (0.07)	0.63 (0.08)	0.91 (0.20)	1.09 (0.22)	1.37 (0.20)	1.35 (0.24)
K-rich (Ch-5,15,16,17,18)	0.82 (0.09)	0.82 (0.22)	0.84 (0.09)	1.10 (0.33)	1.40 (0.19)	2.84 (0.75)
Refractory (Ch-3,4,9,13)	0.96 (0.10)	0.59 (0.21)	0.71 (0.08)	0.52 (0.05)	0.26 (0.03)	0.11 (0.02)
<i>Ungrouped chondrules</i>						
Ch-2	1.33	0.56	0.55	0.55	0.50	0.24
Ch-8	0.94	0.56	0.76	1.19	0.64	0.35
Ch-11	0.41	0.93	0.31	0.94	0.29	0.23
Ch-20	0.72	0.25	0.29	0.05	1.38	1.07

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a radiating pyroxene chondrule (Ch-8), and a radiating olivine-pyroxene chondrule (Ch-11). Ch-2 seems to be genetically related to the refractory group but failed to become as refractory. The other two have apparently unrelated elemental abundances. Both are depleted in alkalis and Cr, have undepleted Mn contents but are either depleted in Sm (Ch-11) or Ca (Ch-8). They also differ in oxidation state (fa 25.2 and fs 5.6, respectively), Fe/Mn ratio (72 and 8 respectively), and mineralogy. Their genetic histories must have been quite different from the rest of the cluster.

Most features of the refractory group can be explained by partial volatilization of an originally chondritic melt. This probably happened during the chondrule formation process. Actually, partial volatilization during melting should be a normal process and it is surprising that only a fraction of chondrules has been affected. The variable Ca contents cannot be explained by a vapor fractionation mechanism. They probably reflect by chance sampling of Ca-fractionated parent matter. A similar indication is provided by the intermediate refractory chondrules (Ch-2, Ch-8, and Ch-11) which have very different Sm, Cr, and Mn contents. Apparently, pre-chondrule matter was fractionated also in these elements.

3.2. Na-K fractionation

The majority of chondrules (12 out of 19) is enriched in Na relative to CI at an approximately similar level but is highly variable in K contents ranging from depleted to enriched.

The K-depleted group has only 2 members, two porphyritic olivine chondrules (Ch-6, Ch-10). They have very similar compositions of the silicate portion as far as the limited number of elements analyzed is concerned (Table 4). Only Mn shows considerable deviations which are also manifested in the variable Fe/Mn ratios of the silicates in Ch-6 and Ch-10 (Table 2) which differ by a factor of 2. Manganese, however, is variable in all groups except the refractory one.

The chondritic group (Na/K ~ CI) consists of 4 members, all of which are porphyritic olivine chondrules (Ch-1, Ch-7, Ch-14, Ch-19). In the Na-K plot Ch-20 also projects into the "chondritic"

group but in almost all other elemental ratios it differs considerably from this group and will therefore be treated separately (see below). The chondritic group is enriched in the volatile elements K, Na, and Mn and depleted in the refractory elements Ca and Sm. There is some variability in the moderately volatile element contents (~20%, Table 4) but little (<10%) in the refractory element contents. There are, however, large differences in oxidation state and Fe/Mn ratios of the silicates between different members of that group (Table 2). Ch-1 is highly reduced (fa 2) and has a high Fe/Mn ratio whereas the other members of this compositional group are more oxidized (fa 11.5–15.5) and have fractionated Fe/Mn ratios (20–35).

The K-rich group plots to the right of the CI Na/K ratio in Fig. 1 and consists of 5 members. They show a variety of textures from quench olivine (Ch-5) and quench pyroxene (Ch-16) to porphyritic olivine (Ch-15, Ch-17, Ch-18). This group is highly enriched in K (~2.8 × CI, Table 4), enriched in Na and perhaps Mn and depleted in Cr, Ca, and Sm. Sm and Cr contents show a variance of ±10% whereas Ca, Mn, Na, and K are variable within ±20–30%. All chondrules are oxidized (fa 11–20) and have fractionated Fe/Mn ratios (13–42).

Ch-20 projects into the primitive chondritic group in Fig. 1 but except for the alkali contents is highly fractionated. It is strongly depleted in Mn (0.05 × CI), Ca (0.25 × CI), Cr (0.25 × CI) and is depleted in Sm (0.72 × CI). It is strongly reduced (fa 0.9) and has a high Fe/Mn ratio.

All three Na-rich chondrule groups have very similar silicate compositions (Table 4), except for the K contents which vary between 0.40 × CI and 2.84 × CI. Either the pre-chondrule matter or the chondrules themselves have experienced a severe Na-K fractionation. The fractionation is of a peculiar type: without any detectable change in Na contents, K is strongly fractionated. None of the other elements included in this study follows that trend, except for Mn, which shows a weak correlation with K (see discussion below). In principle, Na and K can easily be separated in systems which contain a high proportion of Na and K phases because Na and K have quite different ionic radii and tend to enter different phases.

These phases can be separated mechanically and by fractional crystallization from silicate liquids or aqueous solutions. These mechanisms, however, will not work in ultrabasic systems as represented by chondrites because both elements will behave as incompatible elements with respect to the main rock-forming minerals (olivine, orthopyroxene) and Na and K do not separate in the subsolidus region but rather concentrate in Na-rich feldspar. Thus, ordinary geochemical processes cannot account for the observed Na-K fractionation. Standard cosmochemical processes (gas-liquid/solid) can also not explain our observation because both elements should be affected, although to different degrees, as is the case in our volatilization sequence.

In order to account for the observed Na-K fractionation, Na and K have to be preferentially stored in different phases. We can think of two possibilities: (1) halides, and (2) sulfides.

Urey [25] first explored the stability of halides in the solar nebula and found that—under certain circumstances—they are stable species and could account for the mostly undepleted abundances of halogens in chondrites. Recent calculations [26] showed that halides are common gaseous species in the cooling solar nebula and some could also condense under heterogeneous accretion conditions. Since NaCl and KCl have different physical properties, a separation of K from Na seems feasible. A major obstacle, however, is the cosmic abundance of halogens which suffices for converting most of the K into KCl (F, Br, J) but not the other competing cations (Na, Ca, Mg). We therefore consider this possible way of separating K from Na not to be a likely one.

Sulfur is much more abundant than the halogens and it might even be more abundant than anticipated so far [27]. Simple alkali sulfides (like Na_2S and K_2S) are stable condensates in the heterogeneous accretion model [26] but not in the homogeneous one. Anyway, alkali sulfides are stable phases in E chondrites (e.g. [28]) and could provide a vehicle to separate K from Na. If we just take into account the alkali-sulfur compounds known so far, separation of Na and K can easily be achieved. Like in other systems Na and K tend to form separate phases. In E chondrites Na preferentially forms sulfides with Cr like caswell-

silverite [29] whereas K resides in djerfisherite [30].

Therefore, under reducing conditions (or better: high S_2/O_2 ratios) Na and K could be concentrated in different phases. For a separation of K from Na a process has to be found which separates the K sulfides from the Na sulfides. This should be possible via a variety of physical processes because in almost all Na-K phase systems the K compounds are physically weaker than the Na compounds. This is reflected in different melting points and boiling temperatures and many other physical properties. One or some of these properties allowed separation of K sulfides from Na sulfides. The conditions must be unique because the Na compounds were immobile while the K compounds could be transferred from one portion to another. This way K-poor and K-rich precursors could have formed. Sampling of either one of these precursors or a mixture thereof during the chondrule forming process would produce the observed trend in chondrule compositions. Detailed investigation of this fractionation mechanisms should provide a unique opportunity to quite narrowly define the physical-chemical condi-

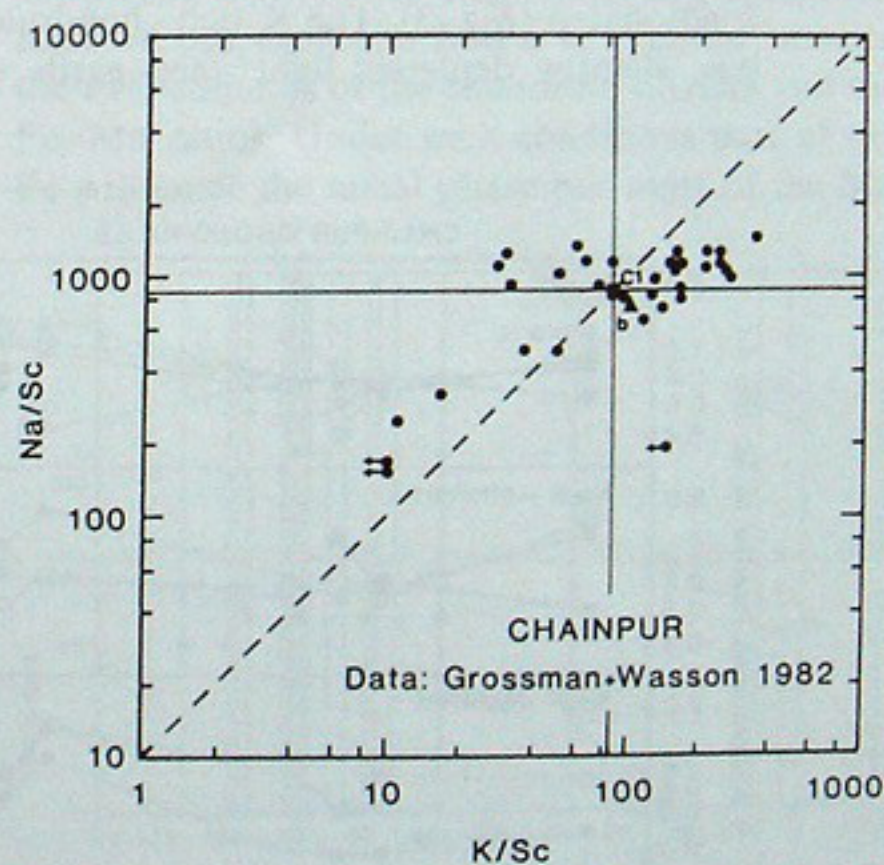


Fig. 2. Logarithmic plot of K/Sc vs. Na/Sc ratios of bulk compositions of chondrules and chondrule-sized fragments from Chainpur [15] compared to Chainpur bulk (b) [15] and carbonaceous chondrite Orgueil (CI, unpublished data, MPI Mainz).

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tions prevailing during the alkali fractionation process and thus of the formation of the pre-Chainpur matter.

Comparison of our data (mostly chondrules) with those published by Grossman and Wasson [15], who analyzed a suite of chondrule-sized particles (including chondrules) from Chainpur suggests that lithic fragment compositions follow a similar trend (Fig. 2). We cannot evaluate the data in detail because of lack of petrographic data but statistically lithic fragments should be abundant among the K-rich compositional group. In fact, the most K-rich particle analyzed by Grossman and Wasson [15] is a microbreccia fragment ("chondrule 2"). The tendency of some compositions determined by Grossman and Wasson [15] towards lower Na contents could also be a feature of lithic fragments. However, this crucial question cannot be resolved without additional investigations devoted exclusively to lithic fragments.

3.3. Rare earth elements

Some REE concentrations have been determined in the second set of chondrules (Ch-11 to Ch-20). All of the patterns obtained are fractionated (Fig. 3). The K-rich chondrule group has slightly depleted light rare earth element

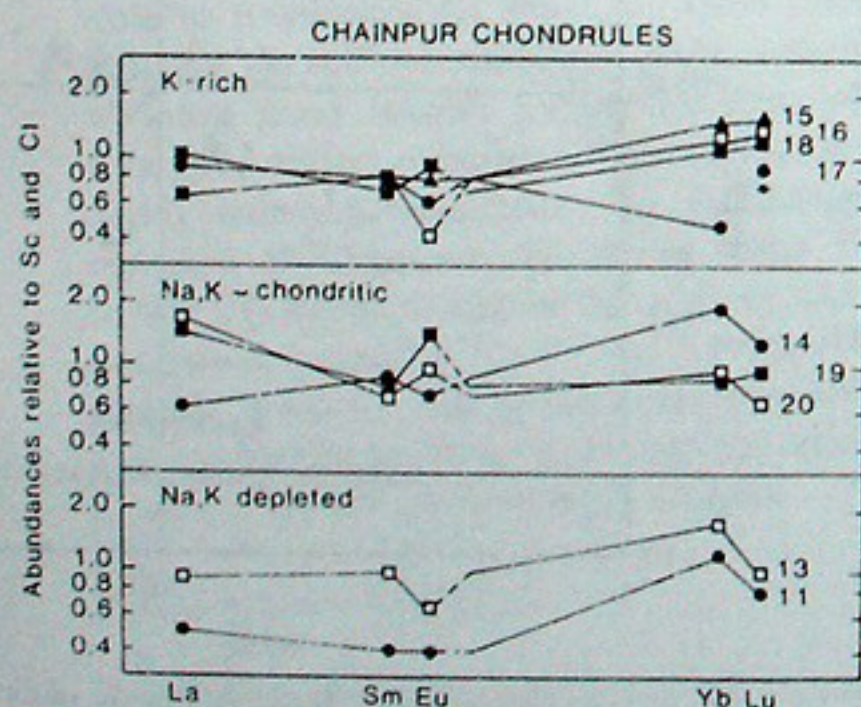


Fig. 3. Abundances of REE in chondrules from Chainpur normalized to Sc and CI (Orgueil, unpublished data, MPI Mainz).

(LREE) abundances with generally weak La/Sm fractionation (+ and -). Most chondrules have a negative Eu anomaly but one chondrule (Ch-18) which has the highest La content has a positive Eu anomaly. The heavy rare earth elements (HREE) are mostly enriched with a Yb/Lu ratio < CI. An exception is Ch-17 which has depleted HREE abundances.

Chondrules with approximately chondritic Na/K ratios have fractionated LREE with La/Sm > and < CI. The Eu anomaly follows the La fractionation. The HREE are depleted for the La-rich chondrules and enriched for La-depleted ones. The Yb/Lu ratio is either larger or smaller than the CI ratio.

One refractory chondrule (Ch-13) has approximately CI LREE abundances, a negative Eu anomaly and a positive Yb anomaly. Ch-11, however, is strongly depleted in LREE, has no Eu anomaly, and is enriched in the HREE with a positive Yb anomaly. Chondrule Ch-20 has a somewhat similar REE pattern to Ch-14 but with much lower HREE abundances.

Interpretation of these patterns is complicated. There is definitely no indication of magmatic processes. Fractionation by volatility [31] can also be excluded.

The fact that mostly Eu and Yb show anomalies is probably related to the high ionization potentials of these elements for transitions from the second to the third ionization state (e.g. [32]). The severe fractionations of Eu and Yb therefore are an additional indication of reducing conditions under which Eu^{2+} and Yb^{2+} should be stable. Eu^{2+} with an effective ionic radius of 1.12 Å is known to follow Ca (1.03 Å). This also holds for sulfides and Eu^{2+} should preferentially follow Ca^{2+} in CaS, an indirect indication of which has been reported from Indarch chondrules [33]. Yb^{2+} has a smaller ionic radius (0.94 Å) and can thus follow either Ca or Na^+ (1.01 Å). This could lead to a fractionation between Eu and Yb. Unfortunately we cannot see any correlation in our data between Na and Yb, mainly because Na is not fractionated except in the refractory chondrules. In these cases temperatures might not have been sufficiently high to volatilize even the most volatile REE together with the alkali elements.

The Eu and Yb anomalies could supply us with a very sensitive S-O barometer. In a recent study [34] it has been shown that CaS from some E chondrites is strongly enriched ($\sim 100 \times \text{CI}$) in all REE. This can be expected for extremely reducing conditions (or extremely high S_2/O_2 ratios). Less severe conditions will selectively reduce those REE with the highest 2–3 ionization potential. Degrees of Eu and Yb fractionations could thus provide an indication on the physical-chemical conditions prevailing during the fractionation process(es).

3.4. Fractionation of Ca

Ca is depleted in almost all chondrules investigated with respect to Sc and CI (Table 4). This result is surprising because Ca is a refractory element and one could expect that it will follow the other refractory elements (Sc, Sm).

The high variability of Ca contents between individual chondrules is a consequence of a Ca-Sc (and Sm) fractionation. Such a fractionation is difficult to achieve through standard cosmochemical processes (vapor fractionation) and geochemical processes (crystal-liquid fractionation). There are several ways to fractionate Ca at low temperature and oxidizing conditions (e.g., via CaCO_3 or CaSO_4). Under reducing conditions it is also possible to fractionate Ca from the other refractory elements via sulfides (like CaS). As outlined above, we have good reasons to believe that the pre-Chainpur matter experienced fractionation under highly reducing conditions. The fractionated Ca contents of Chainpur chondrules (from 0.25 to $0.93 \times \text{CI}$) therefore can be taken as an additional indication for sulfide fractionation being the main process involved. The question remains why during the chondrule forming process the matter depleted in Ca was preferentially sampled.

3.5. Fractionation of Cr

Chromium can be expected to be fractionated with respect to refractory elements (like Sc) because of its moderate volatility. Accordingly, Cr is uniformly depleted in chondrules of the refractory group (Table 4) and only slightly depleted in all Na-rich chondrule groups. Variability of Cr/Sc

ratios is high in the ungrouped chondrule compositions. It is remarkable that Cr and Na are highly correlated in these three chondrules. On the other hand, Ch-20 is chondritic in its alkali contents but strongly depleted in Cr (and Ca and Mn). This peculiar co-depletion of Cr, Ca, and Mn could be an indication of fractionation via sulfides like Cr_2S_3 , CaS, and MnS in the pre-Chainpur matter. Alternatively, the co-fractionation of Na and Cr observed in the three refractory chondrules could be the result of a fractionation via caswell-silverite (NaCrS_2). This interpretation is supported by the Na-rich compositional groups which have rather uniform Cr contents.

3.6. Manganese and FeO

Since Fe is much more siderophile than Mn, fractionation of Fe from Mn can be expected to take place during redox processes. With falling p_{O_2} , Fe will preferentially enter the metal phase but Mn will continue to behave as a lithophile element and will stay in the silicates (for recent experimental data see Rammensee et al. [35]). If chondrules were formed by remelting of primitive oxidized chondritic matter (CI) under reducing conditions than we can expect to find a correlation between the FeO contents of the chondrule silicates and the Fe/Mn ratios. Under such conditions part of the Fe will enter the metal phase but most of the Mn

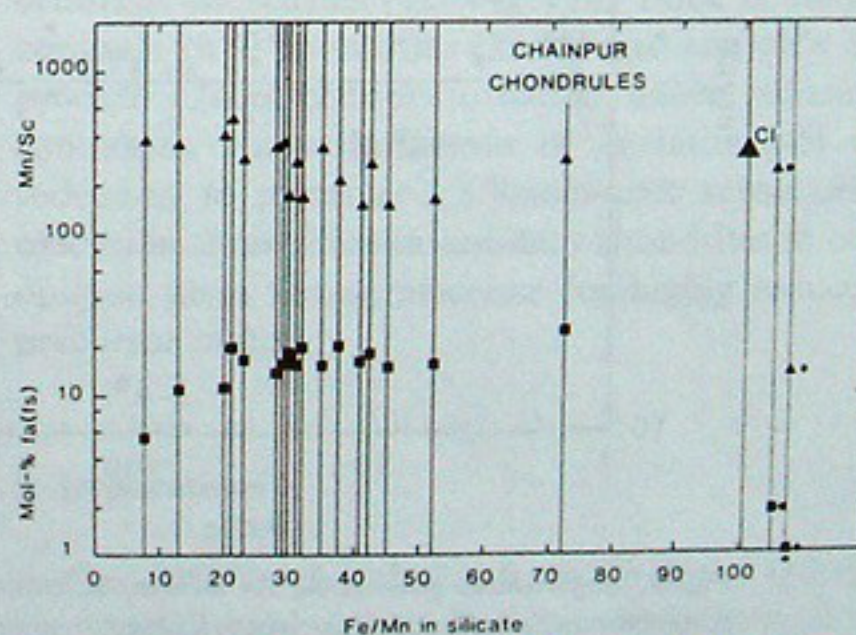


Fig. 4. Silicate Fe/Mn ratios vs. mol.% fa(fs) and Mn/Sc ratios of chondrules from Chainpur. CI ratios are from unpublished data on Orgueil (MPI Mainz). Chondrules with Fe/Mn > 100 (Ch-1, Ch-20) are plotted above the CI ratio.

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will stay in the silicates and consequently the Fe/Mn ratios of the silicates should decrease with decreasing FeO contents. Our data, however, do not show such a simple relationship (Table 2, Fig. 4). The Fe/Mn ratios vary widely and range from > 100 to 8 with the more primitive ratios (the higher ones) showing a reverse relationship to FeO. Furthermore, most chondrules do not show any relationship between Fe/Mg and Fe/Mn ratios. Apparently the Fe/Mn ratio has been established independently of the Fe/Mg ratio. This fact clearly rules out a simple metal-silicate fractionation.

The average Fe/Mg ratio is rather uniform in most chondrule silicates (Fig. 4). This could have been established by a FeO-Fe^o buffer reaction (via a gas phase) in the environment in which the chondrules were formed. This implies that during formation of most chondrules of Chainpur rather oxidizing conditions prevailed. The Fe/Mn ratios were thus established by the amount of Mn already present in the silicates and the amount of FeO added from the environment. Support for this interpretation can be found in the negative corre-

lation between Mn/Sc (= the Mn content of the chondrule's silicate portion) and the Fe/Mn ratio for the main cluster of chondrules in Fig. 4. Apparently, the Mn content of chondrules was established before FeO was added to the system.

Seemingly there is a weak positive correlation between Mn/Sc and K/Sc for all chondrules except Ch-20 (Fig. 5). However, the fractionation trend in this plot resembles closely the Na-K fractionation in Fig. 1. This means that in the refractory chondrules Mn was volatilized together with Na and K. The depletion of Mn relative to Na and K is consistent with the respective volatilities. An exception is Ch-20 which is highly depleted in Mn but undepleted in K. We consider this depletion of Ch-20 in Mn to be an important additional argument in favor of our sulfide fractionation model. Manganese cannot significantly be fractionated from Fe and Mg in silicate systems. Fractionations are possible under strongly oxidizing conditions and under strongly reducing conditions, provided p_{S_2} is sufficiently high. The latter conditions are in accordance with our reasoning above and provide a good mechanism for Mn fractionation via Mn sulfides (MnS and others).

The different states of oxidation of chondrules in Chainpur pose some problems. If we accept that most chondrules acquired their FeO contents via buffering by the atmosphere prevailing during chondrule formation, why are not all chondrules affected? A final explanation cannot be given at this stage of investigation but we suspect that the reduced chondrules represent relics of an earlier chondrule-forming process which took place under reducing conditions.

4. Synthesis

The fractionation of chondritic matter observed in chondrules from Chainpur is of such a peculiar and complex type that it cannot be explained by conventional cosmochemical and geochemical fractionation mechanisms. In addition, most of these fractionations cannot have been established during the chondrule forming process alone. An exception is the refractory chondrule group which has a clear compositional signature of vapor frac-

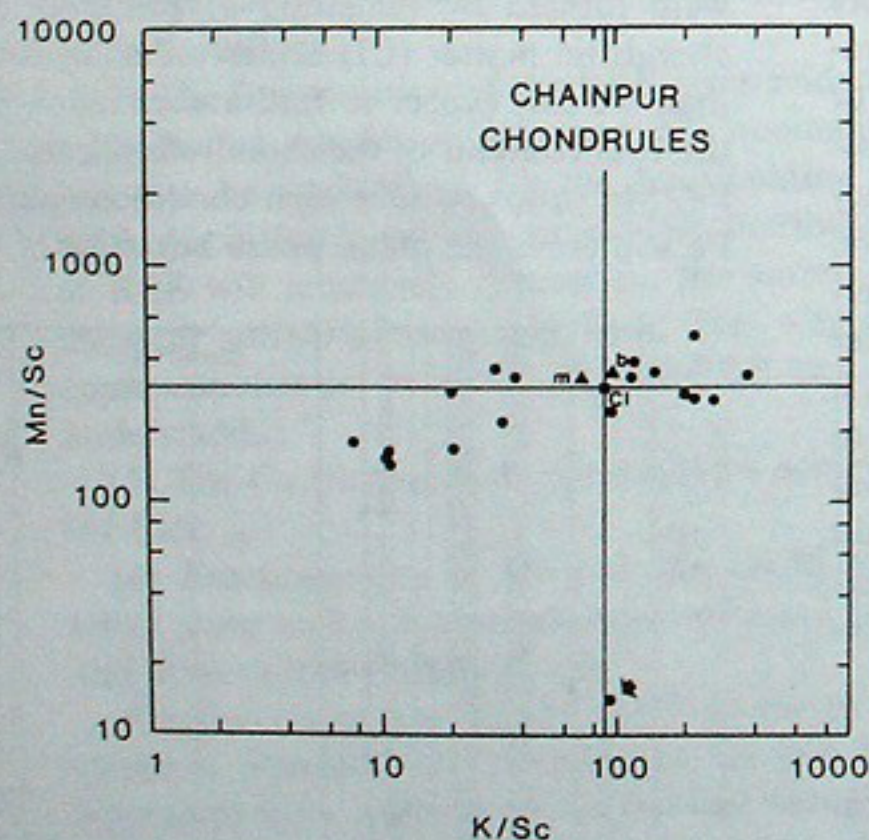


Fig. 5. Logarithmic plot of K/Sc vs. Mn/Sc ratios of bulk compositions of chondrules from Chainpur compared to Chainpur bulk (b) [15], Chainpur "matrix" (m), and carbonaceous chondrite Orgueil (CI, unpublished data, MPI Mainz). Note Ch-20 which plots close to the bottom of the graph (arrow).

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tionation (volatilization). Surprisingly, the majority of chondrules is undepleted in volatile elements and hence somehow escaped extensive volatilization during the chondrule forming process. They, however, show evidence for fractionations of a variety of elements. We believe that these fractionations were established in the chondrule precursor matter via extensive separation of different elements into separate phases. Separation of geochemically and cosmochemically coherent elements forces us to believe that fractionation of the lithophile elements was established via sulfides. This implies that the pre-Chainpur matter formed under conditions which must have been highly reducing and must have been governed by high S_2/O_2 ratios. Under such conditions many of the lithophile elements will become chalcophile and form mostly individual sulfide phases. This way all of the elemental fractionations observed in Chainpur chondrules could be understood:

(1) The Na-K fractionation can be achieved via Na_2S , caswellsilverite ($NaCrS_2$) and other phases, and K_2S and djerfisherite ($K_3Cu[Fe, Ni]_{12}S_{14}$) or other K sulfides.

(2) The fractionation of the REE gives evidence for reducing conditions (Eu and Yb anomalies) and can be understood by the fractionation of REE into different sulfide phases. The distribution of REE will sensitively depend on the variety of different sulfide phases competing. This way the apparent chaotic behavior of the REE can be understood.

(3) The Ca fractionation can easily be achieved via CaS .

(4) Fractionations of Cr and Mn could have taken place via Cr_2S_3 and caswellsilverite and MnS and other sulfides respectively.

Fractionations are mainly observed for minor elements, because their abundances are just high enough to form separate phases but low enough to show variance after small scale sampling. Certainly the major lithophile elements (Si, Mg) must also have suffered fractionations (via sulfides, metals, intermetallic phases and others) but subsequent sampling will not show too large compositional variations. However, such variations do show up among the different chondrite classes and could be taken as an indication for similar processes

being responsible also for large-scale fractionations.

Our sulfide fractionation model for the pre-Chainpur matter finds support from a large amount of detailed observations made in different chondrites, most of which can be explained in the light of our model. Direct support is received from detailed studies of the Qinzhen (E-3) chondrite [36]. There, caswellsilverite is predominantly present in chondrules whereas djerfisherite occurs exclusively in the chondrite matrix. This physical separation (on a millimeter scale) of Na and K also clearly shows up in bulk chondrule analyses from Indarch (E-4) ([37], see also Kurat [2]). Of the 24 chondrules analyzed 23 are K-depleted and only 1 is enriched, but all are rich in Na.

Indirect evidence for a pre-chondritic fractionation under reducing conditions is provided by the rather common association of Na and Cr in chondrules from many different chondrites. Albite-chromite chondrules have been known for a long time [38,39]. Recently a variety of Na-Al-Cr-rich chondrules have been investigated [40] and one peculiar chondrule from Patora (H) has been described [41] which consists mainly of albite and ureyite ($NaCrSi_2O_6$). Clearly, these objects give evidence for Na-Cr co-fractionation as can be expected to take place under reducing conditions via caswellsilverite. Another support for our model is provided by free silica occurring in many ordinary chondrites [42-44]. Free silica is rather common in E chondrites [28,45] and can only be produced from chondritic matter under reducing conditions via sulfurization of enstatite [45] or reduction to metal and silicides and subsequent oxidation. Free silica in ordinary chondrites in our opinion gives strong evidence for highly reduced precursor matter.

5. Implications

Our data on chondrules from Chainpur (LL-3) give additional evidence for chondrule formation from pre-existing solid matter [5]. This material must have had a grain size somewhat smaller than that of chondrules (~ 1 mm) but coarse enough to inhibit homogeneous sampling by the chondrule

forming event. The pre-Chainpur matter appears to have been highly reduced and sulfurized. Some phases were evenly distributed within that matter (Na sulfides, Mg and Si phases), presumably because of generally smaller grain sizes or high abundances. Others (K sulfides, CaS) had a heterogeneous distribution. If the precursor matter was a rock, it could have been similar to Qinzhen [36]. The fact that the trace elements (like the REE) are less fractionated than the minor element K implies that they were distributed among several phases. Since the partition coefficients for the REE between CaS and silicates are very high [34] the other phases must also have been sulfides in order to successfully compete for the REE. These different minerals must have been closely associated in order to level out their REE contents, which implies that they formed rocks. In order to maintain the overall chondritic composition, these rocks must have had dimensions much larger than the average size of a chondrule.

This matter then must have been broken into pieces comparable in size to chondrules. Oxidation probably took place already during that event but became very effective during the following melting event. The conditions must have been rather peculiar: high p_{O_2}/p_{H_2} , high p_{O_2}/p_{S_2} , and high partial pressures of the alkalis and other volatile elements. The latter is required for producing the majority of chondrules, which do not show any sign of volatilization of the alkalis. Furthermore, partial pressures of the volatile halogens must also have been high because of the general enrichments of chondrules in halogens and ^{129}I [46,47]. These facts all point towards a dense, warm, and oxidizing atmosphere prevailing during chondrule formation.

Not all chondrules from Chainpur, however, fit into that scenario. Two chondrules (Ch-1 and Ch-20) are strongly reduced but unfractionated in their alkali contents. They either somehow escaped strong oxidation (by gentle pre-oxidation?) or are relics from a similar but less oxidizing chondrule forming event.

The refractory group of chondrules represents a sample, which we should expect from any melting event in space. An exception is the high oxidation state of these chondrules which is indistinguish-

able from the normal chondrules. The fact that the refractory group experienced severe vapor fractionation could either indicate a separate event (under similarly oxidizing conditions but low total p) or considerable overheating of these particular droplets under otherwise unchanged conditions. The high oxidation state of all of the most refractory chondrules suggests intensive interaction with the oxidizing atmosphere and thus is in favor of the overheating model. This view is supported by the fact that all of the most refractory chondrules (Ch-3, Ch-4, Ch-9, Ch-13) are barred olivine chondrules which suggests that they crystallized from a melt which (homogeneously) produced only one nucleus (probably after considerable undercooling). A melt not overheated to an extent where all foreign nuclei were destroyed should—upon cooling—produce a porphyritic (or mosaic) texture [48]. Oxygen isotope data [49] also point to an extensive oxygen exchange between barred olivine chondrules and the environment. Thus, it is likely that barred olivine chondrules represent melts which received more energy than normal chondrules. This could have been achieved during the same process. The fact that barred olivine chondrules are omnipresent suggests that the chondrule forming heating event could have been an uncontrollable energy transfer event like impact [13,11] or others. An alternative possibility is the heat of oxidation which will be set free during the oxidation process. It will depend on the degree of reduction of the matter involved. Barred olivine chondrules could therefore represent samples of the most reduced pre-chondritic matter.

6. Conclusions

Bulk chemical and petrological data on 19 chondrules from the Chainpur (LL-3) chondrite are inconsistent with an origin by condensation from the cooling solar nebula [50]. They rather reveal a complex sequence of processes which must have been operative under a variety of mostly extreme conditions:

(1) Chondrules from Chainpur were formed by chance mixing and melting of pre-existing solids, similar to what has been found before [5,9,13–15].

(2) The pre-existing matter was rocks consisting of highly reduced and sulfurized mineral assemblages which provided separation of minor and trace lithophile elements into separate phases.

(3) The chondrule forming process sampled and melted small portions of the precursor rocks.

(4) Melting took place under oxidizing conditions which led to a conversion of sulfides into oxides and provided also FeO in almost constant amounts.

(5) Melting probably took place in a dense atmosphere with high partial pressures of volatile elements because most chondrules are enriched in volatile elements as compared to bulk chondrite compositions.

(6) The most common type of chondrules (volatile-rich porphyritic olivine chondrules) could have formed by gentle partial melting of pre-existing matter. However, the refractory chondrule group gives evidence for vapor fractionation, which implies overheating and thus indicates a process which uncontrollably released energy.

The heat source is unknown but we may speculate that it could have been gas drag [51] in combination with liberation of heat of oxidation during burning of the sulfides. A favorable place for this to take place could have been a proto-planetary atmosphere [52].

We can envision that our fractionation mechanism not only works at small scales but could also provide a basis for an understanding of fractionations on a large scale like the Na-K fractionation [53], and the Si-Mg fractionation [54,55] of different chondrite groups and planets.

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