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Chondrules: chemical, mineralogical and isotopic constraints on theories of their origin

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Chondritic meteorites have not been involved in planetary melting for the past 4.5 Ga. They contain millimetre-sized subspherical objects, 'chondrules', dominantly of silicate, but occasionally grading to rare, metal-sulphide chondrules. Some meteorites comprise 70% or more of chondrules by volume. About 30% of chondrules, or less, originated as molten droplets; the remainder formed from solid or plastic rocks. No rock known from the Earth or Moon contains enough glassy spherules to be termed a chondrite, so volcanism and impact on brittle planetary surfaces were not chondrule-forming mechanisms.

Chondrites have chemical compositions close to that of the volatile-free Sun, so a nebular origin for chondrules is often favoured. However, the mineralogical and chemical diversity among chondrules indicates that some had planetary origins. Furthermore, chondrules co-existed in space with disrupted fragments of planetary igneous rocks. Some chondrules may be nebular but others are not. Alternatively, all may be planetary. In either case the mechanism(s) of formation is(are) unknown.

INTRODUCTION

Chondritic meteorites are representatives of Solar System material that has not undergone melting on a planetary scale during the past 4.5 Ga. They comprise nine chemical groups each of which has a 'quasi-solar composition' (Dodd 1981, p. 13), so the story of their first 50 Ma (*ca.* 4.55–4.50 Ga BP) is fundamental to a chemical investigation into the origin of the Sun and planets. Chondrites are aggregates of various silicate and metal-sulphide components each of which must be older than the whole assemblage. Thus the information from chondrules, a major component, may provide an insight into the origin of what are some of the oldest physically identifiable objects now available in the laboratory. The importance of chondrules was recognized in the proceedings of a recent conference, *Chondrules and their origin* (King 1983), but there was no consensus on a preferred theory for their origin, although many authors argued that they formed by melting pre-existing solids.

In this necessarily brief treatment there has had to be considerable selection in the data and criteria chosen for discussion and we rely largely on personal experience. Much of our work over the past decade has centred on members of the three chemical groups that comprise the ordinary chondrites, and the following discussion largely excludes examples from the other groups. However, we believe that our arguments probably apply also to the enstatite and carbonaceous chondrites (see also Scott & Taylor 1983), with some exceptions.

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DEFINITION

There are various definitions of 'chondrule'. Here we use that of Hutchison & Bevan (1983): a chondrule is an object that was undoubtedly liquid before or during the period(s) of accretion that led to the formation of chondrites. This is, by design, a 'catch-all' definition not only including that of Dodd (1981, p. 30 and figure 3.1), which apparently refers only to silicate, but also recognizing that there is sometimes a gradation from essentially silicate chondrules, through silicate with subsidiary metal-sulphide, to metal-sulphide chondrules (Bevan & Axon 1980). Chondrules may be quenched, millimetre- to micrometre-sized, subspherical droplets, irregular masses of quenched material, or subspherical to irregular abraded igneous objects. An important distinction is drawn between 'clast' or 'lithic' chondrules consisting of igneous rock and 'droplet' chondrules of rapidly solidified liquid. Because lithic chondrules clearly are less primitive than droplet chondrules, the emphasis of this paper is on the latter objects. We recognize as 'droplet chondrules' once liquid objects of which the final shape may have been determined by the impingement of neighbouring solid objects upon them (see, for example, Hutchison & Bevan 1983, figures 1 and 2).

CHONDRITES

Before we consider the properties of chondrules we must note several vital facts about the rocks of which they form a part. Within each of the nine groups of chondrites there is a large degree of uniformity in bulk chemical composition, yet their components are highly variable in both mineralogical and chemical composition (see Dodd 1981; Fredriksson 1983). Thus the members of each chemical group must comprise essentially the same mixture of diverse components.

With few exceptions, if any, chondritic meteorites were subjected to a partial internal redistribution of the chemical elements, accompanied by some recrystallization driven by the thermal or hydrothermal conditions that pertained during the first ten megayears, or more, after accretion. Such changes affected the members of the various chemical groups to different degrees: thus all five members of the CI group are hydrothermally altered, but in the LL-group of the ordinary chondrites, with about 100 members, two are known to contain hydrous minerals (Hutchison *et al.* 1987) whereas the remainder have been thermally metamorphosed or annealed to various extents.

The differing conditions that obtained during the post-accretion crystallization of the chondrites are reflected in their mineralogical and textural properties. Van Schmus & Wood (1967) assigned each chondrite to one of six petrologic types, ranging from one for a wholly hydrothermally altered assemblage, through two to three with an anhydrous, unequilibrated mineral assemblage through four and five to six, representative of granulitic facies rocks in which the original chondritic texture is all but destroyed by recrystallization at high temperature. It would seem obvious that the best means of establishing how chondrules formed would be by studying the least altered assemblages pertaining to petrologic type three, and the scope of this paper is limited largely to type-three (unequilibrated) ordinary chondrites (UOCs). However, even among the chondrites assigned to petrologic type three there is considerable variation in the degree of crystallization (Sears *et al.* 1980), and only the most highly unequilibrated members within the type are close to pristine mineral assemblages. It has been argued that equilibrated chondrites of petrologic types five and six could not have been formed from parental material exactly like the type-three assemblage of the same chemical group (Kurat 1969; Dodd 1976; Christophe-Michel-Levy 1981; Hutchison *et al.* 1980; Fredriksson 1983). In general, type five and six ordinary chondrites formed from precursor aggregates of which the components lacked the extremes in composition found in some type-three chondrites. Thus, type five and six chondrites may yield information unobtainable from other sources.

All chondrites are aggregates of material representative of a variety of chemical and physical environments and to some extent may be considered to be breccias (Fredriksson & Wlotzka 1985; Scott *et al.* 1985). However, many chondritic meteorites have a textural fabric indicative of some post-accretion crystallization and lack evidence of shock, other than mild cataclasis presumably associated with compaction on accretion. They have been mechanically and thermally undisturbed since their formation and have radiometric ages close to 4.50 Ga that testify to this (see, for example, Minster & Allègre 1981; Turner *et al.* 1978). In our discussion we exclude surface (regolith) breccias (see, for example, Bischoff *et al.* 1983) and use as examples chondrites that apparently acquired their components within a few mega years during the principal phase of accretion of their parent bodies. Thus we hope (perhaps optimistically) to eliminate all but the oldest objects from this treatment.

ORIGIN OF CHONDRULES

Theories of the origin of chondrules and chondrites may be broadly grouped under 'nebular' or 'planetary' headings. The aim of this paper is not to review individual theories but to examine the evidence for and against each of the two scenarios. A nebular setting for chondrule formation is essentially based on the interpretation of chemical differences between the groups of chondrites as having resulted from the fractional condensation of a gas of 'solar' composition as deduced from thermodynamics (Wood 1963; Larimer & Anders 1967; Grossman 1972; Grossman & Wasson 1982). It also can account for isotopic anomalies produced by the decay of short-lived radioisotopes (see, for example, Begemann 1980; Chen & Wasserburg 1983; Swindle & Grossman 1986) or by unusual fractionation or synthesis among the stable isotopes of (generally) light elements such as H, O and Ne (see review by Pillinger 1984). In many cases there has been a failure to identify the carrier phases of anomalous isotopic abundances in the stable isotopes, so there is still some room for conjecture about their origin. (Isotopic anomalies and their interpretation are the subject of papers by Clayton and Pillinger, this symposium, so will not be reviewed here.)

In contrast, planetary theories of chondrule formation tend to be based on interpretations of texture and mineralogy of chondrules and chondrites (Kurat 1969; King *et al.* 1972; Fredriksson 1983; Hutchison & Bevan 1983) which are based on observation. In a few cases, however, nebular theories have some basis in mineralogical (in addition to chemical) observation, for example, the formation of some chondrules by melting nebular dust (Scott *et al.* 1984; Scott & Taylor 1987) and Dodd (1981) and Kurat *et al.* (1984) favour impacts on chunks of polymineralic rock to produce chondrules by selective sampling, perhaps in a nebular setting.

A further dichotomy between the two groups of theories is that nebular ones generally require cold accretion of the components of chondrites followed by heating to different temperatures to produce the various petrologic types (see, for example, Laul *et al.* 1973). Planetary theories, on the other hand, tend to rely on different temperatures of accretion and/or different cooling rates to achieve the same results (Kurat 1969; King *et al.* 1972; Christophe-Michel-Levy 1981; Hutchison *et al.* 1980; Fredriksson & Wlotzka 1985), and so avoid the need for a second transient source of heat for the small bodies thought to be the source of chondrites. (The first source of heat or energy is required to produce the chondrules.)

The thermal history of chondrules has been the subject of much experimental simulation. Production of the different textural types (outlined below) has been found to require nonlinear cooling rates, incomplete melting of solid precursors, or other special conditions (see, for example, Miyamoto *et al.* 1986). In all cases an initial temperature of perhaps 1300–1500 °C appears to have been required. Hughes (1977) found that the cumulative mass distribution of chondrules obeys a power law, indicating that they formed by fragmentation and thus supporting the experimental evidence that solid precursors were involved.

A major problem faced by a reviewer is that many sets of data on chondrules are incomplete or have not been published in full (Kurat 1984). Workers in the field often have attempted to establish mean compositions of types of chondrules (see, for example, Gooding 1983) which, although useful, overlook extremes in chemistry or mineralogy that must be included in a viable theory of chondrule formation. Here we expand on Hutchison & Bevan's (1983) emphasis on the chemical diversity among chondrules.

TEXTURAL TYPES OF CHONDRULE

Following Dodd (1981), Gooding & Keil (1981) and Kurat (1984) the following types of chondrule have been recognized in ordinary chondrites: microporphyritic chondrules; excentroradial (pyroxene) chondrules; barred (olivine) chondrules; microcrystalline–glassy chondrules; poikilitic chondrules; granular chondrules; dark-zoned chondrules; various types, rich in Ca and Al (Bischoff & Keil 1983).

Microporphyritic chondrules comprise phenocrysts of olivine and/or low-Ca pyroxene set in a glassy or microcrystalline mesostasis. Metal and/or sulphide may be present to a variable extent. Over 70% of the chondrules in UOCs are of this type (Gooding & Keil 1981). Although many such chondrules are 'clastic', some originated as molten 'droplets', for example, a deformed porphyritic olivine chondrule in Tieschitz (Hutchison & Bevan 1983, figure 1).

Excentroradial chondrules, barred olivine chondrules and microcrystalline chondrules are 'droplet' types. In the first, fibres of low-Ca pyroxene appear to radiate from one (or more) point(s) close to the margin; the fibres are set in glassy–microcrystalline mesostasis. Barred olivine chondrules comprise one or more skeletal crystals of olivine enclosing mesostasis. The olivine usually forms a marginal shell from which the crystals grew inwards. Microcrystalline–glassy chondrules are quenched silicate spherules without optically resolvable crystals. The three types together constitute about 15% of the chondrules in UOCs (Gooding & Keil 1981).

Poikilitic chondrules are composed of large crystals of low-Ca pyroxene enclosing anhedral olivines, the whole set in a mesostasis of feldspar-rich material, or even macrocrystalline (Ca) feldspar. Their texture indicates that they are clasts of igneous rock. Granular textured chondrules, common in carbonaceous chondrites, are rare in the UOCs. Fine-grained granular material constitutes the dark zone around chondrules of that name, the interiors being of another textural type. Granulation and darkening were produced by a secondary process (shock?). Calcium-Al-rich chondrules and inclusions constitute only about 1% of ordinary chondrites (Scott & Taylor 1987). They have various textures, but are dominated by calcic pyroxenes and plagioclase, plus other Ca- and Al-rich minerals, like the occurrences in CO and CV chondrites (see, for example, Dodd 1981).

Compound chondrules

In contrast to the deformed chondrules just described, compound chondrules are pairs of partially fused droplets lacking intervening matrix or rim material. In general, the individuals of each pair are of the same type, indicating that they formed together from the same precursor material (Lux *et al.* 1981) and collided before the acquisition of rims.

Mineralogy of droplet chondrules

The most common type of chondrule (though not all are 'droplet' chondrules) has microphenocrysts of olivine and/or low-Ca pyroxene set in a glassy to microcrystalline mesostasis rich in normative feldspar (see, for example, Dodd 1981). If olivine is the only phase occurring as phenocrysts, the mesostasis may be nepheline-normative and highly undersaturated in silica (Kurat 1967; Kurat 1971; Hutchison & Bevan 1983). Such chondrules may be considered to be mixtures of three components, olivine, pyroxene and feldspathic material. Excentroradial pyroxene chondrules and barred olivine chondrules are each essentially two component mixtures of pyroxene and feldspathic material, and olivine and feldspathic material, respectively. Spinel, metal and troilite may occur as minor phases in all three types of chondrule.

Many microporphyritic chondrules are clast chondrules and composed of igneous rock. Others contain grains that are out of equilibrium with their present mesostases and with neighbouring microphenocrysts (Christophe-Michel-Levy 1979; Nagahara 1981; Rambaldi 1981). Such grains are identifiable by their having dusty (metallic?) inclusions and Mg:(Mg+Fe) ratios indicative of a more reducing environment than their current one. They may also have a distinctive minor element signature.

Chemistry of droplet chondrules

Droplet chondrules in UOCs vary in chemical composition not only from one type to another but among members of the same textural type (Dodd 1978*a*; Lux *et al.* 1981). Many of the data are incomplete, partial analyses by neutron activation techniques (see, for example, Gooding 1983; Kurat *et al.* 1984) not having been supplemented by data from other techniques, so that figures for SiO_2 and/or Al_2O_3 and/or CaO abundance may be lacking. Furthermore, 'chemically oriented' investigations are seldom accompanied by mineralogical and/or textural observations (Grossman & Wasson 1982).

Lux *et al.* (1981) provide mean major and minor element contents in the various textural types of chondrule occurring in H3 chondrites. It is clearly seen (table 1, numbers 1 and 4, and figure 1) that there are compositional differences between some types of droplet chondrule, such as barred olivine and excentroradial pyroxene; the former have a mean atomic Ca/Al ratio of 0.33, and the latter, 0.97. Many silicate chondrules are not strongly depleted in volatiles such as Na and K (Wilkening *et al.* 1984; Kurat *et al.* 1984), which is surprising in view of

Table 1. Microprobe analyses and norms of chondrules in H-group chondrites

(1. Mean composition of 7 barred olivine chondrules in H3 chondrites (Lux *et al.* 1981). 2. Deformed chondrule, Tieschitz, H3, (see figure 1). Analyst: R. Hutchison. Wavelength dispersive microprobe analysis, 20 kV accelerating voltage, 2.5×10^{-8} A electron beam. Average of three 'spots' 100 μm diameter. The low total may be due to the presence of water, the chondrule having suffered damage under the electron beam. 3. Spherical chondrule, Dhajala (no. 137, Bischoff & Keil, 1983). 4. Mean composition of eight excentroradial pyroxene chondrules in H3 chondrites (Lux *et al.* 1981). 5. Deformed chondrule, Tieschitz, H3 (see figure 1). Analyst: R. Hutchison. Conditions as for number 2. One 'spot' 100 μm diameter.)

	1	2	3	4	5
SiO_2	46.4	42.0	55.1	55.9	48.4
TiO_2	0.26	0.80	0.69	0.10	0.06
Al_2O_3	6.7	15.9	16.1	1.9	0.06
Cr_2O_3	0.30	0.32	0.21	0.48	0.64
FeO	8.4	7.2	4.9	6.7	7.83
MnO	0.19	0.05	0.10	0.31	0.52
MgO	29.5	14.8	10.8	29.5	20.8
CaO	2.4	2.8	2.12	2.0	8.56
Na_2O	3.0	8.9	8.6	0.83	0.23
K_2O	0.48	0.50	0.47	0.13	—
total	97.71[a]	93.3	99.09	97.89[b]	87.1
mg	86.2	78.4	79.8	88.7	81.6
Ca/Al	0.33	0.16	0.12	0.96	140
			C.I.P.W. (mass) norm†		
Qtz	0.0	0.0	0.0	0.0	1.0
Or	2.8	3.0	2.8	0.8	0.0
Ab	19.8	9.6	50.1	7.0	0.3
An	3.4	2.0	4.0	1.1	0.0
Ne	3.0	35.5	12.2	0.0	0.0
Di	6.8	9.6	5.3	7.0	33.9
Hyp	0.0	0.0	0.0	77.5	50.6
Ol	61.0	31.6	23.1	3.7	0.0
Cm	0.4	0.4	0.3	0.6	0.8
Il	0.5	1.5	1.3	0.2	0.1

mg is 100 Mg:(Mg+Fe) atomic; Ca/Al is atomic ratio. [a] Total includes 0.08% P_2O_5; [b] total includes 0.04% P_2O_5.

their high temperature of formation. In fact, enrichment in Na may have occurred in some porphyritic olivine or barred olivine chondrules (table 1, numbers 2 and 3; also Kurat 1967, 1971), accompanied by enrichment in Al but depletion in Ca. However, Fredriksson (1983) found that in the chondrules of UOCs, Ca and Al are positively correlated, but the examples in table 1 and figure 1 show that exceptions do occur. These are important because Ca should not fractionate from Al below 1550 K during condensation from a cooling gas of solar composition (Ganapathy & Anders 1974; Grossman, 1975).

Enrichment in Al and Na and depletion in Ca in some chondrules should have produced a complementary trend of Ca enrichment with Al and Na depletion in others if all droplet chondrules are fractions from a single source. The latter trend may be observed in pyroxene-rich melts (table 1, numbers 4 and 5) (Hutchison & Bevan 1983). Furthermore, a distinction has been drawn between chondrules with clear glass and chondrules with devitrified glass in the Sharps, H3, chondrite. Glass-containing chondrules generally 'are strongly depleted in Ca and their Ca/Al ratios are below the cosmic...ratio' (Wlotzka 1983, pp. 309–310 and figures

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† This is a well-established convention for expressing a chemical analysis of a rock as a hypothetical mineral assemblage.

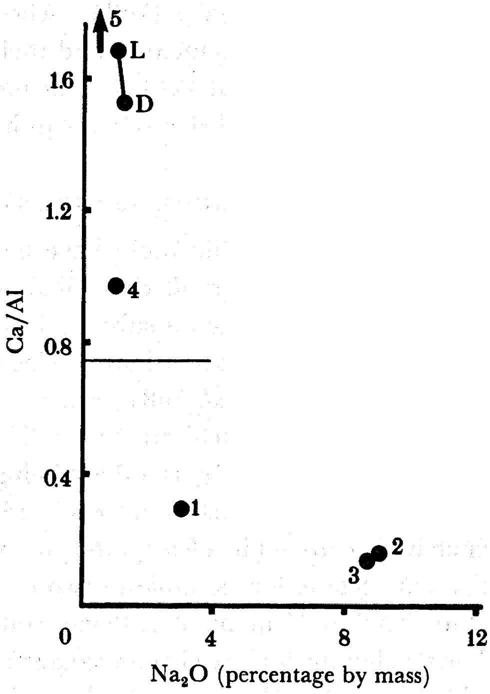

FIGURE 1. Ca/Al atomic ratio plotted against Na_2O content of chondrules. The numbers refer to analyses in table 1. L and D are light and dark devitrified glasses in a chondrule from Manych (L3) (Dodd 1978*a*). The horizontal line represents the 'cosmic' Ca/Al ratio. Note that Ca/Al appears to be inversely correlated with Na_2O in the examples chosen.

9 and 11). In comparison, chondrules with devitrified glass have a higher Ca content, ascribed to the presence of finely exsolved diopside in the devitrified mesostases.

Textural, mineralogical and chemical information is available for two separate suites of chondrules from the Chainpur (LL3) chondrite studied independently by Grossman & Wasson (1982) and Kurat *et al.* (1984). In the earlier work Ca was not determined and Al was determined in about half the chondrules; various minor and trace elements with different chemical affinites were determined. Factor analysis was used which resulted in the identification of five chemical components of chondrules: (1) bulk metal and sulphide; (2) refractory metal; (3) refractory silicate; (4) low-temperature, pyroxene-rich silicate and (5) a volatile-rich component. However, there clearly was fractionation within the refractory silicate component, the CI normalized Al/Sc ratio in chondrules 20–36 (the ones in which Al was *measured*) ranging from 0.89 to 2.27. (Normalization was based on 5.76 p.p.m. Sc and 8620 p.p.m. Al (by mass) in Orgueil, from Anders & Ebihara 1982.)

Kurat *et al.* (1984) did not determine Al in Chainpur chondrules but measured the abundances of Ca, Na, K and various trace elements. They remarked on the range of Ca/Sc ratios, somewhat analogous to Al/Sc ratios, these elements being refractory lithophiles. They found that the CI normalized Na/Sc and K/Sc ratios within their chondrule suite ranged from 0.26 to 1.40 and 0.11 to 2.84, respectively, and that volatile Na was fractionated from volatile K. Thus there appears to have been a chemical fractionation between elements of similar volatility. Different chondrules also appear to have formed under different redox conditions, reflected in increasing Fe/Mn with increasing oxidation (Kurat *et al.* 1984), but there is no simple relation. It was concluded that Mn contents were established in chondrules before the addition of some FeO. This is confirmed by Wlotzka (1983), who found a weak positive correlation between the size of chondrules (and 'fragments') and their Fe:(Fe+Mg) ratio in Tieschitz and Sharps (both H3). He found also that FeO content increases from chondrules with clear glass through chondrules with devitrified mesosatases to irregular chondrules and fragments.

Clast chondrules and rock fragments

Fragments of pre-existing igneous or metamorphic rocks have been observed within the fabric of various UOCs (Dodd 1968, 1969; Graham *et al.* 1976; Rubin *et al.* 1981; Hutchison & Bevan 1983). In most cases abrasion has produced a subspherical shape to produce clast chondrules, but angular fragments also occur. Observations of clastic, foreign inclusions in equilibrated ordinary chondrites are rare (Olsen *et al.* 1981; Prinz *et al.* 1984; Fredriksson & Wlotzka 1985; Christophe-Michel-Levy 1976; Hutchison *et al.* 1986).

In the UOCs, poikilitic chondrules were recognized by Dodd as having the texture of a coarse-grained igneous rock in which rounded olivine crystals are enclosed in poikilitic crystals of (generally) low-Ca pyroxene which in turn are set in a feldspathic mesostasis. In some instances the mesostasis is crystalline calcic plagioclase, for example in two occurrences in Semarkona (LL3). An angular igneous clast in Tieschitz (Hutchison & Bevan 1983) has a similar texture. In other cases large microporphyritic chondrules have been recognized as fragments of plastic to solid pre-existing rock (Dodd 1969, 1978*b*); their subspherical form was achieved by abrasion of larger precursor rocks. Graham *et al.* (1976) described an anorthositic glass inclusion, in Bovedy (L3), with a fractionated rare earth element (REE) pattern which they interpreted as a planetary differentiate, like lunar highlands anorthosite.

In chondrites of types five and six, exotic inclusions have mainly been identified because of their failure to attain complete chemical equilibrium with their hosts. Prinz *et al.* (1984) described two olivine porphyry clasts with the oxygen isotopic signature of H-group chondrites within an L-group chondrite. One clast has a relic barred olivine chondrule. Another, similar clast is present in Barwell (L5–6), an unbrecciated meteorite with a generally uniform fabric. This clast has a light REE enriched pattern with positive Eu anomaly (Hutchison *et al.* 1986). Typically, the presence of plagioclase and spinel more calcic and more aluminous, respectively, than those of their host, has been diagnostic of clasts in equilibrated chondrites (Christophe-Michel-Levy 1976; Fredriksson & Wlotzka 1985), although Olsen *et al.* (1981) identified a cristobalite–pyroxene assemblage as the reaction product of H-group silica with L-group host.

Chondrule rims and interchondrule matrices

In the UOCs, chondrules and clasts are often coated by opaque material (rims) with a grain-size from 10 μm to less than 1 μm. There is no correlation between the chemical composition of a rim and that of the chondrule or clast that it coats (Scott *et al.* 1984). Material similar to the rims fills the spaces between the chondrules and coarse-grained objects and is known as matrix. Fine-grained chondrule rims (distinct from 'dark zones') and opaque, interchondrule matrix were considered to be a low-temperature nebular component and host to volatiles (Larimer & Anders 1967; Nagahara 1984; Scott & Taylor 1987). Rims and opaque matrices have highly variable chemical compositions, there being a fivefold variation in the mean abundances of Mg, Ng, Al and Ca within a single chondrite (Scott *et al.* 1984).

Detailed study using the analytical transmission electron microscope (ATEM) indicates that rims and opaque matrices are essentially composed of clastic olivine and pyroxene accompanied by a minor feldspathic component. In Bishunpur (LL3) the clastic grains are cemented by amorphous feldspathic material whereas in Tieschitz (H3) the feldspathic component is clastic also and fills channels between the opaque rims of chondrules. Rims and matrices were probably derived from the comminution of chondrules (Barber *et al.* 1988); rims presumably formed by the welding of clastic grains to the surfaces of hot chondrules. In addition, metal-rich and sulphide-rich varieties of rim and matrix may occur (Allen *et al.* 1980). The size-distribution of grains in rims and matrices obeys a cumulative power law indicating that they formed by the fragmentation of pre-existing solids (Ashworth 1977; Barber *et al.* 1987), as for chondrules (see, for example, Hughes 1977). Coarse olivine and pyroxene grains in rims and matrices have cores with Mg:(Mg+Fe) ratios within the range of these minerals in chondrules, but their margins and small grains are more Fe-rich. Furthermore, the pyroxene is usually the polysynthetically twinned variety with very low Ca content thought to have been produced by the inversion of protopyroxene from quenched chondrule liquids (Ashworth 1980; Barber *et al.* 1988). The textures of the finest grained rims and matrices are often witness of the effects of recrystallization, probably in the solid state, but fluids might have been involved.

There is an intimate association between chondrules and rims and/or matrices; in fact, some chondrules have included lumps of matrix material (Scott *et al.* 1984). In the Tieschitz (H3) chondrite, opaque rims were emplaced on chondrules while some of the latter were still plastic (Hutchison & Bevan 1983; Holmen & Wood 1986). From their deformation after accretion we know that in Tieschitz, chondrules of several textural types were still hot after they had received their rims. These deformed chondrules have a variety of chemical compositions (cf. numbers 2 and 5, table 1; figure 1) indicating that materials resulting from different chemical trends coexisted, while hot, during the accretion of the meteorite.

Isotopic constraints

Clayton and co-workers (Clayton *et al.* 1983, 1986) have shown that chondrules in the ordinary chondrites have oxygen derived from a mixture of a ^{18}O-rich and ^{17}O-rich reservoir with a component enriched in ^{16}O. On the conventional three-isotope plot the chondrules lie on a mixing line with a slope close to unity. Rims and matrices are ^{16}O-enriched, and there is a negative correlation between chondrule size and ^{16}O-enrichment in chondrules. This is manifest in the H-group of chondrites, which typically have small chondrules, having bulk O isotopic ratios richer in ^{16}O than the L-group or LL-group. The systematics within the carbonaceous chondrites are more complex.

Relative ages of chondrules and chondrites may be obtained from I–Xe systematics if it is assumed that there was isotopic homogeneity in I in the early Solar System; that is, that the ^{129}I/^{127}I ratio varied (decayed) only with time. This ratio is obtained from the (measured) radiogenic ^{129}Xe/^{127}I ratio, the Xe isotope being the daughter of ^{129}I, with a half-life of 16 Ma. Various ordinary chondrites of types five and six are apparently up to some tens of megayears older than bulk UOCs or their separated chondrules (see, for example, Swindle & Grossman 1986). The discovery by Hutchison *et al.* (1987) of the products of hydrothermal alteration in some UOCs led Swindle & Grossman (1986) to speculate that the I/Xe systematics may have been reset, resulting in the apparently younger ages of their chondrules. However, it seems unlikely that strongly bound I and Xe, corresponding to the high-temperature release of Xe, could have been affected. It is noteworthy that the initial $^{129}I/^{127}I$ ratio (1.4×10^{-4}) inferred for the igneous clast in Barwell (Kirschbaum 1986) is greater than that measured in the chondrules of UOCs.

Discussion

The occurrence together of droplet and clastic chondrules indicates that two types of material were involved in chondrule formation, in its widest sense. Liquids co-existed with solid or plastic rock fragments some of which were abraded to become subspherical objects. These fragments were originally produced from melts. In addition, fine-grained, opaque rims were added to droplet and clastic chondrules and to crystalline fragments of igneous rock before aggregation and before some chondrule melts had completely solidified (Hutchison *et al.* 1979; Hutchison & Bevan 1983; Holmen & Wood 1986). Thus, the three types of material co-existed in space or in a hot regolith. However, as Dodd (1981) has suggested, there is no reason to believe that all chondrules necessarily came from a single source or originally formed in a single melting process.

In contrast, the oxygen isotopic data (Clayton *et al.* 1983) indicate that most, if not all, chondrules in all three chemical groups of UOCs were derived from a single population. This reinforces Dodd's (1981, p. 124) suggestion that in Manych (L3), clast and droplet chondrules are genetically related. Isotopic differences between chondrules may be the product of secondary partial equilibration with oxygen from another reservoir. But it is possible that some, primitive, chondrules were produced by melting of solids or condensation of liquids while others represent reworking of the primary materials without fractionation of the isotopes of oxygen. The occurrence of pre-existing grains within some chondrules tends to favour an origin by reworking pre-existing solids.

The identity of the (hypothetical) solid precursors of chondrules has been sought in different ways. Dodd (1981, for example) argued that because chondrules are essentially composed of three minerals – major olivine and/or pyroxene, with minor feldspar – they could have formed by the random fusion of portions of a coarse-grained harzburgitic rock. Such a rock would have been composed of large (5 mm?) olivine and pyroxene crystals with minor interstitial feldspar. The minimum size of a chondrule precursor rock must have been larger than the largest chondrule and greater than about 10 cm. To account for the fractionation of elements (Ca, Na, K) with various chemical and physical properties, Kurat *et al.* (1984) suggested that the precursor of chondrules was a rock with a highly reduced mineral assemblage. The fractionated elements were distributed between different sulphide and silicate minerals that were dispersed throughout the rock. Random melts from different parts of the rock produced chondrules with different primary Ca, Na and K contents. However, Al is fractionated relative to Sc, both of which are highly refractory lithophile elements and which could not have been vapour fractionated except under the most extreme conditions (Davis & Hinton 1985). Both elements would have been present in silicate and not distributed between silicate and sulphide. Thus the fractionation of Al apparently was geochemical rather than cosmochemical; perhaps crystal–liquid fractionation within a planetary body was involved.

Scott *et al.* (1984) and Scott & Taylor (1987) noted the similarity in chemical composition between interchondrule matrices and bulk ordinary chondrite, allowing for the more reduced state of the latter. They argued that the chondrule precursors were dust balls of matrix composition formed in a presolar nebula. Chondrules formed by melting and reduction of dust balls, and matrix material is the unmelted remnant. However, a recent investigation of interchondrule matrices (and opaque rims on chondrules) at the high spatial resolution of the transmission electron microscope (Barber *et al.* 1988) indicates that they were probably derived by the fragmentation of chondrules. The matrix material now present in UOCs apparently could not have been representative of chondrule precursors. Both suggestions of genetic links between chondrules and matrices face difficulties over their different oxygen isotopic signatures. One possibility is that the present oxygen isotopic ratios in matrix resulted from mixing with an extraneous component, the fine-grained matrix having been more susceptible to isotopic exchange than coarse-grained or glassy chondrules. This interpretation is supported by the evidence that the finest grained matrix ('holy smoke') in equilibrated chondrites differs from that in UOCs (Rambaldi *et al.* 1981). Chondrules in the equilibrated chondrite, Allegan (H5), have oxygen isotopic ratios like those of chondrules in UOCs (Clayton *et al.* 1983), which implies that the 'holy smoke' has ratios like those of opaque matrices. Two different types of material, therefore, appear to have similar oxygen isotopic ratios which may have been established by a secondary process common to both. Finally, the highly oxidized mineral assemblage in the matrix of Semarkona (LL3) was probably produced by secondary oxidation of a more reduced primary assemblage, possibly by the action of CO or CO_2 and/or water (Hutchison *et al.* 1987).

Vapour fractionation of some elements has been invoked to a greater or lesser degree in theories of the origin of chondrules. On a grand scale, Grossman & Wasson (1982) suggested that the five chemically identifiable components of chondrules were fractionated by fractionation of dust during different stages in the condensation of a presolar nebula. Chondrules did not form until the nebula had cooled below 648 K, the temperature at which troilite would have formed. Chemical differences between chondrules were produced by melting of different batches of dust with different relative abundances of the five components. It is difficult to explain the fractionation of Ca between chondrule types by this mechanism. In fact, Wlotzka (1983, p. 310), interpreting Ca/Al ratios, comments that: 'The compositional differences between chondrules with clear glass and chondrules with devitrified glass is the opposite of what one would expect from a condensation model.'

On a lesser scale, Kurat *et al.* (1984) require vapour fractionation in an oxidizing atmosphere to account for enrichments in chondrules in Na, K and oxidized Fe. There is abundant evidence that vapour fractionation played some part in establishing the compositions of chondrules. New experimental data have led us to reject Hutchison & Bevan's (1983, p. 168) conclusion that vapour fractionation could not have been responsible for the positive correlation between refractory Al_2O_3 and volatile Na_2O in many chondrules. Biggar (1986) found that among neighbouring experimental charges in a furnace, Al_2O_3-rich charges tended to gain Na_2O at the expense of Al_2O_3-poor charges; charges with low Al_2O_3 and Na_2O could lose the latter oxide to charges with higher initial abundances of both oxides. Hence we conclude that solid-state partitioning of elements between phases in chondrule precursors, and/or crystal liquid fractionation, coupled with vapour fractionation, were responsible for the chemical heterogeneity among chondrules.

The fact that igneous rocks or their derivatives co-exist with chondrules indicates that a planetary process such as solid–liquid fractionation need not be excluded from hypotheses of chondrule formation. Indeed the igneous rock, with fractionated REE and 'old' I–Xe age, in Barwell, suggests that planetary melting and differentiation had taken place before the formation of the chondrules in the UOCs.

CONCLUSIONS

1. The evidence bearing on the mode of formation of chondrules is still far from conclusive.

2. Nebular condensation probably produces dust rather than molten droplets; chondrules possibly formed by the melting of dust.

3. There now seems to be no direct evidence supportive of a nebular dust precursor of chondrules.

4. Chunks of coarse-grained harzburgite or coarse-grained enstatite chondrite-like rock could have been chondrule precursors, but could they have formed in a nebular environment?

5. Alternatively, such precursor rocks could have been the product of planetary processes, perhaps followed by planetary fragmentation. A planetary atmosphere may have been one reservoir of oxygen with a distinctive isotopic ratio. A planetary setting for chondrule-formation is consistent with the coexistence, in chondrites, of chondrules and objects with REE distribution patterns indicative of planetary processes.

6. If chondrules are planetary, they did not form on asteroids Moon or Earth, by impact or volcanism during the past 4 Ga, in sufficient abundance to produce rocks called chondrites (Taylor *et al.* 1983). The physical environment of chondrule formation may have differed from present planetary environments.

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