# The Semarkona meteorite: First recorded occurrence of smectite in an ordinary chondrite, and its implications

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Abstract—Semarkona is an unshocked unequilibrated ordinary chondrite. Much of the interchondrule matrix and the mesostases of some chondrules and clasts have been hydrothermally altered. Analyses of altered materials and opaque matrix are presented. Ca and Fe have been redistributed from primary, anhydrous phases into calcite and Na, Fe smectite, respectively. In Semarkona the process possibly requires open system behavior inconsistent with the conventional view of "metamorphism" of the ordinary chondrites. The low petrologic type previously assigned to Semarkona is the result of retrograde metamorphism, under aqueous conditions, of a higher temperature mineral assemblage. Semarkona, and possibly Bishunpur, should be assigned to petrologic type 2.

#### **INTRODUCTION**

THE UNEQUILIBRATED ordinary chondrites (UOCs) have largely been unaffected by heat since their accretion, so they provide a more complete record of the conditions then prevailing than their more thermally processed relatives. Because of this, UOCs have been the focus of chemical (e.g. GROSSMAN and WASSON, 1985) and stable isotopic studies (e.g. ROBERT et al., 1979; GRADY et al., 1982; MCNAUGHTON et al., 1982) aimed at deciphering their record. In addition to chondrules, clasts and the products of their comminution, many UOCs have an opaque, fine-grained interchondrule matrix (DODD et al., 1967), interpreted as having formed at low-temperature, and host to volatiles (LAUL et al., 1973). Largely because of their fine grain-size and heterogeneity, interchondrule matrices have been difficult to study, notable attempts being those of CHRISTOPHE-MICHEL-LEVY (1976), ASHWORTH (1977, 1981), ALLEN et al. (1980), HUSS et al. (1981) and NAGAHARA (1984). An attempt, using thermoluminescence, to measure the degree of thermal processing in the UOCs was made by SEARS et al. (1980).

The present work is part of a program aimed at elucidating the origin of chondrules, interchondrule matrices and the ordinary chondrites in general (HUTCH-ISON *et al.*, 1980; HUTCHISON and BEVAN, 1983). Microprobe and analytical transmission electron microscope (ATEM) techniques have been used to obtain analyses of chondrules, of opaque rims to chondrules, of interchondrule matrices, and of their respective constituents. Semarkona was selected for study because SEARS *et al.* (1980) identified it, with Krymka and Bishunpur, as one of the least metamorphosed ordinary chondrites. Surprisingly, although various workers have undertaken different specialised investigations of the meteorite, no general description appears to exist. This

is to some extent remedied here, for our techniques allow us to integrate observations over a scale from the millimetre to the submicrometre range. Our observations constitute what we believe to be the first compelling evidence for hydrothermal alteration and calcite precipitation in an ordinary chondrite, which suggest that the ordinary chondrites formed in an environment like that of the carbonaceous chondrites. We recognise, however, that earlier studies of Tieschitz by KURAT (1969) and CHRISTOPHE-MICHEL-LEVY (1976) implied that the meteorite had undergone some hydrous alteration, and that NAGAHARA (1984) recognized "fluffy particles" in Semarkona and other UOCs and suggested that the particles might be of phyllosilicate. Ours, we believe, is the first direct evidence.

# TEXTURAL OBSERVATIONS

The aim of this part of the paper is to provide a general description of Semarkona and to demonstrate that it is essentially unshocked. Furthermore, textural relationships provide evidence on the relative ages of the various components of the stone and allow us to reconstruct its history.

Three polished thin-sections of total area about 3  $cm^2$  were examined by transmitted and reflected light microscopy and selected areas were analysed by electron microprobe. One section (USNM 1805-5), kindly loaned to us by R. S. Clarke, Jr, of the Smithsonian Institution, is only about 10  $\mu$ m thick. The other sections were prepared from part of the same slice as 1805-5 by the method of BARBER (1981), so that portions could be removed and ion-thinned for the ATEM. It should be noted that the hydrous silicates and calcite are randomly distributed within each of the three sections.

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The meteorite was seen to fall in 1940 and has suffered no obvious terrestrial weathering. It comprises chondrules and clasts, with occasional droplets of metal and/or sulfide in their interiors. The proportions of the various types of chondrules

conform to the estimate of GOODING and KEIL (1981), the porphyritic olivine and pyroxene type being dominant, barred olivine and cryptocrystalline types being rare. Many chondrules and clasts have opaque rims, the whole being set in interchondrule matrix of variable reflectance.

The matrix is generally fine-grained, dominantly of silicate and ranges from opaque through transpucent brown to clear olive-green in color, although transparency is enhanced in 1805-5 by its thinness. In addition to silicate, the matrix contains strings of magnetite crystals, usually associated with carbide, and/or metal, and/or sulfide (TAYLOR et al., 1981). Subspherical objects composed of mixtures of the last three phases are situated in matrix; they usually are rimmed by concentric layers rich in carbide or sulfide, followed by magnetite adjacent to matrix (Fig. 1). Concentric layering is present also around metal/sulfide that occurs in embayments on the margins of silicate chondrules or clasts. Fracturing in metal/carbide objects is common (TAYLOR et al., 1981), and their layered rims may be discontinuous.

For example, one oval, carbide-rich object on the margin of a chondrule is fractured, the two parts being displaced by 30  $\mu$ m. Its sulfide rim is also displaced, exposing the carbide interior (It has about 87% Fe, 4% Ni, 0.35% Co. 0.9% Cr and 0.2% P. so is probably cohenite. cf. analysis no. 9, Table 1 of TAYLOR et al., 1981), which makes contact with pure magnetite that poikilitically encloses angular fragments of enstatite from the margin of the chondrule. The fracture stops at the magnetite, which, therefore, crystallized after the formation of the carbide and its sulfide rim, and after their subsequent displacement with the fracturing of the enstatite.

An example of a spherical object appears in Fig. 1. It has a central area composed of polycrystalline, anisotropic carbide.



FIG. 1. Back-scattered electron micrograph, spherical carbide/metal/sulfide object with sulfur-rich silicate rim (midgray). Within the rim lies a circumferential carbide vein (lightgray)  $1-3 \mu m$  thick. Arrow indicates analyzed portion of bifurcating carbide vein in interchondrule matrix. Insets, scale bars 10  $\mu m$ . Upper: Detail of circumferential carbide vein, showing locations of analyses of contiguous carbide grains. Lower: Detail of circumferential carbide vein with radial apohyses, and radial and circumferential (shrinkage?) cracks.

with fine-grained intergrowths of carbide, metal. sulfide and silicate. Around the object is a rim comprising four concentric zones; from the interior, a sulfide-rich silicate zone is followed by a carbide layer only a few micrometres thick, then comes a second sulfide-rich silicate zone and, finally, an irregular zone with magnetite, carbide and sulfide, some of which is pentlandite with 16.5% Ni. The carbide in the outer zone, with 88% Fe, 1.4–1.7% Ni and 0.4% Co, is contiguous in places with the thin carbide layer bounded by sulfide-rich silicate. Radial offshoots of this carbide layer penetrate the inner and outer sulfide-rich silicate (Fig. 1, insets) and extend outwards into matrix. Further away from the object an irregular, branching carbide vein of the same composition traverses interchondrule matrix.

Carbide veinlets commonly cut the opaque matrix and, in a few cases, silicate grains within it. Sulfide veins are rarely observed in a similar, cross-cutting, relationship. Magnetite occasionally occurs as discrete grains in matrix, apparently unassociated with metal or carbide. Embayments filled with matrix are not uncommon in the magnetites against which matrix abuts.

# CHONDRULES AND CLASTS

Chondrules range from several millimetres to less than 10  $\mu$ m in diameter; together with rock clasts, all are set in the translucent brown to olive green or opaque matrix. Many chondrules and clasts are surrounded wholly or partly by opaque rims that may be zoned on a textural and/or compositional basis (MATSUNAMI, 1984). The larger silicate objects range from crystalline clasts with no mesostasis (one is composed of magnesian olivine, low-Ca pyroxene and minor, interstitial, anorthite) through porphyritic objects with clear, isotropic glass, to rare, wholly microcrystalline chondrules.

However, the mesostases of porphyritic objects have been selectively devitrified, especially around the margins. Some chondrules have clear, isotropic glass in their centers and brown, microcrystalline material near their rims, indicating that devitrification worked inwards.

In one porphyry, phenocrysts of low-Ca pyroxene (En<sub>84</sub>) are set in translucent brown mesostasis (Fig. 2) which is anisotropic, fine-grained, and porous on a micrometre scale. Material similar to the mesostasis in visual appearance occurs on the margin of the clast where it is intimately associated with opaque interchondrule matrix. It is difficult to determine the boundary between the mesostasis of the clast and the adjacent matrix. Similar difficulties occur with the chondrules and clasts lacking opaque rims, where mesostases make direct contact with enclosing matrix.

One chondrule of note (located over 1 cm from fusion crust) is composed of a granular mosaic of twinned clinoenstatite crystals (En<sub>93</sub>) (Fig. 3). Several dendritic structures, one of which extends inwards from the chondrule rim, are poikilitically enclosed within enstatites, indicating that enstatite crystallized after the dendrites had formed. The dendrites, however, are now composed of brown, fine-grained material that is not porous on a sub-micrometre scale (scanning electron microscope observation). One apparently contains a 20  $\mu$ m crystal that is straight extinguishing and pleochroic from mid- to dark brown, the stronger absorption being parallel to the cleavage traces. Its optical properties indicate that it may be micaceous. Similar "crystals" occur around the margin of the chondrule and range up to  $50 \times 10 \,\mu m$ . From their textural relationship to the enstatite crystals the dendrites are interpreted as having originally crystallized as olivine which was subsequently altered.

#### INTERCHONDRULE MATRIX

The interchondrule matrix in Semarkona is different from that in the other UOCs that we have studied (Bishunpur, Chainpur, Krymka, Ngawi, Sharps and Ties-



FIG. 2. Porphyritic pyroxene clast, plane polarized light, field 700  $\mu$ m wide. Phenocrysts of low-Ca pyroxene (light) in devitrified mesostasis (dark). The circle indicates the location of three analyses of mesostasis, Table 2, no. 1.

chitz). In transmitted light its variation from opaque through translucent brown to olive-green is unusual, but within it, the presence of trains of calcite crystals and rare, irregular, sometimes branching, fissures filled with translucent, anisotropic material is, as yet, unique in a UOC. The presence of calcite in Semarkona was, however, noted by NAGAHARA (1984).

Opaque areas have a grain-size in the micrometre range, or less. They have a higher general reflectivity than translucent matrix, probably associated with the higher Ni and FeS contents of the former (Table 2, analyses 7 and 8). The high reflectance may be due to the presence of sulfides, a pentlandite-like phase with 20% Ni and a pyrrhotite-like sulfide, but not troilite, having been observed in the ATEM. Also identified by ATEM diffraction data are nickel-poor maghemite and a carbide without an ideal cohenite composition (see also TAYLOR *et al.*, 1981), but probably lying somewhere between Fe<sub>3</sub>C and Fe<sub>2</sub>C (see JACK, 1950). The composition of the carbide around the spherical object (Fig. 1) is consistent with this diagnosis.

Translucent brown and olive-green matrix are birefringent on a very fine scale, indicating that they are microcrystalline. Within all three types of matrix lie angular fragments and sub-spherical microchondrules up to  $60 \ \mu m$  across. Some of the fragments are of olivine or pyroxene, but others are microcrystalline and, like the microchondrules, range from translucent brown through olive-green to colorless.

Veins in matrix are invariably of lower reflectance

than the material of their host. In some cases veins continue into chondrules or clasts, along angular courses presumably controlled by the geometry of the coherent objects encountered by propagating fractures. Calcite, its birefringence diagnostically higher than that of neighboring olivines, rarely occurs as an infilling. It also occurs occasionally as trains of crystals following irregular courses sub-parallel to the rough outlines of the margins of the chondrules or clasts bounding the matrix in which they lie (Fig. 4). Clumps of crystals and isolated crystals were seen more frequently. Many calcites are twinned and contain central dustings of silicate, an observation confirmed by ATEM. The composition is virtually pure  $CaCO_3$ , with (FeO + MgO) less than 1% (wt.).

The ATEM results show the matrix and some chondrule mesostases to be a highly oxidized mineral assemblage in which the primary ferro-magnesian minerals have undergone alteration, but not to completion (Fig. 5). The dominant alteration product is a fibrous phyllosilicate (Fig. 6) which we have identified as a smectite on the basis of non-basal interplanar spacings (Table 1). It is an unusual mineral in terms of both structure and chemistry, most closely resembling nontronite.

Electron diffraction shows that the basal interplanar spacings of the smectite are small, 9.7-10.0 Å, compared with 12-13 Å for typical terrestrial sodium smectites. However, it is known that basal spacings of about 10 Å can be produced by heating terrestrial



FIG. 3. Granular pyroxene chondrule, plane polarized light, field 500  $\mu$ m wide. Arrow, 2, indicates analyzed dendrite, Table 2, no. 2. Arrow, 3, indicates location of twinned "micaceous" crystal, Table 2, no. 3.



FIG. 4. Interchondrule matrix, plane polarized light, with dusty calcite crystals (mid-gray). The large calcite crystal (see inset) is 15  $\mu$ m long. The calcite crystals are concentrated in an irregular train roughly parallel to the margins of chondrules and clasts (light).

smectites above 200-300°C, whereupon loosely bound water is driven off (BRINDLEY and BROWN, 1980, p. 213). Semarkona is not particularly rich in water (JA-ROSEWICH, 1966; MCNAUGHTON *et al.*, 1982) and it is therefore likely that its smectite formed in an environment that fostered incomplete hydration.



FIG. 5. 200 kV Transmission electron micrograph. Semarkona interchondrule matrix with a low-Ca pyroxene fragment (PX) partially altered to fibrous smectite. Note especially the corroded margin between the arrows. Differential erosion of the sample during ion-beam thinning has produced holes in places, around which the smectite has become amorphous, due to thinning and electron irradiation.



FIG. 6. 200 kV Transmission electron micrograph. Semarkona interchondrule matrix consisting of porous, fibrous smectite with twinned grains of maghemite (arrowed). The holes are artifacts.

The general formula for a dioctahedral smectite is:

 $(M_{x+y})(R_{2-y}R_y)(Si_{4-x}Al_x) \cdot O_{10}(OH)_2$ 

(BRINDLEY and BROWN, 1980, p. 169). The analysis of Semarkona smectite obtained by ATEM yields the formula:

 $(Na_{0.81}, K_{0.08}, Mg_{0.29}, Ca_{0.01})$ 

 $\times$  (Fe<sub>1,46</sub>, Mg<sub>0.54</sub>)(Si<sub>3.05</sub>, Al<sub>0.44</sub>, Fe<sub>0.51</sub>)

and the composition of the twinned "micaceous" crystal (Fig. 3 and Table 2, no. 3) becomes:

 $(Na_{0.28}, K_{0.05}, Mg_{0.60}, Ca_{0.02})(Fe_{1.28}, Mg_{0.72})$ 

 $\times$  (Si<sub>3.15</sub>, Al<sub>0.34</sub>, Fe<sub>0.51</sub>).

In each case the formula is calculated assuming that all the Fe is trivalent, and the results indicate that considerable Fe is required to fill tetrahedral sites (*i.e.* substituting for Si). Even if the analyses are calculated as tri-octahedral smectites, with divalent iron present, there is still a deficiency in tetrahedrally co-ordinated cations unless some Fe<sup>3+</sup> is allocated to this site. Matrix and altered mesostases, therefore, appear to be highly oxidized. The smectite is very poor in Ca. most of

Table	1.	Me	asur	ed	interplanar
spac	ing	s	(Å)	in	smectites

	Semarkona	Terrestrial (non-basal)
001	9.87 0.15	
002	4.83	
	4,56-4,65 (broad)	4.51-4.61
003	3.25	
	2,55-2.66 (broad)	2.55-2.66
	2.42 + 0.01	
	1.92 + 0.01	
	1,75 + 0.01	1.69-1.75
	$1.53 \pm 0.01$	1.49-1.52
	$1.32 \pm 0.01$	1.29-1.32
	$0.99 \pm 0.02$	0.97-0.99
	0.88 <u>+</u> 0.02	0.86-0.88

Data for terrestrial smectites from Brindley and Brown (1980, Table 2.7).

which is present as calcite. Because the calcite is so Fepoor, we were able to use its interplanar spacings as a ruler against which to confirm the interplanar spacings of the smectite. (This is a desirable cross-check because of the normal uncertainty in electron diffraction camera length.)

We also have identified a smectite in the matrix of the Bishunpur, LL3, meteorite, but in this case the phyllosilicate is much richer in Ca than in Semarkona. Thus, it seems likely that in the latter meteorite there has been transport of Ca from the precursors of the phyllosilicate to the sites of calcite crystallization.

Some magnesian olivines and striated low-Ca pyroxenes remain in contact with the matrix but they show clear signs of *in situ* alteration (Fig. 5). There is also an Fe-rich mineral with a non-stoichiometric olivine composition that may be related to the ferrifayalite-laihunite series. It is often found with a Zn-bearing Fe-Si-S mineral association, which may be particularly significant because GROSSMAN and WASSON (1985) noted that chondrules in Semarkona are depleted in Zn.

Evidence of oxidation is not confined to the finest grained matrix, most metal inclusions having been oxidised to magnetite, taenite and pentlandite. The taenite contains up to 65 wt% Ni but our ATEM shows it to be strained taenite rather than ordered tetrataenite as might be expected. This possibly resulted from alteration at a very low temperature.

# CHEMISTRY OF CHONDRULE MESOSTASES AND INTERCHONDRULE MATRIX

The composition of the mesostasis in the porphyritic pyroxene clast (Fig. 2) is given in Table 2 (no. 1). A similar composition was determined for the translucent brown matrix associated with opaque matrix immediately outside the clast. The material appeared to decompose under the electron beam (15  $\mu$ m diameter, 20 kV accelerating voltage) and the analysis totals only about 80%. In this case, microporosity may have contributed to the low total. The low CaO content, 0.25 wt%, coupled with normal abundances of the alkali oxides (1.73% Na<sub>2</sub>O; 0.45% K<sub>2</sub>O) seemed unusual, especially since no obvious calcium-bearing phase, such as Ca-pyroxene, was found. These properties alerted us to the possibility that the mesostasis may have been altered, and calcium redistributed into carbonate. Calcite was sought and found as rare crystals within the clast.

The altered dendrite and an apparently twinned "micaceous" crystal in the porphyritic pyroxene chondrule (Fig. 3) have compositions (Table 2, nos. 2 and 3) similar to that of the mesostasis of the porphyritic pyroxene clast. Here, however, porosity cannot be invoked to account for the low totals, and the altered dendrite did not appear to decompose under the electron beam.

Another chondrule contains olivine dendrites (Fo99) up to 2 mm long, with overgrowths of feathery pi-

Table 2. Chemical analyses of hydrated materials and opaque matrix in Semarkona

		-						
	1	2	3	4	5	6	7	8
510,	41.3	44.6	41.6	39.4	48.7	35.9	37.5	38.8
10,	0.05	<0.05	<0.05	0.14	0.20	0.46	0.06	0.07
1,203	2.54	3.83	3.80	1.53	3.52	4.27	3.27	4.30
r_01	<0.05	<0.05	<0.05	0.27	0.43	0.14	0.29	0.25
°eÒ í	17.4	20.6	28.4	30.8	11.5	21.5	25.9	24 0
(n0	0.05	0.11	0.14	0.08	0.42	0.10	0.21	0 15
(gO	16.0	10.4	11.7	7.61	24.5	11.2	11.5	12.0
ao	0.25	0.20	0.28	0.60	2.42	0.78	0.73	1.05
la <sub>2</sub> 0	1.73	1.57	1.90	0.66	0.74	2.26	2.53	2.30
( <sub>2</sub> ð	0.42	0.45	0.48	0.27	0.49	0.87	0.6*	0.63
re S	0.44	0.25	0.44	0.70	0.55	0.38	3.15	2 40
li	<0.05	0.11	<0.05	<0.05	<0.05	<0.05	1.11	0.90
Տատ	80.2	82.1	88.7	82 1	93.5	77 9	86.9	86.8

Analyst: R. Hutchison. Analyses by wavelength dispersive microprobe with 20 kV accelerating voltage and 2.5x10  $^8$  Amp current. Standards used were: wollastonite (Si,Ca), Eagle Citiki: Station olivine (Fe,Mg) jadette (Na,Al), sylvine (K), rutile (Ti), pyrite (S) and pure, Cr, Mn.Fe and Ni. \*16 points, EDS analysis, 15 kV, 0.4x10<sup>-8</sup> Amp.

Mean, 3 analyses, mesostasis of clast, Fig.2, 15 µm beam

Dendrite Fig. 3. 3

Denoirte II..... Twinned "micaceous" crystal, Fig.3. Microchondrule, in interchondrule opaque matrix, 12x10 سبر 4.

raster 5. Angular inclusion in interchondrule opaque matrix, 10 µm

6. Mesostasis, 60 um chondrule, mean of 2 analyses, 10 um bean

Opaque matrix, mean of 6 analyses, 10 µm beam, this work

8. Opaque matrix, recalculated from Huss et al. (1981)

geonite. In the center these are associated with clear, isotropic glass with almost no Fe, but with 14.5 wt% CaO, and analyses total 96.7%. Towards the margin of the chondrule the mesostasis becomes brown, devitrified and has 24.8% FeO and only 5.2% CaO, the analysis having a total of 86%.

Analyses of objects situated in opaque matrix are presented in Table 2 (nos. 4-6). Number 4 is of a microcrystalline microchondrule, number 5 of a microcrystalline angular inclusion, and 6 of mesostasis of a microporphyritic microchondrule some 60  $\mu$ m in diameter. All three analyses have low totals, but the angular inclusion has 2.42% CaO, and, if the low total and the K<sub>2</sub>O content are ignored, has the composition of a stoichiometric pigeonite, Wo5Fs20En75. The microcrystalline microchondrule has abnormally high FeO and low MgO contents (30.8 and 7.61%, respectively), but otherwise is not unlike the mesostasis of the clast or the altered dendrite.

The mesostasis of the microporphyritic microchondrule is silica-poor, tended to decompose under the electron beam and the analysis has a very low total (no. 6). The microchondrule contains clear microphenocrysts with straight, sharp margins and square outlines; one has the composition of a fassaite, Wo48En50Fs2, with 12.0% Al2O3. The crystals could not have crystallized from a liquid with the present FeO content of the mesostasis, 21.5%, because the distribution coefficient between pyroxene and liquid, 0.6-1.0 (HENDERSON, 1982) indicates that the crystals should have a minimum FeO content of 12 wt%, instead of the reality of 0.76%. Furthermore, it is unlikely that the mesostasis, with its present content of CaO, 0.78%, could have precipitated phenocrysts of Ca-rich pyroxene. Finally, the euhedral form and lack of embayments indicate that the crystals were not out of equilibrium with the enveloping mesostasis so they cannot be interpreted as pre-existing grains. We conclude that the mesostasis originally was Fe-poor and Ca-rich when the phenocrysts formed, and that it was subsequently altered.

The composition of opaque matrix of HUSS *et al.* (1981) was confirmed (Table 2, no. 8), except for the high  $Al_2O_3$  content (*cf.* no. 7). It is noteworthy that the CaO content of Semarkona opaque matrix is lower than that of opaque matrix in all other UOCs studied by these authors.

# DISCUSSION

#### 1. The formation of veins

The stone is essentially unshocked, lacking the pervasive veining, with metal and sulfide droplets, typical of heavily shocked chondrites (HEYMANN, 1967). However, minor cataclastic fracturing is common and probably occurred by compaction, accompanied by cooling and contraction of some of the components of the stone. Carbide in the circumferential and radial "shrinkage" cracks in the spherical object (Fig. 1) may have been deposited by gaseous carbonyls (BLOCH and MULLER, 1971). Deposition from a fluid seems preferable to shock emplacement as the potential origin of the delicate, micrometre thick carbide veins that intersect at about 90° (Fig. 1, inset). If this were the case, carbide veins in matrix presumably had a similar origin.

The movement of fluids through veins is also invoked to account for the origin of smectite and calcite.

# 2. Chemistry and origin of mesostases, interchondrule matrix and smectite

Analyses nos. 1–4, and 6, Table 2, roughly have the interelement ratios of the smectite determined by ATEM. It is therefore inferred that smectite constitutes the bulk of the material in the devitrified, brown or green matrix, and of the mesostases of the clast, microchondrules and of the dendritic structures. Furthermore, the mesostasis of the clast is similar in composition to that of the adjacent, translucent interchondrule matrix. We interpret the dendrites, then, as resulting from the alteration of olivine to Na, Fe smectite. Optical continuity within each dendrite presumably reflects a parallelism among constituent microcrystals of smectite.

The chemistry of translucent interchondrule matrix and green or brown, devitrified mesostases of chondrules, clasts and microchondrules is interpreted as the result of hydrothermal alteration of precursor materials, accompanied by redistribution of Ca and Fe. Calcium was leached from the precursor material and reprecipitated as calcite. Sometimes there were structural controls that led to precipitation within veins or as trains of crystals in matrix, so a fluid presumably was involved. Iron was introduced into at least some chondrule and clast mesostases during the devitrification and hydrous alteration, and certainly into that of the fassaite-bearing microchondrule. The partial, *in situ*, attack of pyroxenes (Fig. 5) and olivines in the matrix testifies that alteration was not confined to glassy mesostases. The Zn-bearing Fe-Si-S association described above suggests that Zn may have been mobilized also, and partially removed with Ca from some chondrules. The source of the Fe may have been matrix kamacite, oxidised with the production of the residual strained taenite with up to 65 wt% Ni, although some Fe ultimately was fixed as maghemite.

## 3. The source of water

MCNAUGHTON et al. (1982) showed that Semarkona contains a phase or phases in which deuterium (D) is highly enriched relative to H. They suggested that such an enrichment, with  $\delta D > 5700$  relative to SMOW. could only have been produced by ion-molecule reactions in the interstellar medium. The release pattern of water from Semarkona mimics that of terrestrial smectites (Ross and HENDRICKS, 1945), so there is no need to invoke the presence of more than one waterbearing compound in the meteorite. The highest temperature release, with greatest  $\delta D$  in Semarkona, corresponds to the release of bound water above 500°C. A fraction of the water, or at least its hydrogen, in the meteorite might therefore derive from an interstellar source. The story is more complicated, however, because water released at lower temperature is less enriched in D so presumably contains a component from a different source. If all the water released by pyrolysis had come from the decomposition of smectite, the system must have been open with respect to hydrogen and metamorphism did not occur in a closed system.

It is worth noting that if all the water released in the pyrolysis of bulk Semarkona (MCNAUGHTON *et al.*, 1982) and all the CO<sub>2</sub> released by phosphoric acid attack (GRADY *et al.*, 1982), occurred as vapor, their total pressure at 550°C (the temperature of major water release) would have been some 40 atmospheres (20 atm. each, approximately). It seems unlikely that such a pressure could have been sustained in the porous, near surface layers of a small body. If volatiles were sealed in, we would expect to see evidence for a closed system in the isotope systematics. It is therefore possible that the volatiles were transient and that a proportion of them was mixed into a regolith from an extraneous source.

# 4. History of reaction

We do not want to speculate here on the origin of chondrules, rims and opaque matrix in Semarkona. The relic pyroxene and olivine grains in the matrix and inferred presence of metal, now residual, high-Ni taenite, indicate that the assemblage originally was essentially dry. If we accept a primary origin for the subspherical objects composed of metal, carbide, sulfide and magnetite (TAYLOR *et al.*, 1981), we recognize that the last three minerals were also formed after aggregation. Indeed, some carbide may even post-date the hydrous alteration, for veinlets of it apparently crosscut translucent brown veinlets in matrix.

The poikilitic form of some magnetites and the example of the crystal that post-dates displacement within carbide on a chondrule margin are reliable evidence that some crystallization was post-accretion. It probably preceded hydrous alteration because magnetites in matrix show evidence of corrosion in the form of matrix-filled embayments. Perhaps some Fe from the magnetites was reprecipitated as maghemite in the matrix.

The time of formation of the sulfides is more difficult to constrain. Veins very rarely cut matrix and so there is little evidence in favor of a major, post-accretion formation of sulfide. Furthermore, fragmentation in concentrically zoned metal/carbide/sulfide/magnetite objects indicates that sulfide-rich zones may pre-date their association with matrix, so could be pre-accretion in origin. Alternatively, and more simply, the sulfiderich concentric zones may have formed around metal, carbide objects near the surface of the parent body while stirring by impact occurred. Otherwise we have to postulate that sulfide rims formed before accretion, while some magnetite, carbide, a little sulfide, calcite and smectite crystallized as the result of parent body processes.

We can therefore postulate the following history:

1. (Oldest) chondrules, clasts, metal/carbide assemblages, with magnetite.

2. Formation of sulfide concentric rims.

3. Accretion, followed/accompanied by mild brecciation.

4. A second period of magnetite crystallization.

5. Crystallization of carbide in veins.

6. Hydrous alteration and calcite precipitation, from fluids, resorption of some magnetite, precipitation of maghemite.

# CONCLUSIONS

We have demonstrated that the mesostases of many chondrules and clasts have been wholly, or partially, subjected to hydrothermal alteration. Microcrystalline feldspar within these mesostases would have been destroyed. Thus, the abundance of the main phosphor producing thermoluminescence (TL) (SEARS *et al.*, 1980) would have decreased during hydrothermal alteration. The low TL in petrologic types 3.0–3.2 is therefore ascribed to the effect of retrograde, hydrothermal metamorphism of a primary assemblage of petrologic type 3.3 or 3.4. An initial decrease in TL in a type 3.4 chondrite has been produced in hydrothermal experiments (GUIMON *et al.*, 1986), lending support to this conclusion.

The formation of smectite and calcite *in situ* in Semarkona indicates that the meteorite is from an environment like that of CM2 meteorites (BUNCH and CHANG, 1980; BARBER, 1985). Semarkona, and possibly Bishunpur, should be recognized as LL2 chondrites.

The carbonaceous chondrites include abundant members of petrologic types 1–3, with a few of types 4 and 5. The ordinary chondrites are dominantly of types 4–6, with a few of type 3, and perhaps two of type 2. The structure of the parent bodies may, however, have been similar, the relative abundances of the various petrologic types being the result of sampling bias.

Retrograde metamorphism in the Semarkona parent body possibly did not occur in a completely closed system.

Smectite, magnetite, carbonate, carbides, sulfides, metal, olivine and pyroxene have been identified in chondritic interplanetary dust particles (IDPs) (BROWNLEE, 1985). The occurrence of these minerals in Semarkona indicates that there may be a link between some chondritic IDPs and the ordinary chondrites.

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#### REFERENCES

- ALLEN J. S., NOZETTE S. and WILKENING L. L. (1980) A study of chondrule rims and chondrule irradiation records in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* 44, 1161–1175.
- ASHWORTH J. R. (1977) Matrix textures in unequilibrated ordinary chondrites. *Earth Planet. Sci. Lett.* 35, 25-34.
- ASHWORTH J. R. (1981) Fine-structure in H-group chondrites. Proc. Roy. Soc. London A374, 179-194.
- BARBER D. J. (1981) Demountable polished thin-sections and their use in transmission electron microscopy. *Mineral. Mag.* 44, 357-359.
- BARBER D. J. (1985) Phyllosilicates and other layered structured materials in meteorites. Clay Minerals 20, 415-454.
- BLOCH M. R. and MULLER O. (1971) An alternative model for the formation of iron meteorites. *Earth Planet. Sci. Lett.* 12, 134–136.
- BRINDLEY G. W. and BROWN G. (1980) Crystal Structures of Clay Minerals and their Identification. Mineral. Soc., London. 495p.
- BROWNLEE D. E. (1985) Cosmic dust: Collection and research. Ann. Rev. Earth Planet. Sci. 13, 147–173.
- BUNCH T. E. and CHANG S. (1980) Carbonaceous chondrites—II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* 44, 1543–1577.
- CHRISTOPHE-MICHEL-LEVY M. (1976) La matrice noire et blanche de la chondrite de Tieschitz (H3). Earth Planet. Sci. Lett. 30, 143–150.
- DODD R. T., VAN SCHMUS W. R. and KOFFMAN D. M. (1967) A survey of the unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* **31**, 921–951.
- GOODING J. L. and KEIL K. (1981) Relative abundances of chondrule primary textural types in ordinary chondrites and their bearing on conditions of chondrule formation. *Meteoritics* 16, 17-43.
- GRADY M. M., SWART P. K. and PILLINGER C. T. (1982)

The variable carbon isotopic composition of type 3 ordinary chondrites. Proc. Lunar Planet. Sci. Conf. 13th; J. Geophys. Res., Suppl. 87, A289-A296.

- GROSSMAN J. N. and WASSON J. T. (1985) The origin and history of the metal and sulfide components of chondrules. *Geochim. Cosmochim. Acta* 49, 925-939.
- GUIMON R. K., LOFGREN G. E. and SEARS D. W. (1986) A study of the effect of devitrification on thermoluminescence in type 3.4 ordinary chondrites. *Lunar Planet. Sci. XVII*, 297-298.
- HENDERSON P. (1982) Inorganic Geochemistry. Pergamon Press. 353p.
- HEYMANN D. H. (1967) On the origin of hypersthene chondrites; ages and shock effects of black chondrites. *Icarus* 6, 189-221.
- HUSS G. R., KEIL K. and TAYLOR G. J. (1981) The matrices of unequilibrated ordinary chondrites: implications for the origin and history of chondrites. *Geochim. Cosmochim. Acta* 45, 33-51.
- HUTCHISON R. and BEVAN A. W. R. (1983). Conditions and time of chondrule accretion. In *Chondrules and their Origins* (ed. E. A. KING), pp. 162-179. Lunar and Planetary Institute, Houston, TX.
- HUTCHISON R., BEVAN A. W. R., AGRELL S. O. and ASH-WORTH J. R. (1980) Thermal history of the H-group of chondritic meteorites. *Nature* 287, 787-790.
- JACK K. H. (1950) Results of further X-ray structural investigations of the iron-carbon and iron-nitrogen systems and of related interstitial alloys. Acta Cryst. 3, 392-393.
- JAROSEWICH E. (1966) Chemical analyses of ten stony meteorites. Geochim. Cosmochim. Acta 30, 1261-1265.
- KURAT G. (1969) The formation of chondrules and chondrites and some observations on chondrules from the Tieschitz

meteorite. In Meteorite Research (ed. P. M. MILLMAN), pp. 185-190. Reidel, Dordrecht.

- LAUL J. C., GANAPATHY R., ANDERS E. and MORGAN J. W. (1973) Chemical fractionation in meteorites—VI. Accretion temperatures of H-, LL-, and E-chondrites, from abundance of volatile trace elements. *Geochim. Cosmochim. Acta* 37, 329-357.
- MCNAUGHTON N. J., FALLICK A. E. and PILLINGER C. T. (1982) Deuterium ratios in type 3 ordinary chondrites. Proc. Lunar Planet. Sci. Conf. 13th: J. Geophys. Res., Suppl. 87, A297-A302.
- MATSUNAMI S. (1984) The chemical compositions and textures of matrices and chondrule rims of eight unequilibrated ordinary chondrites. Proc. 9th Symp. Antarctic Meteorites. pp. 126-148. Tokyo, Nat. Inst. Polar Res.
- NAGAHARA H. (1984) Matrices of type 3 ordinary chondrites—primitive nebular records. Geochim. Cosmochim. Acta 48, 2581-2595.
- ROBERT F., MERLIVAT L. and JAVOY M. (1979) Deuterium concentration in the early solar system: hydrogen and oxygen isotope study. *Nature* 282, 785-789.
- Ross C. S. and HENDRICKS S. B. (1945) Minerals of the montmorillonite group. U.S. Geol. Surv. Prof. Pap. 205B, 23-79.
- SEARS D. W., GROSSMAN J. N., MELCHER C. L., ROSS L. M. and MILLS A. A. (1980) Measuring metamorphic history of unequilibrated ordinary chondrites. *Nature* 287, 791– 795.
- TAYLOR G. J., OKADA A., SCOTT E. R. D., RUBIN A. E., HUSS G. R. and KEIL K. (1981) The occurrence and implications of carbide-magnetite assemblages in unequilibrated ordinary chondrites. *Lunar Planet. Sci. XII*, 1076– 1078.