# Magnetite in CI Carbonaceous Meteorites: Origin by Aqueous Activity on a Planetesimal Surface

Abstract. *The composition and morphology of magnetite in CI carbonaceous meteorites appear incompatible with a nebular origin. Mineralization on the meteorite parent body is a more plausible mode of formation. The iodine-xenon age of this material therefore dates an episode of secondary mineralization on a planetesimal rather than the epoch of condensation in the primitive solar nebula.*

Magnetite, $Fe_3O_4$, in CI carbonaceous meteorites (*1*) has attracted attention because of its bizarre morphologies and apparently ancient age (*2*). These observations have provoked speculation that this material formed in the primitive solar nebula, either by direct condensation (*3, 4*) or by reaction between water vapor and previously condensed Fe-rich phases at about 400°K (*5*). This report describes morphologic, crystallographic, and compositional information which casts doubt on a nebular origin and suggests rather that the magnetite formed during low-temperature mineralization on the meteorite parent body (*6-9*). It follows that the age recorded in this material does not date the epoch of nebular condensation and that no conclusions may therefore be drawn concerning the time interval between the cessation of nucleosynthesis and the onset of solar system condensation.

In the elemental analysis of polished thin sections and polished grain mounts, we used an electron microprobe (ARL EMX) operated at 15 kV. We used standard data reduction procedures, leading to compositions which were identical for all morphological varieties and for all meteorites studied (Orgueil, Alais, and Ivuna) and which were indistinguishable from a nominally pure magnetite standard. Thus, an upper limit of about 100 parts per million (ppm) may be assigned to all elements except Fe and O. Assuming a compositionally homogeneous population, we combined data for 50 grains to yield a mean Ni content of $50 \pm 15$ ppm (*11*). These results agree with those obtained by neutron activation analysis of magnetic separates from Orgueil (*12*); CI magnetite is depleted in siderophile elements by a factor of about $10^{-3}$ relative to Fe.

We investigated morphological details by scanning and transmission electron microscopy of meteorite sections, replicas, and grain mounts, as appropriate. Some of the morphologies exhibited by CI magnetite are forms that may be plausibly related to its crystal structure (spinel group); such varieties are unlikely to yield unambiguous genetic information. Consequently, we focused our attention

on unusual forms, not obviously controlled by internal symmetry, for which specific antecedent conditions may reasonably be argued.

The commonest occurrence, perhaps accounting for half of the total magnetite, is as aggregates containing typically some thousands of crystallites of submicron size. Individual crystals are equant, exhibiting forms common among terrestrial magnetites, although the trapezohedron is apparently absent (*13*). Aggregates are typically subrounded, ranging from irregular to precisely circular in section (Fig. 1). The resemblance to so-called "framboidal" pyrite ($FeS_2$) from marine sediments, is marked. Random accumulation of particles might produce irregular aggregates, but precisely regular framboids (Fig. 1) demand a more specific origin. Such an origin, based on the results of laboratory synthesis, has been advanced by Sweeney and Kaplan (*14*) for terrestrial pyrite framboids; an analogous origin for CI framboidal magnetite seems most plausible. Figure 2a shows a pyrite framboid identical in shape, diameter, and particle size to the meteoritic aggregate illustrated in Fig. 1, except that pyrite cubes substitute for magnetite polyhedra. It was formed by the sulfurization of synthetic pyrrhotite ($Fe_7S_8$) in aqueous solu-

tion; exclusion of water inhibited the reaction. Sweeney and Kaplan showed that the framboidal texture was controlled by the spherical shape adopted by a cryptocrystalline intermediate reaction product [greigite ($Fe_3S_4$) in the sulfide system] within which the pyrite nucleated and grew. The factors controlling the sphericity of the greigite were not defined. The nature of the putative spherical precursor for CI magnetite cannot be specified at present; a reasonable speculation is that it was a poorly crystallized Fe hydroxide, such as limonite, which has been reported in these meteorites (*9*).

Spherical forms are, in fact, common among CI magnetites. Figure 2b illustrates such a grain, sectioned to reveal a spherulitic internal texture; the individual radiating fibers, which constitute the spherulitic texture and whose development leads to an overall spheroidal shape, may be clearly seen. Possibly all spherical CI magnetites possess such texture; "smooth" spheres observed in sections may have lost their texture during polishing. Spherulitic textures are well known in terrestrial mineralogy (Fig. 2c). The high surface/volume ratio of the individual fibers makes this texture a nonequilibrium form. Studies of synthetic and natural systems (*15*) have shown that spherulite formation requires crystallization from a melt or amorphous material (for example, glass) under conditions which maintain a subtle balance between the rate of diffusion of impurities away from the growing crystal and the growth rate of the crystal itself. Because of the high melting point of magnetite, 1590°C, and the improbability of achieving a suitably high oxygen fu-
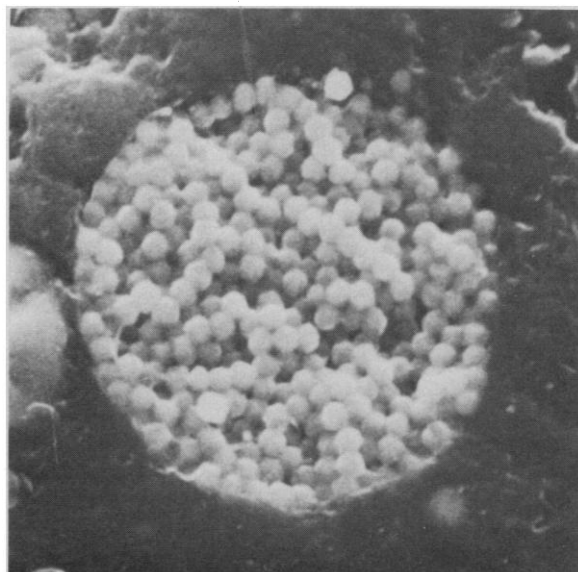


Fig. 1. Scanning electron micrograph of framboidal magnetite in the Orgueil carbonaceous meteorite. Formation of this structure appears to have required aqueous activity on the meteorite parent body. The width of the field of view is 27 $\mu$m.

gacity at such a temperature during meteorite formation, a molten stage for CI magnetite is implausible. The requisite amorphous medium for spherulite growth was probably supplied by an aqueous gel containing a colloidal Fe hydroxide such as limonite. Thus, both spherulitic and framboidal textures probably share a closely similar origin, namely, crystallization from an amorphous or cryptocrystalline precursor, most likely a limonite-like hydroxide. The spheroidal form necessary to produce the framboidal texture may have been generated by the spherulitic growth of an intermediate phase characterized by a somewhat greater degree of crystallinity than that of the gel.

Possibly the most unusual, and therefore potentially informative, morphology is exhibited by the variety termed "plaquettes" (Fig. 2d). A careful study of the disymmetric nature of these stacks of platelets, including apparent evidence for dislocation-induced growth spirals on platelet surfaces, caused Jedwab (13) to propose an origin as condensate from nebular vapor. He noted that such platy forms had been predicted for nebular condensates (16). However, two lines of evidence argue against this possibility.

First, it is very difficult to form pure magnetite as a nebular condensate. Under equilibrium conditions magnetite forms, not as a condensate, but by alteration of an Fe-rich phase (5). The nebula may have become supersaturated with respect to Fe metal (17), but, even with very large degrees of supersaturation, fayalite ($Fe_2SiO_4$) and troilite (FeS) would have formed, removing Fe from the gas before magnetite condensation.

If, for some unknown reason, no other Fe-rich phase formed, other elements present in the gas, for example, Ni, would have co-condensed to yield a Ni-bearing magnetite. Similarly, if the elements condensed from a hot, ionized gas as they became neutralized upon cooling (4), magnetite formed in such an environment would have contained significant amounts of elements with similar ionization potentials, such as Co, Cu, and Ni.

Second, there is strong crystallographic evidence that the platy morphology was controlled by the microenvironment in which nucleation and growth occurred rather than by the underlying crystal structure. (The latter would be expected for the case of vapor condensation.) This conclusion is based upon evidence, first noted by Jedwab (13), that terminating platelets sometimes reveal a fourfold symmetry axis perpendicular to the principal plane of the platelets (see Fig. 2d). This identifies these planes as belonging to {001} of the cubic magnetite structure; however, the close-packed planes in this structure, within which growth would be preferred (18), belong to {111}. A crystal face parallel to such a close-packed plane would exhibit three- or sixfold symmetry, which is not observed here. This precludes not only morphological control by the magnetite structure but also similar control for any precursor phase, of which the observed magnetite might be a pseudomorph, because all topotactically related oxides and hydroxides of Fe possess close-packed (that is, sixfold-coordinated) layers of oxygen as a common structural unit.

A possible explanation for this morphology is suggested by the frequent, although not universal, occurrence of plaquettes within carbonate grains (19). If magnetite nucleated and grew upon a rhombohedral carbonate face, epitaxial matching of oxygen networks in carbonate and magnetite would cause the fourfold 001 axis of magnetite to lie within about 12° of the normal to the carbonate, and hence magnetite, face (20). Preferential growth of magnetite along the rhombohedral carbonate face would produce a platelet with the observed symmetry. This could occur either by exsolution within carbonate cleavage planes or by simultaneous crystallization along carbonate growth faces.

If such a mechanism were responsible for the production of plaquettes, it makes them contemporary with, or somewhat younger than, the carbonates, generally believed to have crystallized during an epoch of mineralization on the meteorite parent body (7-9). Production of an Fe hydroxide gel and crystalliza-
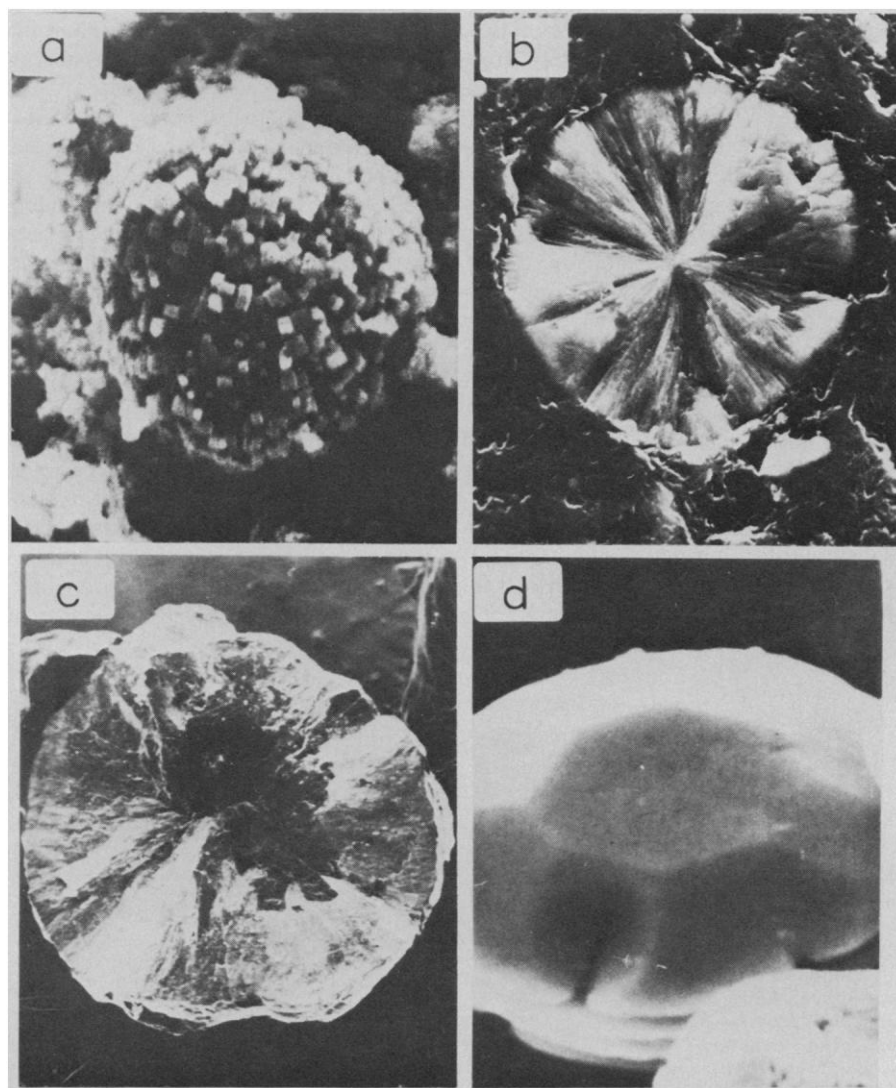


Fig. 2. (a) Scanning electron micrograph of framboidal pyrite synthesized in the laboratory by the sulfidation of pyrrhotite (14). The width of the field of view is 20 μm. (b) Scanning electron micrograph of spherulitic magnetite in the Orgueil carbonaceous meteorite. The width of the field of view is 20 μm. (c) Scanning electron micrograph of spherulitic feldspar from rhyolitic ash flow, Superior, Arizona. The width of the field of view is 2.2 mm. (d) Scanning electron micrograph of a magnetite "plaquette" from the Orgueil carbonaceous meteorite. Note the fourfold symmetry exhibited by the terminal platelet. The width of the field of view is 11 μm.

tion of carbonate both suggest aqueous alteration, most plausibly on a planetesimal surface, of material produced earlier, possibly in the nebula. A similar origin has also been inferred for all other major minerals in CI chondrites (21). Such mineralization does not appear compatible with an origin directly in the nebula. Therefore, the I-Xe age determined for the Orgueil magnetic separate (5) apparently records alteration on a parent body rather than nebular condensation (22). Thus, aqueous activity, chondrule formation, and planetesimal differentiation all occurred within a period of $16 \times 10^6$ years, the "sharp isochronism" (23). Aqueous alteration apparently took place in a system that was closed, at least to nonvolatile elements, because the elemental abundances determined by bulk analyses of CI chondrites closely match solar elemental abundances (10).

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#### References and Notes

1. The category CI in the classification by J. T. Wasson [*Meteorites* (Springer, Berlin, 1974)] is equivalent to category C1 in the scheme of W. R. Van Schmus and J. A. Wood [*Geochim. Cosmochim. Acta* **31**, 747 (1967)].
2. A magnetic separate, consisting mostly of magnetite, from the Orgueil CI meteorite gave a $^{129}$Xe retention age of $4 \times 10^6$ years prior to the Bjurböle standard (5). This was the oldest age recorded at that time and was interpreted as dating the era of nebular condensation, linking that event to the neucleosynthesis of $^{129}$I (5). An apparently older age, by $6 \times 10^6$ years, has since been reported for the chondrite Arapahoe [R. J. Drozd and F. A. Podosek, *Earth Planet. Sci. Lett.* **31**, 15 (1976)].
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6. Such a suggestion is not new (7-9). However, recent emphasis on the primitive nature of carbonaceous meteorites [(10); A. G. W. Cameron, *Int. Astron. Union Symp. 52* (1973), p. 545; L. Grossman and J. W. Larimer, *Rev. Geophys. Space Phys.* **12**, 71 (1974)] has caused the significance of evidence for secondary alteration, for example, well-crystallized dolomite, $(Ca,Mg)CO_3$, and veins of epsomite, $MgSO_4 \cdot 7H_2O$ [(7); S. M. Richardson, *Meteoritics* **13**, 141 (1978)] to be overlooked.
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18. Thus, magnetite exsolved from pyrrhotite $(Fe_{1-x}S)$ containing dissolved $O_2$ can produce lamellae parallel to $(111)_{magnetite},(001)_{pyrrhotite}$ [C. E. G. Bennett, J. Graham, T. C. Parkes, M. R. Thornber, *Am. Mineral.* **57**, 1876 (1972)]; dehydration of Green Rust I can produce hexagonal plates of magnetite (A. L. Mackay, paper delivered to the Mineralogical Society, London, 23 March 1961); and reduction of hematite $(Fe_2O_3)$ yields magnetite lamellae parallel to $(111)_{magnetite},(001)_{hematite}$ [N. J. Tighe and P. R. Swann, in *Electron Microscopy in Mineralogy*, H.-R. Wenk, Ed. (Springer, Berlin, 1976), p. 209].
19. Genetically informative mineral associations are rare in CI meteorites. Thus carbonate apparently did not enclose sulfides during crystallization, and sulfates are only occasionally found in contact with their presumed precursor, pyrrhotite.
20. An identical orientation relationship to that suggested here is found when magnetite is produced by thermal decomposition of siderite $(FeCO_3)$ despite loss of more than half of the oxygen from the carbonate lattice [J. D. Bernal, D. R. Dasgupta, A. L. Mackay, *Clay Miner. Bull.* **4**, 15 (1959)].
21. J. F. Kerridge, *Earth Planet. Sci. Lett.* **29**, 194 (1976); _____ and J. D. Macdougall, *ibid.*, p. 341; _____, K. Marti, *ibid.*, in press.
22. A magnetic separate from the Murchison carbonaceous meteorite was shown to be contemporaneous with the Orgueil separate (5). Therefore, aqueous activity may have occurred simultaneously on more than one parent body.
23. F. A. Podosek, *Geochim. Cosmochim. Acta* **34**, 341 (1970).
24. We thank R. W. Fitzgerald, E. Flentye, I. R. Kaplan, H. Lem, G. Lofgren, J. D. Macdougall, and R. E. Sweeney for advice and assistance. Meteorite samples were kindly supplied by K. Fredriksson and P. Pellas. We thank G. Lofgren for the spherulite illustrated in Fig. 2c and R. E. Sweeney and I. R. Kaplan for permission to use Fig. 2a. Supported by NASA grants NGR 05-007-289, NSG 7121, and NSG 7335. Publication 1896 of the Institute of Geophysics and Planetary Physics, University of California.

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# Sulfur Volcanoes on Io

Abstract. *Widespread volcanism on Jupiter's satellite Io, if it occurred over the age of the solar system, would quickly reduce the inventory of most common volatiles needed to drive such volcanism. One exception is the volatile element sulfur. It is therefore postulated that sulfur is the driving volatile for Ionian volcanism. Its presence is consistent with a carbonaceous-chondrite-like bulk composition for the original material that formed Io 4.5 billion years ago. The ubiquity of sulfur on Io today demonstrates the importance of this element in the processes that formed its surface.*

In a recent report Peale *et al.* (1) examined the dissipation of tidal energy in Jupiter's satellite Io and predicted that "widespread and recurrent surface volcanism would occur, leading to extensive differentiation and outgassing" of that body. Recent photographs of Io by Voyager 1 appear to confirm this prediction (2).

If such extensive outgassing has occurred over 4.5 aeons, as would seem to be implied by the model of Peale *et al.* (assuming the Galilean satellites have occupied their current positions over the age of the solar system), then one would expect the outgassing of Io to have been completed long ago.

For example, let us assume Io started with the composition of a very volatile-rich C1 carbonaceous chondrite—20 percent water and 5 percent carbon by mass. This is similar to the composition proposed by Fanale *et al.* (3). On eruption, gases such as $H_2O$ and $CO_2$ will be at roughly 1000°C; their molecules will have mean velocities of 1.4 and 0.9 km/sec, respectively, compared to the escape velocity of material from Io into Jupiter orbit, which can be as low as 1.78 km/sec. [Such escape is trajectory-dependent; the average escape velocity is 2.0 km/sec (4).] Thus one would expect much of the $H_2O$ to escape immediately. More importantly, the molecules that did not escape would be subject to dissociation and ionization by solar ultraviolet (UV) radiation (5) and their products would be quickly lost by Jeans escape or the sweeping action of Jupiter's magnetic field. Thus one can assume that any $H_2O$ or $CO_2$ outgassed by a volcanic event would be lost to the system. To lose an entire Io inventory of such volatiles, assuming an initial C1 composition, one would have to erupt these gases at the rate of $10^8$ g/sec.

This is of the same order as the volatile loss for a single Earth volcano. The Laki flow in Iceland erupted 15 km³ of material over 7 months, or $2 \times 10^9$ g of material per second (6). The average rate for most Earth lavas is about an order of magnitude less; however, eruption rates an order of magnitude greater have been estimated for a section of the Columbia River plateau (7). Estimates of the volatile content of Earth lavas have ranged from 0 to 50 percent; best estimates for the solubility of water in magma at kilobar pressures are 10 percent (6). Thus one large Earth volcano with a volatile content of 10 percent could degas a very vol-