

Reports

Cliftonite in Meteorites: A Proposed Origin

Abstract. *Cliftonite, a polycrystalline aggregate of graphite with cubic morphology, is known in ten meteorites. Some workers have considered it to be a pseudomorph after diamond, and have used the proposed diamond ancestry as evidence of a meteoritic parent body of at least lunar dimensions. We have synthesized cliftonite in Fe-Ni-C alloys in vacuum, as a product of decomposition of cohenite [(Fe,Ni)₃C]. We therefore suggest that a high pressure origin is unnecessary for meteorites which contain cliftonite, and that these meteorites were formed at low pressures. This conclusion is in agreement with other recent evidence.*

The origin of cliftonite, which has been found in nine iron meteorites (1, 2) and one enstatite chondrite (3) has been a subject of controversy for more than a century. One group of workers (4, 5) has considered cliftonite to be a pseudomorph after diamond, and some (5) have used the proposed diamond ancestry of cliftonite as evidence of a high pressure origin for iron meteorites, and hence have postulated a parent body of at least lunar dimensions.

Other workers (2, 6-9) have proposed that cliftonite is not a pseudomorph after diamond. The major arguments presented are: (i) the inter-

nal structure of cliftonite differs from that of graphitized diamond (8); (ii) there is no evidence of the considerable volume change that occurs in the transition of diamond to graphite (2); (iii) cliftonite, if derived from diamond at high temperature, would dissolve in the metal during the slow cooling of iron meteorites; therefore, cliftonite must have another origin (9); and, (iv) other evidence of high pressure in meteorites has proved illusory, hence a proposed diamond origin for cliftonite must be suspect (10). In view of the important implications of cliftonite on the genesis of iron meteorites, we decided to investigate cliftonite and its occurrence

both from a mineralogical and metallurgical viewpoint.

Cliftonite occurs ordinarily in kamacite (α -Fe,Ni) which surrounds troilite (FeS)-graphite-silicate nodules in iron meteorites. It is occasionally found in schreibersite [(Fe,Ni)₃P] and cohenite [(Fe,Ni)₃C] rims surrounding the nodules and in kamacite which veins nodules composed of almost pure graphite (2, 11, 12). It is very rarely present in plessite (Fig. 1). It does not occur within the interior of nodules even though they may contain plentiful graphite. Cliftonite bodies occur in dodecahedra (7) and more commonly in cubes, octahedra, cubo-octahedra, and cubo-dodecahedra. In polished sections, the cliftonite bodies appear as squares, rectangles, parallelograms, triangles, and hexagons (Figs. 1 and 2), whose sides may be curved. There is commonly a gradation from cliftonite squares to polygons to true spherulites within the same polished section. Intergrown cliftonite bodies are common (Fig. 2). Spectrographic analysis of separated cliftonite cubes reveals that the graphite is composed of carbon of exceptionally high purity; no other elements are present within the limits of detection.

Cliftonite bodies commonly have identical orientation in any given grain of kamacite or schreibersite (Figs. 1 and 2). Careful repeated sectioning and microscopic examination of a cliftonite cube from Canyon Diablo disclosed that it was composed of six apparently single crystals of pyramidal shape with a cube face for a base and an apex at

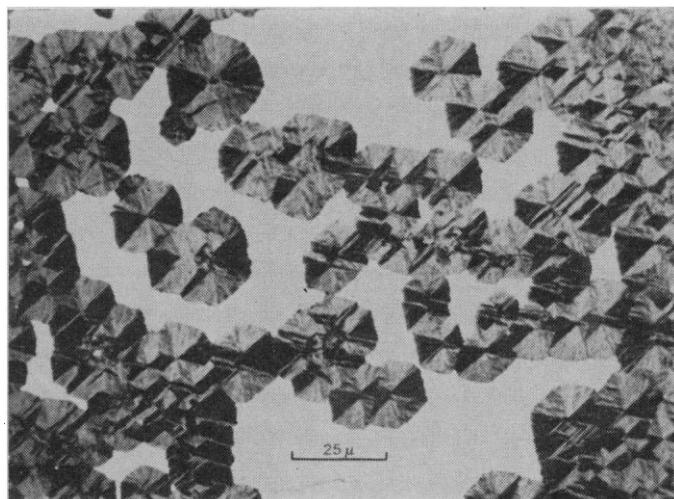
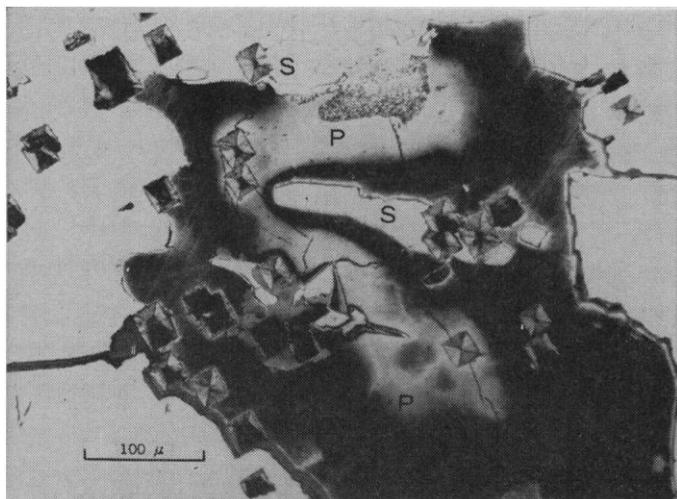


Fig. 1 (left). Cliftonite (squares and rectangles) in kamacite (white) in Canyon Diablo. *P* is plessite, *S* is schreibersite, material in fractures is secondary oxide. [Photograph by B. Nielsen, courtesy of E. Anders] Fig. 2 (right). Cliftonite (grey) with hexagonal cross section in kamacite from Canyon Diablo. Graphite hexagons have spherulitic extinction under crossed nicols. [Photograph courtesy of A. El Goresy]

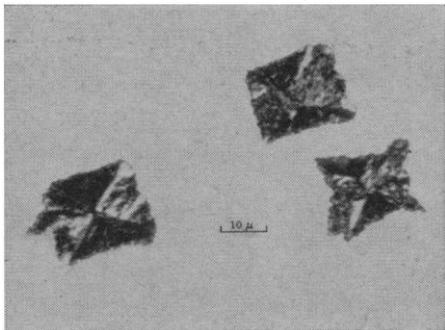


Fig. 3. Synthetic cliftonite in kamacite.

the center of the cube. Precession x-ray diffraction studies revealed that each of these apparent single crystals is composed of a large number of crystallites, which have a preferred orientation such that their *c*-axes are approximately perpendicular to the corresponding morphological cube faces, in agreement with the conclusions of Grenville-Wells (8). The internal structure of cubo-octahedra of cliftonite is similar to that of the cubes except that sheaves of spherulitic graphite crystals radiate from the center of the cubo-octahedron to form the octahedral faces.

We have synthesized graphite aggregates in a Fe-Ni-C alloy (13) which are indistinguishable optically from cliftonite in meteorites (Fig. 3). The cubes have identical orientation within any given metal grain. The homogeneous alloy was annealed at 950°C and air-cooled to form cohenite [(Fe,Ni)₃C] plus kamacite. Specimens were then annealed in evacuated silica glass tubes at 550°C for times ranging from 270 to 1000 hours. In all experiments the carbide partially or totally decomposed to form cliftonite-like graphite, and additional kamacite. By annealing the same composition in a 4:1 argon-oxygen mixture at 1 atm pressure at 550°C for 1000 hours, spherical aggregates of fine-grained graphite were formed instead of cubes. Higgins and Jeminson (14) annealed Ni-free alloys of similar Fe to C ratio at temperatures ranging from 300° to 700°C in the argon-oxygen mixture referred to above and in vacuum for times ranging from 270 to 1000 hours. They did not synthesize cliftonitic graphite.

All evidence from the synthetic alloys indicates that the conditions of formation of cliftonitic graphite differ only slightly from those under which graphite spherulites form. This is sup-

ported by meteoritic evidence: a complete gradation between spherulites and cliftonite may occur. Spherulitic growth of graphite in steels and cast irons as a product of carbide decomposition is well known to metallurgists and is promoted by a high S:Mn ratio, a slow-growth rate, and the presence of hydrogen in the annealing atmosphere (15).

The presence of Ni and a low oxygen fugacity in the annealing atmosphere is probably necessary for the growth of cliftonitic graphite. It may be that the greater size and perfection of meteoritic cliftonite compared to synthetic cliftonite is due to the much longer annealing times available for meteorites than for the laboratory alloys.

The meteorites, except Linwood, which contain cliftonite also contain partially decomposed cohenite (16, 17); in addition, all the other requirements specified above for cliftonitic or spherulitic growth of graphite are present during the cooling of such meteorites.

We therefore propose that cliftonite in meteorites was formed by the diffusion of carbon, a product of the decomposition of cohenite, to nucleation sites, and subsequent growth of graphite in cubic morphology. The orientation of the cubes is determined by the crystallographic orientation of the metal. Schreibersite which was formed in the solid state at temperatures around 600°C (18) and later cohenite partially replaced the metal, resulting in the assemblages schreibersite-cliftonite and cohenite-cliftonite.

The present proposal for the origin of cliftonite by cohenite decomposition also explains why cliftonite has not been reported in meteorites containing more than 8 percent Ni by weight, as conditions were unfavorable for these meteorites to form cohenite (16).

We disagree with those who believe that cliftonite is a pseudomorph after diamond, and we favor a low pressure origin for the following reasons. (i) The origin of meteoritic cliftonite may be explained by decomposition of cohenite at relatively low temperatures. (ii) The crystallographic orientation of graphite in cliftonite does not correspond to that of graphite after diamond (8). (iii) The lack of cliftonite in the interior of troilite-graphite nodules in meteorites that contain cliftonite elsewhere is consistent with its formation by decomposition of cohenite with kamacite, but is inconsistent with

a diamond ancestry. (iv) The gradation from cliftonite to masses of intergrown cliftonitic and spherulitic graphite may readily be explained in terms of our proposed origin, but gradation from masses of intergrown natural or synthetic diamond crystals of similar morphology to the cliftonite masses is unknown. (v) Our proposed low-pressure origin for cliftonite is consistent with other recent work on the pressures pertaining during the formation of iron meteorites (16, 19); a diamond-derived origin is inconsistent with almost all other relevant evidence. We therefore propose that the meteorites which contain cliftonite formed in bodies of asteroidal size or near the surface of large bodies.

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13. Composition in percent by weight: C, 0.16; Si < 0.01; Ni, 0.94; Al, 0.007; S, 0.005; Mn < 0.1; Mo < 0.1; Cr < 0.01; V < 0.01; P < 0.001.
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