OCCURRENCE OF CARBIDES AND GRAPHITE IN IRON METEORITES AND ORIGIN OF C-RICH IRONS. Edward R. D. Scott[1] and Joseph I. Goldstein[2], [1] Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI, 96822, USA. [2] Department of Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003, USA. E-mail: escott@hawaii.edu

Introduction: Although carbon concentrations in iron meteorites may exceed those of sulfur and phosphorus, the effects of carbon on fractional crystallization and Widmanstätten growth of kamacite are generally neglected, and few clues to the origins of irons have been derived from the occurrences of carbon-bearing phases. As an important step towards understanding how carbon affects the solidification of iron meteorites and the growth of kamacite (from which cooling rates are inferred) we present an overview of graphite and carbide occurrences with analyses of carbides, and address the origin of these phases and C-rich irons. C analyses of kamacite and taenite in carbide-rich and carbide-poor iron meteorites are given by Goldstein et al. [1]. Winfield et al. [2] provide cooling rate estimates for ten carbide-rich irons.

Carbon and carbides in irons: Carbon in irons is present in solution in Fe-Ni, as graphite, shock-formed carbon polymorphs, and the carbides, cohenite, $(Fe,Ni)_3C$, and haxonite, $(Fe,Ni)_{23}C_6$. [3, 4]. A third carbide, $Fe_{2.5}C$, was reported in Wedderburn (IIID) but has not been fully characterized [5]. $Fe_{23}C_6$ like Fe_3C is metastable relative to graphite and Fe. Calculations suggest that the former may be more stable, even though the latter is the most common precipitate in steels [6].

Haxonite can be distinguished from cohenite as it has a cubic structure and is isotropic in reflected light whereas cohenite is orthorhombic and more anisotropic than schreibersite. Mixed grains were not observed. Concentrations of Fe+Ni+Co should ideally total 94.7 wt.% for stoichiometric haxonite vs. 93.3 wt.% for cohenite. Our analyses of ~80 grains of each phase in 16 iron meteorites (Fig. 1) give Fe+Ni+Co totals that averaged 94.4 % for haxonite and 92.9 % for cohenite. The small offset of 0.3-0.4 wt.% from stoichiometry can readily be attributed to correction errors in the electron probe analyses. Note that because of these and other errors, carbides can be misidentified if the sole basis is the total Fe+Ni+Co from analyses of a single carbide phase [7]. Fig. 1 shows that the Ni range of haxonite (3.5-5.6 wt.%) in iron meteorites approaches that of kamacite (5-7%) and exceeds that for cohenite (0.7-2.3 wt.% Ni).

Occurrences and origins of graphite and carbide occurrences:

IAB main group. Rare graphite nodules up to 5 kg in mass, which have Fe-Ni veins, are found in Canyon Diablo irons [ref. 4, Fig. 488] and as separate nodules. These presumably formed in molten Fe-Ni-S-C and, like silicates, were unable to separate gravitationally. This suggests that bulk C contents exceeded a few wt.%, as in cast iron. Much more common are cm-sized nodules composed of graphite-troilite intergrowths, which probably formed from residual Fe-S-C melt near eutectic temperatures. Cliftonite is a polycrystalline graphite aggregate up to 100 μm wide with cubic morphology and spherulitic structure, formed by precipitation in kamacite [8]. Similar spherulitic textures are observed in graphite rims around silicate and troilite nodules and these appear to have formed simultaneously [4]. Graphite also forms skeletal veins in low-Ni kamacite regions that mark the prior location of carbides that decomposed in impact-heated irons like Dungannon.

Cohenite forms mm-wide elongated crystals that are aligned along the kamacite plates enclosing rounded kamacite and taenite grains [e.g., ref. 4, Fig. 197-8]. Cohenite also forms rims, which are 50-300 μm wide, around phosphides and phosphide-coated sulfide nodules. Haxonite occupies some fields of fine plessite enclosing μm-sized grains of taenite and kamacite.

Other IAB complex irons. Three low-Au subgroups of the IAB complex [9] are also C-rich. Most sLL subgroup irons have minerals that are typical of IAB main group. The sLM subgroup (formerly IIIC) and the sLM subgroup (formerly IIID) are both rich in haxonite, or graphite plausibly formed from carbide decomposition. In Edmonton (KY) and Carlton, some plessite fields contain haxonite up to several mm across, which are laden with micrometer-sized spheroidized taenite blebs and some inclusions of spheroidized plessite. Kamacite in small plessite volumes inside haxonite contains up to 4% Co cf. 0.6% elsewhere. In some areas of Tazewell, haxonite pseudomorphed the Widmanstätten kamacite, elesehwhere haxonite platelets are abundant in plessite.

Mundrabilla (IAB-ungr.) contains extensive metal-graphite intergrowths including unusual fan-shaped aggregates, in which graphite precipitated in taenite [4]. Abundant troilite nodules lack graphite and carbides appear to be absent. Graphite failed to form from the melt, either because cohenite formed instead and later decomposed or because bulk C was too low (<1-2 wt.%).

Other groups: IC. These irons contain large cohenites resembling those in IAB MG irons but lack the cm-sized graphite-troilite nodules of IAB irons.

IIAB. Cohenite forms rims on schreibersite and sulfides. Cohenite and, less commonly, haxonite form minor euhedral precipitates up to 50 µm across on rhabdites. Carbides decomposed to graphite and kamacite in about half the IIA irons, which were impact heated.

IIIAB. Carbides and graphite are rare in group IIIAB. A few IIIA irons contain small grains of cohenite (or more rarely haxonite) in plessite fields, or graphite from carbide decomposition.

IIIE. Plessite fields contain abundant haxonite (or in two irons, graphite from carbide decay).

IVA and IVB. Graphite and carbides are absent in group IVA and IVB irons and also in ungrouped irons with similarly low Ga and Ge contents.

Discussion: **Formation of carbides and graphite.** After crystallization was complete, graphite and carbides precipitated because the maximum solubility of C in kamacite is >10× less than in taenite and the solubility of C in both phases decreases with falling temperature. Graphite precipitated as cliftonite and other spherulitic morphologies but growth of graphite was effectively halted by its high degree of structural anisotropy, which generates high-energy boundaries and lattice strain. Carbides formed at low temperatures after kamacite and schreibersite, and appear to be among the last phases to appear. Cohenite was favored in low-Ni irons like those in groups IAB and IIIA whereas haxonite was favored in irons with >8-9% Ni like IIICD and IIIE in which carbide growth occurred predominantly at lower temperatures. However, the two carbides appear to have formed simultaneously, e.g., in Freda (IIID) and in IIA. Graphite growth recommenced in some irons via carbide decomposition following shock heating and deformation.

Haxonite may nucleate on taenite as suggested by [6] on the basis of the match in cell parameters of the two phases. However, haxonite can also nucleate on schreibersite in the absence of taenite, e.g., in hexahedrites. Low-temperature growth of carbides below 500°C is consistent with the high concentrations of Co observed locally in enclosed kamacite grains in plessite. These inferences appear to be consistent with the Fe-Ni-C phase diagram [10] and can be tested with ion probe carbon analyses [1].

Bulk C analyses of iron meteorites [11] show scarcely any correlation with chemical group or carbide abundance. However, ion probe analyses show taenite in carbide-rich groups is richer in C than taenite in carbide-poor irons [1]. We infer that the groups with the lowest C concentrations are IVB and IVA. The highest C concentrations are found in MG-IAB irons and a few other IAB complex irons. Groups IIAB and IIIAB where carbides are sparse probably have intermediate amounts of carbon.

Why do group I irons have more C than group IV irons? Bulk Ge increases through the sequence—IV, III, II, I—like bulk C values. Hence C and Ge appear to be correlated in iron meteorite groups. Since Ge is moderately volatile and C is highly volatile under nebula conditions, the bulk carbon concentration in iron meteorites appears to have been controlled by nebula conditions when the chondritic precursors formed.

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Fig. 1. Co vs. Ni concentrations in cohenite and haxonite from electron probe analyses of 16 iron meteorites. Haxonite grains all contain higher Ni concentrations than cohenite, and tend to have higher Co concentrations also. Bars show approximate ranges for each occurrence. Key: An: Angelica, IIIA; Ca: Carlton, IIIC (IAB-sLM); Cb: Carbo, IID; CC: Chihuahua City, IC; CD: Canyon Diablo, IAB-MG; Co: Coopertown, IIIE; Coa: Coahuila, IIA; De: Deport, IAB-sLL; Ed: Edmonton (KY), IIIC (IAB-sLM); Fr: Freda, IIID (IAB-sLH); Mb, Mbosi, ungr.; Murnpeowie, IC; NC: North Chile, IIA; SC: San Cristobal, IAB-ungr.; Ta: Tazewell, IIID (IAB-sLH).