

CARBON CONTENTS OF METALLIC PHASES IN IRON METEORITES. J. I. Goldstein¹, G. R. Huss², and E. R. D. Scott², ¹ Department of Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003, USA. ² Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI, 96822, USA. E-mail: jig0@ecs.umass.edu

Introduction: In order to understand the effects of C on the growth of phases in iron meteorites and their microstructures, we used the Cameca ims 1280 ion microprobe at the University of Hawai'i to measure the C content and the distribution of C between kamacite, taenite, and plessite regions. We analyzed IAB-IIICD irons, the iron meteorites that have the highest abundances of graphite and/or carbides, as well as meteorites that lack these phases. These data provide critical information about the effect of C on the nucleation and growth of the Widmanstätten pattern and the cloudy zone microstructure and the formation of carbides (cohenite and haxonite) during the cooling process. The ion probe allows us to measure C in kamacite, where solubility limits are <0.001 wt% (<10 ppm) at low temperatures (<400°C) [1].

Previous attempts to measure the spatial distribution of C in iron meteorites have been made using a nuclear microprobe [2] and a Cameca ims 6f ion microprobe [3]. These studies showed that martensite has a higher C content than taenite and plessite and that kamacite has the lowest C concentration. The abundances were poorly quantified in both previous studies and the C abundance in kamacite was below detection limit.

Method: One-inch round samples of the meteorites were carefully polished and areas for measurement were preselected and documented by optical microscope and SEM. Ion probe measurements were made using a Cs⁺ primary ion beam of ~0.5 nA focused to ~5-7 μm. Negative ions of ¹²C, ³¹P, ³²S, ⁵⁶Fe, ⁵⁹Co and ⁶⁰Ni ions were measured at a mass resolving power of ~7400, sufficient to resolve all molecular interferences. Before each spot was measured, the beam was rastered over a 25×25 μm² area for 10 minutes to eliminate surface contamination. Analysis time was ~30 minutes per spot including pre-sputtering. The measurements were standardized using a suite of Fe and Fe-Ni metals from the European Committee for Iron and Steel Standardization and from NIST with certified concentrations of C (0.055 to 0.79 wt%), P, S, and other minor elements. The detection limit for C is ~1 ppm wt. at 1% precision or 50-100 ppb wt. at 10% precision. Data reduction was carried out in varying combinations of 3 routines: normalizing to Fe, normalizing to Ni, and using ratios of counts/sec/nAmp.

Results: Traditional IAB irons Canyon Diablo, and Toluca have between 4±1.9 and 18±2.7 ppm (0.0004 – 0.0018 wt%) C in kamacite. Maximum taenite C contents range between 120±60 and 248±37 ppm (0.012 – 0.025 wt%), similar to values reported by Sugiura [2] for IAB irons. Figure 1 shows the distribution of C across a taenite

particle surrounded by kamacite on both sides. The C variation shows a classical “M” profile similar to the Ni variation. In these meteorites, the central portions of original taenite has decomposed into plessite, a fine-grained intergrowth of kamacite and taenite. The C is highest in the taenite next to the taenite-kamacite interface. In the plessite the C content reflects the abundance of kamacite in this region of the decomposed plessite. Figure 2. shows the direct variation of C content with Ni throughout the composition profile across the same taenite band.

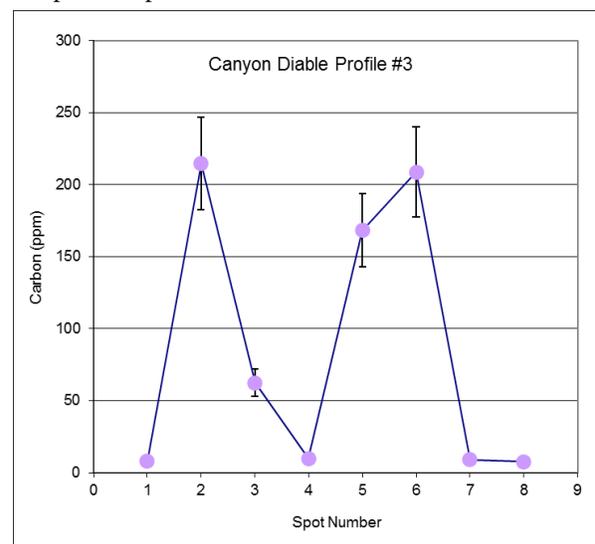


Figure 1. C variation across a Canyon Diablo (IAB) taenite band.

Measurements of C content on either side of the kamacite-taenite interface provides an opportunity to measure the partition coefficient, defined here as the taenite/kamacite ratio. The calculation is complicated by the relatively low spatial resolution of the ion probe. The 5-7 micron spot integrates the steep C concentration gradient in taenite adjacent to the boundary. Thus, the measured C abundances for taenite are lower limits on the abundance at the boundary. The maximum partition coefficients determined from the measurements for Canyon Diablo and Toluca are ~30. The actual taenite C content at the interface can be estimated, since the C content tracks directly with Ni content (Fig. 2). Extrapolation of C vs Ni to the Ni content of tetraetaenite, ~50 wt%, which is present at the kamacite/taenite boundary using Fig. 2 would give a C content of ~450 ppm and a C taenite/kamacite partition coefficient of ~65.

Results: Traditional IIICD irons Carlton IIIC, Edmonton IIIC and Dayton IIID have between 10±9 to 15±2 ppm (0.0010 to 0.0015 wt%) C in kamacite. Max-

imum taenite C contents range from 325 ± 285 and 1205 ± 181 ppm (0.0325 – 0.1205 wt%). The maximum partition coefficient calculated directly from the Edmonton measurements is ~ 150 . For Carlton, we can extrapolate the C concentration gradient to the boundary, giving an inferred C concentration in tetraetaenite of ~ 1356 ppm and a partition coefficient of ~ 135 .

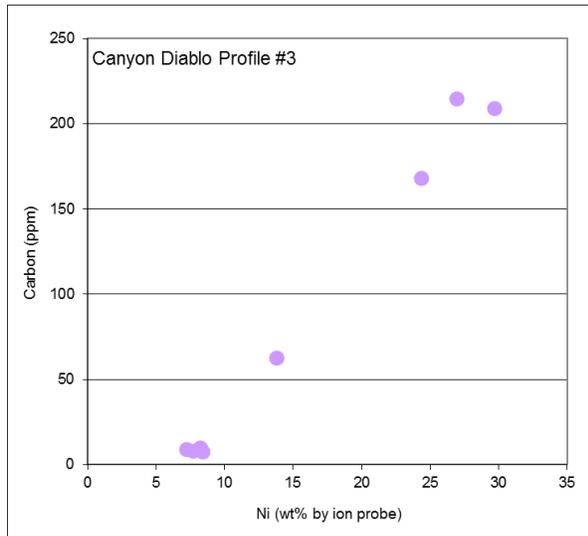


Figure 2. Variation of C with Ni content in Canyon Diablo

Results: Other irons We analyzed North Chile (IIAB), Tawallah Valley (IVB), Woodbine (Pitts Grouplet in the IAB complex), Tishomingo (ungrouped), and Estherville (Mesosiderite). The lowest kamacite C content in kamacite of ~ 4 ppm, 0.0004 wt% was measured for Tawallah Valley, a IVB. Tawallah Valley plesite, the major microstructure of this meteorite has a C content of $< \sim 6.4$ ppm. The mesosiderite Estherville also contains low C in kamacite of 3 to 6 ppm. Tishomingo which has a Ni content of ~ 32 wt%, contains a C content of 3.5 ± 1.1 ppm. The meteorite contains a matrix of martensite, distorted bcc kamacite, which formed during cooling and untransformed taenite. Woodbine, which is an ungrouped iron belonging to the IAB complex, contains the highest C in kamacite, 32 to 39 ppm. We measured 470 to 700 ppm C in the taenite in Woodbine.

Discussion: Carbon and Carbide formation. We observe a clear correlation between the measured carbon concentrations in metallic phases and the abundance of carbides and graphite in the meteorite. Estherville, Tawallah Valley and Tishomingo, which do not contain any carbides or graphite, have the lowest C concentrations in plesite, taenite and among the lowest C concentrations in kamacite. In the IAB irons, Toluca and Canyon Diablo and the IAB-related Woodbine, which are rich in graphite and carbides, and in the IIICD irons, Carlton, Edmonton, and Dayton, which have abundant haxonite, we measured maximum carbon concentrations in taenite of

100-1200 ppm. Their kamacite carbon concentrations were also systematically higher than in the three meteorites lacking graphite and carbides.

From microstructural observation, haxonite, $(\text{Fe-Ni})_{23}\text{C}_6$, forms in high Ni (> 10 wt%) taenite during cooling as taenite decomposes to a structure containing carbide and kamacite. Therefore the mineral haxonite, forms after kamacite has nucleated and the Ni “M” profile is established ($< 600^\circ\text{C}$).

According to the Fe-Ni-C phase diagram [4], there are three ways that cohenite might form in iron meteorites. Cohenite might form directly from taenite during cooling in IAB-IIICD irons, for example if the C content is above 0.5 wt% at 650°C . Cohenite can also form after Widmanstätten pattern formation in the 3 phase kamacite + taenite + cohenite field of the Fe-Ni-C phase diagram with decreasing temperature and C contents. The third mechanism for cohenite formation is exsolution directly from C supersaturated kamacite during cooling. Carbon measurements in a larger suite of IAB irons are required for a more detailed scenario for carbide formation.

Discussion: Blocking temperature and cooling rates According to the Fe-C phase diagram the solubility of C in kamacite decreases from ~ 100 ppm at 650°C to ~ 60 ppm at 600°C and ~ 20 ppm at 500°C . Our measurements of C in kamacite of ≤ 20 ppm indicate equilibration at the kamacite-taenite interface below 500°C . The rapid interstitial diffusion of carbon in bcc Fe-Ni at 500°C and below allows carbides (cohenite and haxonite) to form and grow at low cooling temperatures.

The nucleation temperature of the Widmanstätten-pattern formation is controlled by the P content of the meteorite [5]. According to the Fe-Ni-C phase diagram ~ 0.5 to 0.3 wt% C are soluble in taenite as the Widmanstätten nucleates (650 to 550°C). This range of C will not measurably increase the diffusion of Ni [6]. Meteorite cooling rates will control 1) the lowest temperature at which C equilibrium between kamacite and taenite [2] can no longer be attained, and 2) the measured partition coefficient of C between kamacite and taenite at the kamacite-taenite interface. Preliminary measurements of IAB-IIICD cooling rates and possible cooling rate variations are available to investigate these effects [7].

References: [1] Kleemola H. J. and Kuusisto E. A. (1976) *Scand. J. Met.*, 5, 151-158. [2] Makjanic J., et al. (1988) *Nucl. Instrum. Methods Phys. Res.*, B30, 466-469. [3] Sugiura N. (1998) *MAPS.*, 33, 393-409. [4] Scott E. R. D. and Wasson J. (1975) *Rev. Geophysics Space Physics*, 13, 527-546. [5] Romig A. D. and Goldstein J. I. (1978) *Met Trans A*, 9A, 1599-1609. [6] Yang J. and Goldstein J. I. (2005) *MAPS*, 40, 239-253. [7] Wells C. and Mehl R. G. (1941) *Trans. Met. Soc. AIME*, 145, 329-338. [7] Winfield T., et al.. (2012) *LPS* 43.