Igneous graphite in enstatite chondrites

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Abstract

Igneous graphite, a rare constituent in terrestrial mafic and ultramafic rocks, occurs in three EH and one EL enstatite chondrite impact-melt breccias as 2–150 μm long euhedral laths, some with pyramidal terminations. In contrast, graphite in most enstatite chondrites exsolved from metallic Fe-Ni as polygonal, rounded or irregular aggregates. Literature data for five EH chondrites on C combusting at high temperatures show that Abee contains the most homogeneous C isotopes (i.e. $\delta^{13}C = -8.1 \pm 2.1‰$); in addition, Abee's mean $\delta^{13}C$ value is the same as the average high-temperature C value for the set of five EH chondrites. This suggests that Abee scavenged C from a plurality of sources on its parent body and homogenized the C during a large-scale melting event. Whereas igneous graphite in terrestrial rocks typically forms at relatively high pressure and only moderately low oxygen fugacity (e.g., ~5 kbar, $\log f_{O_2} \sim -10$ at 1200°C), igneous graphite in asteroidal meteorites formed at much lower pressures and oxygen fugacities.

KEYWORDS: igneous graphite, enstatite chondrite, impact-melt breccia, oxygen fugacity.

Introduction

GRAPHITE is a rare constituent of terrestrial igneous rocks, primarily occurring in mafic and ultramafic xenoliths in kimberlites and alkali basalts (e.g. Hatton and Gurney, 1979; Robinson, 1979; Kornprobst *et al.*, 1987; Pearson *et al.*, 1990; Field and Haggerty, 1990) and in intercumulus regions of layered intrusions (e.g. Hollister, 1980; Balhaus and Stumpfl, 1985). On plots of $\log f_{O_2}$ *vs.* $1/T$, the graphite surface (i.e. the $C-CO+CO_2$ buffer) is pushed toward higher $\log f_{O_2}$ values by higher pressures. Because most terrestrial igneous rocks did not form at very low oxygen fugacities, most igneous graphite occurs in rocks that formed at relatively high pressures and moderately low f_{O_2}: e.g. $P \sim 5$ kbar (~ 0.5 GPa) at $\log f_{O_2} \sim -10$ and $T \sim 1200$°C for ultramafic xenoliths in alkali basalt from a strombolian cone in the Algerian Sahara (Kornprobst *et al.*, 1987).

Except for small numbers of lunar and martian meteorites, meteorites are derived from asteroids. Because asteroids are far smaller than planets (in the TRIAD survey of asteroids $\geqslant 10$ km in diameter, 95% were found to have diameters <200 km; Fig. 1 of Hughes, 1982), high internal pressures cannot be achieved. The pressure P at the centre of a 200 km diameter body with a uniform density of 3.6 g cm^{-3} can be determined to be ~ 200 bar (~ 0.02 GPa) from eqn 1 (after eqn 2-63 of Turcotte and Schubert, 1982):

$$P = (2/3)\ \pi\ D^2\ G\ (a^2 - r^2) \qquad (1)$$

where D is the density, G is the gravitational constant, a is the radius of the body and r is the radius minus the depth. Thus, if igneous graphite occurs in asteroids it must form at low pressure and very low values of f_{O_2} rather than at high pressure and only moderately low f_{O_2}.

Primary igneous graphite has been reported in two relatively unshocked ureilites (carbonaceous olivine-pyroxene achondritic meteorites) where it occurs as euhedral laths, some of which possess pyramidal terminations (Berkley and Jones, 1982; Treiman and Berkley, 1994). These rocks are inferred to have formed at $P \geqslant 100$ bar (i.e. $\geqslant 0.01$ GPa) on bodies $\geqslant 200$ km in diameter at $\log f_{O_2}$ values of -14 ± 1.5 and $T \sim 1200$°C (Warren and Kallemeyn, 1992; Walker and Grove, 1993).

Some of the graphite crystals within shock-melted clasts in the Krymka LL3.1 ordinary chondrite occur as euhedral laths with pyramidal terminations (Semenenko, 1996; Semenenko and Girich, 1995). These graphite grains probably formed via crystallization of a cooling impact melt. The probable source of the carbon is organic material found within

Mineralogical Magazine, October 1997, Vol. 61, pp. 699–703

several carbonaceous inclusions in Krymka (Semenenko *et al.*, 1991).

We report here the first occurrences of igneous graphite (i.e. graphite grains that crystallized from a melt) in EH and EL enstatite chondrites, the most reduced chondritic meteorites. These rocks are characterized by the presence of graphite, Si-bearing kamacite, low-FeO enstatite and several unusual sulphides with cations that, under more oxidizing conditions, partition into silicate and oxide minerals: oldhamite [CaS], niningerite [(Mg,Fe)S] or ferroan alabandite [(Mn,Fe)S], Ti-bearing troilite [FeS], Mn-bearing daubréelite [$FeCr_2S_4$], caswellsilverite [$NaCrS_2$] and djerfisherite [$K_6Na(Fe,Cu)_{24}S_{26}Cl$]. Oxide phases other than free silica are absent.

Petrography

Graphite is a common, albeit accessory phase in enstatite chondrites. In most enstatite chondrites it occurs as polygonal, rounded or irregular aggregates of randomly oriented laths inside kamacite (e.g. Figs. A32 and A37 of Ramdohr, 1973). Because the solubility of C in kamacite is very low ($\sim$0.2 mg/g; Scott, 1971), the graphite is presumed to have exsolved from taenite during cooling from $\geqslant$700°C.

In contrast, abundant euhedral laths of graphite were identified in three EH chondrites (Abee, Yamato 791790 (Y-791790) and Yamato 791810 (Y-791810); Rubin and Keil, 1983; Rubin and Scott, 1997) and one EL chondrite (Queen Alexandra Range 94368 (QUE94368); Rubin, 1997). A single euhedral graphite lath was identified in another EH chondrite, Adhi Kot (Rubin, 1983). Although most graphite in Adhi Kot occurs as aggregates within metallic Fe-Ni, all of the graphite in Abee, Y-791790 and Y-791810, and most of the graphite in QUE94368, occur as euhedral laths. The euhedral laths exhibit excellent {0001} cleavage, moderate bireflectance and extreme anisotropy.

Euhedral graphite laths in Abee vary significantly in size: 0.3–6 μm × 8–75 μm; those in Y-791790 and Y-791810 are somewhat smaller and have narrower size distributions (i.e. 0.5–1.5 μm × 2–23 μm, and 0.6–4 μm × 4–19 μm, respectively). Euhedral graphite in QUE94368 varies from 4 × 34 μm to 16 × 150 μm (Rubin, 1997). Some of the graphite laths in Abee and QUE94368 have pyramidal terminations. In some instances, two or three graphite laths form clusters. Many of the clusters in Abee are V-shaped (Fig. 1); in a few cases, the clusters form second-order dendrites, some of which radiate from the surface of silicate grains into the surrounding sulphide. Many of the euhedral graphite laths occur in silicate-rich areas, surrounded mainly by enstatite; I observed one lath in Abee that is almost entirely inside a euhedral enstatite grain and is aligned perpendicular to the *c*-axis of the enstatite. Other euhedral graphite laths in Abee are surrounded by troilite and/or niningerite. Many of the laths on the margins of silicate grains or protruding from silicate into sulphide are slightly bent. None of the laths occurs entirely within metallic Fe-Ni.

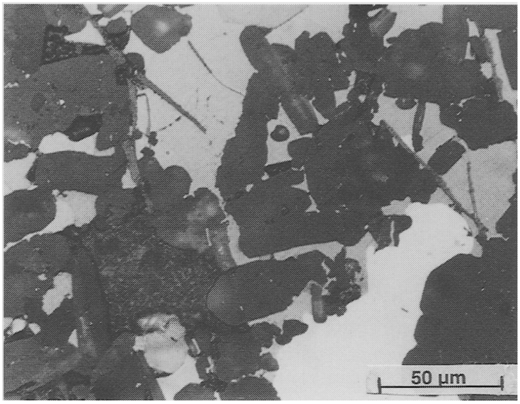

FIG. 1. Reflected light photomicrograph of branching euhedral graphite laths (medium grey, upper left and far right) in the Abee EH enstatite chondrite. The graphite laths occur inside troilite (light grey) and adjacent to silicate grains (dark grey). White region at bottom right is kamacite. The graphite laths, which closely resemble primary igneous graphite in terrestrial ultramafic rocks, most likely crystallized from an enstatite-chondrite impact melt.

Discussion

Igneous character of the whole rocks. It is unlikely that the euhedral graphite grains in Abee, Adhi Kot, Y-791790, Y-791810 and QUE94368 are products of metamorphism. All of these rocks are impact-melt breccias (Rubin and Scott, 1997; Rubin, 1997). The surface energy anisotropy of graphite is much lower than that of orthopyroxene [i.e. $\sim$50 *vs.* $\sim$250 erg cm^{-2} ($\sim 5 \times 10^{-6}$ *vs.* $\sim 2.5 \times 10^{-5}$ J cm^{-2}); Table 7 of Spry, 1969]; thus, orthopyroxene grains in metamorphic rocks would be idioblastic towards graphite and most graphite grains would be bent and restricted to silicate grain boundaries. In contrast, most graphite grains in Abee, Y-791790, Y-791810 and QUE94368 are euhedral and not appreciably bent; it therefore seems likely that they are igneous crystals. If this is the case, their host chondrites must have contained significant amounts of melt. Rubin and Scott (1997) argued that these meteorites are impact-melt breccias. Because Abee is the largest enstatite chondrite (107 kg) and the subject of numerous investigations, the remainder of the discussion focuses on this rock. The low abundance of chondrules in Abee (~2–3 vol.%) compared to unmelted EH3 chondrites (15–20 vol.%) suggests that 80–90% of Abee's chondrules were melted; many of the remaining chondrules were partly resorbed. These relict chondrules served as nucleation sites for euhedral enstatite grains that crystallized from the silicate impact melt. As the melt cooled, the euhedral enstatite crystals were entrained in the residual metal-sulphide melt. This melt collected into voids and formed kamacite globules and metal-sulphide-rich regions.

Carbon in Abee. Abee contains 4.212 mg/g total carbon (Grady *et al.*, 1986), most of which occurs in four distinct forms: (1) euhedral laths of graphite (the most abundant form, described above), (2) ~100 nm to ~1 μm size diamonds which constitute ~100 μg/g of Abee (Russell *et al.*, 1992) and most likely formed from graphite by shock-compression/transformation (Rubin and Scott, 1997), (3) thin cohenite exsolution lamellae within kamacite implying that Abee metal cooled from ~700°C to 200°C within several hours (Herndon and Rudee, 1978; Rudee and Herndon, 1980), and (4) small amounts (~320 ng/g) of light hydrocarbon gases (e.g. methane, benzene, ethylene, acetylene and ethane) trapped between crystal boundaries (Belsky and Kaplan, 1970).

Grady *et al.* (1986) measured the C isotopic composition of Abee and four unmelted EH chondrites (Indarch, Kota-Kota, South Oman and St. Mark's). In order to minimize problems with the data associated with possible contamination with terrestrial C, Grady *et al.* considered only the C combusting at the five temperature steps between 800°C and 1200°C inclusive. The mean $\delta^{13}C$ values and standard deviations for the five steps in each EH chondrite are as follows: Abee, -8.1 ± 2.1‰; Indarch, -10.6 ± 5.7‰; Kota-Kota, -3.3 ± 4.4‰; South Oman, -10.6 ± 2.6‰; St. Mark's, -7.7 ± 5.4‰. The average $\delta^{13}C$ value of the five high-temperature steps for the set of five EH chondrites is -8.1‰.

These data show that, among the five EH chondrites studied, Abee contains the most homogeneous C isotopes and has an average high-temperature C isotopic composition identical to the mean EH $\delta^{13}C$ value. These results suggest that Abee scavenged C from a plurality of sources on the EH parent body and that some process (e.g. large-scale melting) homogenized this C. This could have been accomplished by an impact-melting event as suggested by Rubin and Scott (1997). Prior to impact melting, the carbon in Abee may have occurred as graphite aggregates within kamacite (formed by exsolution of C from metallic Fe-Ni during cooling) and/or as organic material within the matrix (as in EH3 Qingzhen and other enstatite chondrites; Huss and Lewis, 1995; Grady *et al.*, 1986).

Formation conditions of Abee graphite. The presence of euhedral graphite laths completely enclosed within silicate implies that the graphite crystallized from a silicate-rich melt prior to or commensurate with crystallization of silicate. As is the case for the euhedral-graphite-bearing ureilites (Treiman and Berkley, 1994), some Abee graphite grains span different silicate grains; this suggests that the silicate-rich melt was abundant and not just an intergranular film.

The temperature of the Abee impact melt is difficult to constrain, but a lower limit can be estimated from the CaS component in niningerite (Skinner and Luce, 1971); the temperature is a minimum because it is unknown how much CaS exsolved from niningerite during cooling. Plotting the data of Keil (1968) on the FeS-MgS-CaS phase diagram, Skinner and Luce (1971) obtained a temperature of 880°C. Fogel *et al.* (1989) used recent thermodynamic data to modify the enstatite-oldhamite geothermometer of Larimer and Buseck (1974) and obtained a temperature of 910°C for Abee.

In order to estimate the $\log f_{O_2}$ value of the impact melt from which the euhedral graphite laths in Abee crystallized, it is necessary to construct a model of the EH parent body and estimate the temperature of the melt. I assume that the body was 100 km in diameter and had a uniform density of 3.6 g cm^{-3}. The assumption of uniform density is reasonable for a body that is undifferentiated and too small to have elevated densities due to internal compression. The assumed density is that of Abee (Mason, 1966). I also assume the temperature of the impact melt to be 900°C (the estimated lower limit obtained above). Because Abee is an impact-melt breccia, it is likely that the melt formed relatively near the surface. I make three estimates of the depth of melting: 0.1 km, 1 km and 10 km. Using eqn 1, I find that these depths correspond to lithostatic pressures of ~0.2 bar, ~2 bar and ~20 bar, respectively.

Figure 2 is an extrapolation of the $\log f_{O_2}$ *vs.* $10^4/T$ equilibrium diagram of Brett and Sato (1984). This plot is not strictly applicable to the Abee impact melt because it was a disequilibrated assemblage, i.e. it was not in equilibrium at the lithostatic pressure where it formed in its parent body. Thus, the oxygen fugacity of the impact melt was determined by highly localized conditions. Because these conditions are extremely difficult to model, I use Fig. 2 to obtain very rough estimates of the oxygen fugacity of the Abee melt. For depths of 0.1 km, 1 km and 10 km, the $\log f_{O_2}$ values are ~−20, ~−19 and ~−18,

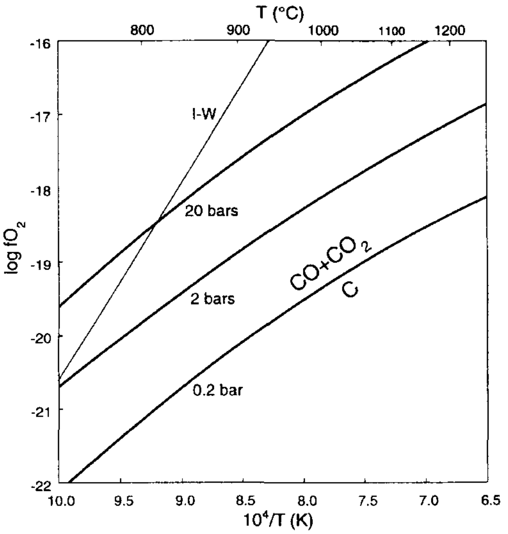

FIG. 2. Variation in the log f_{O_2} values of the graphite surface (i.e. the $C-CO+CO_2$ buffer) with temperature. There is a positive correlation between log f_{O_2} and pressure. The iron-wüstite (I-W) buffer is shown for reference. After Brett and Sato (1984).

respectively. If the temperature of the impact melt were 1000°C instead of 900°C, the log f_{O_2} values would be ~ -19, ~ -18 and ~ -17, respectively. If the temperature were 1200°C, the log f_{O_2} values would increase by <1.0. [If the EH parent body were 50 km in diameter instead of 100 km, the log f_{O_2} values would not change significantly (i.e. ~ -20, ~ -18 and ~ -17, respectively, at 1000°C for depths of 0.1 km, 1 km and 10 km).] These oxygen fugacities are far below those of terrestrial melts containing igneous graphite (e.g. log f_{O_2} ~ -10; Kornprobst *et al.*, 1987) and somewhat lower than those of the parent melts of ureilites (log f_{O_2} ~ -14; Warren and Kallemeyn, 1992; Walker and Grove, 1993).

Although the oxygen fugacity values for the Abee impact melt are only rough estimates, it seems reasonable to conclude that igneous graphite in asteroidal meteorites formed at much lower oxygen fugacities than typical graphite-bearing terrestrial igneous rocks.

Acknowledgements

I thank P. Warren for useful discussions, G.W. Kallemeyn for technical assistance, and M.M. Grady for a helpful review. This work was supported in part by NASA grant NAGW 3535 (J.T. Wasson, P.I.).

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[*Manuscript received 5 June 1996: revised 23 January 1997*]