

Explicating the behavior of Mn-bearing phases during shock melting and crystallization of the Abee EH-chondrite impact-melt breccia

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Abstract—Literature data show that, among EH chondrites, the Abee impact-melt breccia exhibits unusual mineralogical characteristics. These include very low MnO in enstatite (<0.04 wt%), higher Mn in troilite (0.24 wt%) and oldhamite (0.36 wt%) than in EH4 Indarch and EH3 Kota-Kota (which are not impact-melt breccias), low Mn in keilite (3.6–4.3 wt%), high modal abundances of keilite (11.2 wt%) and silica (~7 wt%, but ranging up to 16 wt% in some regions), low modal abundances of total silicates (58.8 wt%) and troilite (5.8 wt%), and the presence of acicular grains of the amphibole, fluor-richterite. These features result from Abee's complex history of shock melting and crystallization. Impact heating was responsible for the loss of MnO from enstatite and the concomitant sulfidation of Mn. Troilite and oldhamite grains that crystallized from the impact melt acquired relatively high Mn contents. Abundant keilite and silica also crystallized from the melt; these phases (along with metallic Fe) were produced at the expense of enstatite, niningerite and troilite. Melting of the latter two phases produced a S-rich liquid with higher Fe/Mg and Fe/Mn ratios than in the original niningerite, allowing the crystallization of keilite. Prior to impact melting, F was distributed throughout Abee, perhaps in part adsorbed onto grain surfaces; after impact melting, most of the F that was not volatilized was incorporated into crystallizing grains of fluor-richterite. Other EH-chondrite impact-melt breccias and impact-melt rocks exhibit some of these mineralogical features and must have experienced broadly similar thermal histories.

INTRODUCTION

Abee, the largest (107 kg) enstatite-chondrite fall, is an EH-chondrite impact-melt breccia (Dawson et al. 1960; Marti 1983; Rubin and Scott 1997; Rubin et al. 1997) with a ^{53}Cr age of ~4565 Ma (Shukolyukov and Lugmair 2004). The Abee breccia comprises ~50 vol% subangular to subrounded clasts up to 22 cm in maximum dimension (Rubin and Keil 1983; Kempton 1996), ~50 vol% interclastic matrix, and ~0.2 vol% subcentimeter-size oldhamite-rich dark inclusions.

Most of the chondrules that were present initially in Abee were melted; relict chondrules served as nucleation sites for some of the euhedral enstatite grains that crystallized from the impact melt (Fig. 2d of Rubin and Scott 1997). Euhedral enstatite grains also occur in other EH impact-melt breccias (e.g., Yamato [Y-] 791790 and Y-791810; Fig. 6 of Rubin and Scott 1997) and EH impact-melt rocks (e.g., Y-86760; Fig. 1e of Kimura and Lin 1999).

Euhedral graphite laths with pyramidal terminations, morphologically similar to those produced magmatically on Earth in some ultramafic rocks (e.g., Kornprobst et al. 1987),

occur throughout Abee (Rubin 1997). Euhedral graphite is also present in other EH impact-melt breccias (e.g., Adhi Kot Y-791790, Y-791810; Rubin and Scott 1997) and EH impact-melt rocks (e.g., Queen Alexandra Range [QUE] 94204; Weisberg et al. 1997).

Compared to the mineral compositions in most unmelted EH3–5 chondrites, many of the phases in Abee have extreme (or near-extreme) concentrations (high or low) of Mn. Several of the Mn-bearing phases have extreme modal abundances compared to typical EH3–5 chondrites. An understanding of the compositions and abundances of the different Mn-bearing minerals can shed light on Abee's complex, multi-stage shock-melting and crystallization history.

DISCUSSION

Unusual Mineralogical Features

The Abee breccia exhibits several unusual mineralogical characteristics (Table 1) that resulted from shock processes and their aftereffects. Several other EH chondrites have

Table 1. Unusual mineralogical characteristics of Abee.^a

1.	Very low MnO in most grains of enstatite (below detection limit). Most EH3–5 chondrites have enstatite with 0.13–0.20 wt% MnO.
2.	High concentration of Mn in troilite (0.24 wt%). Most EH3–5 chondrites have troilite with 0.05–0.11 wt% Mn.
3.	High concentration of Mn in oldhamite (0.36 wt%). EH4 Indarch has oldhamite with 0.22 wt% Mn.
4.	Low concentrations of Mn in keilite (3.6–4.3 wt%). Most EH3–5 chondrites have keilite or niningerite with 6.5–11.8 wt% Mn.
5.	Highest modal abundance of keilite (11.2 wt%). Other EH3–5 chondrites have 0.32–3.4 wt% niningerite or keilite.
6.	Low modal abundance of total silicates (58.8 wt%). Other EH3–5 chondrites have 68–73 wt% silicates.
7.	Low modal abundance of troilite (5.8 wt%). Other EH3–5 chondrites have ~7–10 wt% troilite.
8.	High modal abundance of silica (~7 wt%); up to 16 wt% in some clasts. Most EH3–5 chondrites have 1 wt% silica; many have <0.1 wt%.
9.	Occurrence of euhedral graphite blades. This graphite morphology is absent in most EH3–5 chondrites.
10.	Occurrence of fluor-richite. This phase is absent in most EH3–5 chondrites.

^a1–7 from Keil (1968); 8, 9 from Rubin and Keil (1983); 10 from Douglas and Plant (1969).

similar mineral compositions, grain morphologies, and/or modal abundances.

There are two compositional varieties of enstatite grains in enstatite chondrites. Low-MnO enstatite exhibits blue luminescence under electron bombardment; MnO-bearing enstatite exhibits red luminescence (e.g., Keil 1968; Leitch and Smith 1982; Weisberg et al. 1994).

Manganese in enstatite chondrites occurs as an MnS component in sulfide and, to a small extent, as MnO in enstatite. EL6 enstatite is essentially MnO free, whereas enstatite in most EH3–5 chondrites averages 0.13–0.20 wt% MnO (Keil 1968). The MnO contents of most enstatite grains in Abee are below the electron-microprobe detection limit (Keil 1968), although Leitch and Smith (1982) reported some red-luminescing grains in Abee that average 0.16 wt% MnO. Weisberg et al. (1994) found that some FeO-rich pyroxene grains in EH3 and EL3 chondrites are rimmed by enstatite with low MnO contents. Enstatite with low MnO also occurs in the EH impact-melt rocks Y-82189, Y-8414 and Y-86004 (Lin and Kimura 1998), in EH6 Y-8404, EH6-an Y-793225, and in EH5 St. Sauveur (Lin and Kimura 1998; Keil 1968).

Keil (2007) found that keilite [(Fe,Mg)S] (Shimizu et al. 2002) occurs instead of niningerite [(Mg,Fe)S] only in enstatite-chondrite impact-melt rocks and impact-melt breccias; the occurrence of keilite in St. Sauveur suggests that this understudied rock might also be an impact-melt breccia. Keil (2007) identified large euhedral enstatite crystals surrounded by kamacite in St. Sauveur. This texture resembles that of Abee (e.g., Fig. 1 of Rubin and Keil 1983) and other enstatite-chondrite impact-melt breccias and impact-melt rocks (e.g., Fig. 6 of Rubin and Scott 1997; Fig. 1 of Lin and Kimura 1998); it is consistent with the crystallization of St. Sauveur enstatite from a metal- and

sulfide-bearing, silicate-rich impact melt. From quenching-rate experiments on solid solutions of sulfides, Skinner and Luce (1971) concluded that both Abee and St. Sauveur cooled through the temperature interval 800–500 °C at rates exceeding 0.1 °C s⁻¹. Such a rapid quench is consistent with both Abee and St. Sauveur being impact-melt breccias.

During impact heating of EH impact-melt breccias and impact-melt rocks, MnO was lost from enstatite and underwent sulfidation, slightly enriching the melt in MnS. Such MnO sulfidation also occurred during heating of many EL6 chondrites (e.g., Rubin 2006), whether the heating was caused by thermal metamorphism or impact events. This inference is consistent with the occurrence of detectable MnO in most enstatite grains in the precursors of enstatite-chondrite impact-melt breccias, i.e., in unmelted EH3 chondrites (<0.04–0.34 wt% MnO; Fig. 1 of McKinley et al. 1984; Table 3 of Lusby et al. 1987) and unmelted EL3 chondrites (e.g., 0.05–0.19 wt% MnO; Schneider et al. 2002). Subsequent annealing homogenized the mineral compositions in EL6 chondrites and EH impact-melt rocks, causing any unmelted enstatite grains within relict chondrules to develop low MnO contents. In contrast, Abee (an impact-melt breccia) underwent little annealing and thus retained enstatite of diverse compositions (see below).

Troilite in Indarch, an unmelted EH4 chondrite, averages 0.11 wt% Mn (Keil 1968). Abee contains troilite with much higher Mn (0.24 wt%; Keil 1968); among EH chondrites, only Adhi Kot, another EH impact-melt breccia (Rubin 1983a), has a higher value (0.34 wt% Mn). Troilite with high Mn is also found in St. Sauveur (0.17 wt% Mn; Keil 1968) and in EH6 Y-8404 and the EH impact-melt rocks Y-8414 and Y-86004 (0.19–0.22 wt% Mn; Lin and Kimura 1998).

Oldhamite in Indarch averages 0.22 wt% Mn (Keil 1968). Abee oldhamite has appreciably higher Mn concentrations (0.36 wt%), only slightly lower than those in Adhi Kot and St. Sauveur (0.39 wt%) (Keil 1968). Oldhamite in the Y-8414 EH impact-melt rock contains 0.2–0.3 wt% Mn (Lin and Kimura 1998). Troilite and oldhamite in Abee crystallized from the impact melt after it had been enriched in Mn by the melting of pre-existing niningerite; MnS is soluble in both FeS and CaS (Skinner and Luce 1971).

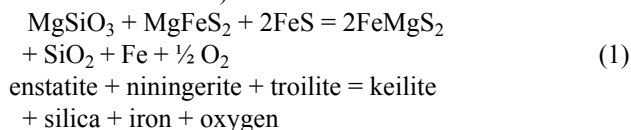
Abee has relatively low Mn concentrations in keilite (4.0 wt%; Keil 1968), similar to that in the (Mg,Mn,Fe)S phases in EH6 Y-8404 and the EH impact-melt rocks Y-8414 and Y-86004 (3.8 wt% Mn; Lin and Kimura 1998). Keilite and niningerite in other EH chondrites contain appreciably higher Mn, i.e., 6.5–11.8 wt% (Keil 1968).

The extremely high modal abundance of keilite in Abee (11.2 wt% versus <0.1–7.0 wt% keilite and niningerite in other EH chondrites; Keil 1968; Lin and Kimura 1998), indicates that a larger proportion of Mn occurs in sulfide in Abee than in other EH chondrites. In Abee, post-impact crystallization resulted in the formation of relatively Mn-rich troilite, relatively Mn-rich oldhamite, abundant enstatite with

very low MnO, and abundant (but only moderately Mn-rich) keilite. The relatively low Mn contents of keilite resulted from the dilution in the impact melt of Mn (and Mg) from the original niningerite by the concomitant melting of troilite (FeS). Hence, the impact melt had higher Fe/Mg and Fe/Mn ratios than the original niningerite grains.

Abee has the lowest modal abundance of silicates among EH chondrites: 58.8 wt% versus 72.6 wt% in EH4 Indarch and 77.7 wt% in EH6-an Y-793225 (Keil 1968; Lin and Kimura 1998).

The unmelted EH4 chondrite Indarch contains 7.3 wt% troilite (Keil 1968). In contrast, Abee has the second lowest modal abundance of troilite among EH chondrites (5.8 wt%; Keil 1968); the Y-8414 EH impact-melt rock has 4.3 wt% (Lin and Kimura 1998). Adhi Kot also has a low modal abundance of troilite (6.1 wt%; Keil 1968). These modal abundances may reflect production of Fe-Mg sulfide (keilite), silica, and metallic Fe at the expense of enstatite, niningerite and troilite via a reaction similar to that illustrated in Reaction 1 (wherein the formula units used for niningerite and keilite are doubled):



This reaction is broadly consistent with the occurrence of high mean modal silica in Abee (~7 wt%) and the occurrence of up to 16 wt% silica in some centimeter-size clasts in Abee (Table 1 of Rubin and Keil 1983). High modal silica also occurs in EH6 Y-8404 (13.0 wt%), and the EH impact-melt rocks Y-8414 (5.8 wt%) and Y-86004 (6.5 wt%) (Lin and Kimura 1998). (Volumetric data from Lin and Kimura were converted into wt% assuming the following mineral specific gravities: enstatite, 3.2; plagioclase, 2.61; silica, 2.32; kamacite, 7.6; schreibersite, 7.1; niningerite, 3.6; and troilite, 4.6.)

Silica-rich clasts (3–5 mm in size) in Adhi Kot (Rubin 1983a) contain abundant keilite (3–15 wt%) and up to twice as much silica (18–28 wt%) as enstatite (12–14 wt%). These clasts lack chondrules and are probably impact-melt products.

Silica is present in other enstatite chondrites; e.g., EH3 Safara 97096 contains 4.3 vol% silica (Weisberg and Prinz 1998). However, in most enstatite chondrites the modal abundance of silica is low. For example, EH6-an Y-793225 contains 0.26 wt% silica (Lin and Kimura 1998). The two analyzed chondrule-rich clasts in Adhi Kot contain <0.1 and 1 wt% silica, respectively (Table 1 of Rubin 1983a). No silica was reported in EL6 Atlanta (Rubin 1983b) or EL6 Hvittis (Rubin 1983c). Although Binns (1967) reported accessory cristobalite in EL6 Blithfield, Rubin (1984) failed to find any silica grains. Sears et al. (1984) reported no silica in EH5 Reckling Peak (RKP) A80259; Fagan et al. (2000) reported that one chondrule fragment in this meteorite has relatively abundant silica, but that elsewhere, silica occurs only in trace amounts.

The silica in enstatite chondrites is present as quartz, tridymite, cristobalite and SiO₂-rich glass (Kimura et al. 2005). Abee and other EH impact-melt breccias contain tridymite and/or cristobalite; quartz is rare in these rocks and SiO₂-rich glass is absent (Kimura et al. 2005). Although Dawson et al. (1960) reported quartz and cristobalite in Abee, Mason (1966) and Rubin and Keil (1983) reported only cristobalite, and Kimura et al. (2005) reported only tridymite and cristobalite.

Summary of Abee's Shock History

I assume that Abee, like all EH chondrites, started off as EH3 material. This is consistent with the presence in Abee of readily recognizable relict chondrules (e.g., Fig. 2d of Rubin and Scott 1997) and the inferred presence of SiC (the host phase of Ne-E (H), trace amounts of which were identified in an Abee acid-etched residue; Huss and Lewis 1995). Unrecrystallized chondrules and SiC are abundant in EH3 chondrites.

The EH3 material from which Abee is inferred to have formed probably contained MnO-bearing enstatite (as in EH3 Kota-Kota and ALHA77156; Table 3 of Keil 1968; Fig. 1 of McKinley et al. 1984). The Abee progenitor may have had typical EH3 modal mineral abundances, broadly similar to those in EH4 Indarch (Table 2 of Keil 1968), but also including minor forsteritic olivine (Mg₂SiO₄), diopside (CaMgSi₂O₆) and perryite [(Ni,Fe)₅(Si,P)₂], and accessory sphalerite [(Zn,Fe)S], djerfisherite [K₆Na₉(Fe,Cu)₂₄S₂₆Cl], and caswellsilverite (NaCrS₂). Prior to impact melting, the principal Mg- and Fe-bearing sulfide in Abee was probably niningerite rather than keilite (Keil 2007).

Rubin and Scott (1997) inferred that an energetic impact event caused melting of much of the Abee whole rock; 80–90% of the chondrules were destroyed. The presence of euhedral enstatite grains that crystallized from the melt indicates that temperatures probably reached at least 1500 °C (McCoy et al. 1999; Keil 2007). During the shock event, MnO from enstatite underwent sulfidation, slightly enriching the melt in an MnS component. During cooling, euhedral enstatite grains crystallized from the melt and, in some cases, nucleated on partially resorbed relict chondrules. Euhedral graphite laths also crystallized from the melt. The oldhamite-rich dark inclusions (Fig. 1 of Marti 1983; Fig. 2 of Rubin and Keil 1983) formed at this time from melts that had drained away from most of the Abee residuum. Abundant keilite, along with relatively Mn-rich troilite and relatively Mn-rich oldhamite, crystallized from the melt.

Some of the melt filled voids in the rock and formed kamacite-rich globules (Dawson et al. 1960), which occur in both the clasts and the matrix. Euhedral grains of enstatite crystallized in many of these metal-rich melt-filled voids prior to the solidification of these filled voids as kamacite-rich globules (e.g., Fig. 2c of Rubin and Scott 1997).

After the initial impact-melting episode, Abee cooled

through the Curie temperatures of kamacite [α -(Fe,Ni)] (~750 °C) and cohenite [(Fe,Ni,Co)₃C] (215 °C) (with cohenite having the more stable magnetic component) and acquired a uniform magnetic orientation (Rubin and Scott 1997).

One or more subsequent impact events shattered the Abee impact-melt rock producing a poorly sorted mixture of sand, granules, pebbles and cobbles ranging in maximum dimension from <0.1 cm to 22 cm (Rubin and Keil 1983; Rubin and Scott 1997; Kempton 1996). The fragments were jumbled by these impacts, randomizing their magnetic orientations (Sugiura and Strangway 1983).

Another energetic impact event preferentially melted the fine-grained Abee material and engulfed the pebbles and cobbles (which survived to become clasts). Heat lost to the cold clasts caused the groundmass (matrix) melt to quench, producing a dearth of clasts <1 mm in size (Wacker 1982). The matrix acquired a uniform magnetic orientation (Sugiura and Strangway 1983) as it cooled through the Curie temperatures of kamacite and cohenite; the interiors of the clasts remained cold (at temperatures below the Curie points of kamacite and cohenite) and retained their near-random magnetic orientations.

Quenching of the melt to ~500 °C was responsible for the retention of keilite; if Abee had cooled slowly (or had been subsequently annealed), the keilite would have exsolved into troilite and niningerite (Keil 2007). Quenching of Abee with little or no subsequent annealing is consistent with the occurrence in this rock of tridymite and cristobalite and the absence of quartz (Kimura et al. 2005). It is also consistent with the preservation of enstatite grains of diverse MnO contents (Fig. 7 of Leitch and Smith 1982). The presence of cohenite exsolution lamellae in Abee kamacite indicates rapid cooling (700 °C to 200 °C in ~2 hours; Herndon and Rudee 1978; Rudee and Herndon 1980). Finally, the quenching-rate studies of Skinner and Luce (1971) are consistent with cooling of Abee from 800 °C to 500 °C in approximately 2 days.

Similar igneous textures in Abee were produced in the matrix as in the clasts, but, because of quenching, the reaction did not proceed in the matrix as far as it did in the clasts during the first extensive impact-melting event. This would account for the matrix regions containing more enstatite (49 ± 4 versus 32 ± 9 wt%), less silica (3 ± 2 versus 9 ± 7 wt%) and less keilite (3 ± 0 versus 9 ± 6 wt%) than the clasts (Table 1 of Rubin and Keil 1983). Metal-sulfide melts froze in place at the margins of the clasts and dark inclusions (e.g., Fig. 3 of Rubin and Keil 1983); many of these metal-sulfide melts contain euhedral enstatite grains (Fig. 1 of Rubin and Keil 1983).

Also present in the Abee matrix are rare 3.5 mm long acicular grains of the amphibole fluor-richterite [Na₂Ca(Mg,Fe)₅Si₈O₂₂F₂] (Douglas and Plant 1969; Olsen et al. 1973). These grains occur in clusters of radiating

crystals within kamacite globules in association with enstatite, troilite, keilite, (and, possibly, albite and graphite) (Douglas and Plant 1969). Fluor-richterite also occurs as ~40 × 100 μm size subhedral grains in St. Sauveur (Table 2 of Rubin 1983a). The morphologies of these grains and their occurrence in two impact-melt breccias indicate that fluor-richterite crystallized from the impact melt.

Fluorophlogopite, a phyllosilicate of formula KMg₃(Si₃Al)O₁₀F₂ that averages 5.1 wt% F, is present in the EH impact-melt rock Y-82189; it occurs as rare subhedral 10–30 μm size grains in association with enstatite, silica and albite (Lin and Kimura 1998). Fluorophlogopite crystallized from the impact melt of Y-82189.

Although EH chondrites are rich in bulk F (238 μg/g, compared to only 64 μg/g in CI chondrites; Wasson and Kallemeyn 1988), there are no primary F-rich phases in pristine (unmelted) enstatite chondrites. The observation that 8% of the total F in EH4 Indarch is leachable, in contrast to 0% in Abee (Reed 1964), suggests that a minor fraction of F in pristine EH chondrites occurs in friable phases and/or as phases that were adsorbed onto grain surfaces during condensation. After impact melting, most of the F in Abee, St. Sauveur and Y-82189 that was not driven off was scavenged by the crystallizing grains of fluor-richterite and fluorophlogopite.

Small diamonds (0.1–1 μm) with platy and lath-shaped morphologies, low N contents (<50 μg/g), and N and Xe isotopic compositions that are characteristic of solar-system materials (Russell et al. 1992) formed from graphite during one or more of the impact events (Rubin and Scott 1997). However, any diamonds that were produced during the initial impact could have been destroyed by subsequent impact heating.

CONCLUSIONS

Unusual mineralogical characteristics of the Abee EH-chondrite impact-melt breccia include very low MnO in most grains of enstatite (below microprobe detection limits), relatively high Mn in troilite (0.24 wt%), relatively high Mn in oldhamite (0.36 wt%), low Mn in keilite (3.6–4.3 wt%), high modal abundances of keilite (11.2 wt%) and silica (~7 wt%), low modal abundances of total silicates (58.8 wt%) and troilite (5.8 wt%), and the occurrence of fluor-richterite and euhedral blades of graphite. Abee's complex shock history is responsible for producing these features. Other EH impact-melt breccias (e.g., Adhi Kot; St. Sauveur) that share some of these characteristics have broadly similar shock and crystallization histories.

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