Fayalite in the Vigarano CV3 carbonaceous chondrite: Occurrences, formation age and conditions

Kaori Jogo, Tomoki Nakamura, Takaaki Noguchi, Mikhail Yu. Zolotov

ABSTRACT

We have performed petrographic characterization, $^{53}$Mn–$^{54}$Cr age determination and thermodynamic stability evaluations of fayalite in Vigarano meteorite that belongs to the reduced subgroup of CV3 chondrites. Vigarano is a breccia consisting of clasts which are separate chondrules surrounded by olivine-rich fine-grained materials. Four out of twenty three explored clasts contain fayalites that represent materials of the Bali-like oxidized subgroup of CV3 chondrites. The fayalites (Fa$_{90}$) with grain sizes typically $<$ 20 µm occurs in veins that extend from chondrules into the fine-grained materials. The fayalite commonly coexists with troilite and/or magnetite. The fayalite-bearing veins terminate at the boundaries of clasts. No evidence of strong impact enough to make melt veins is found in materials adjacent to the veins. These observations suggest that the fayalite-bearing veins in the Bali-like clasts formed through aqueous alteration in an asteroid prior to fragmentation and re-accretion to the Vigarano parent body. In saponite-rich fine-grained materials, we also found troilite–magnetite veins, which are similar to the fayalite-bearing veins in morphology. Morphological evidences and thermochemical equilibrium calculations suggest that fayalite replaced magnetite, and that replacement occurred at temperatures $<$ 200 °C and low water/rock mass ratios from 0.07 to 0.18, which represent aqueous to metamorphic transition. Fayalite grains typically show iron-magnesium zoning (fayalite content decreases towards the grain edges). Based on equilibrium models, this zoning may have occurred at increasing temperature. The observed initial ratio of ($^{53}$Mn/$^{55}$Mn)$_0$ = (2.3 ± 0.5)$\times 10^{-8}$ suggests that fayalite formed $\sim$ 5 Ma before the timing when the Mn–Cr system was closed in angrite NWA 4801 and has an absolute age of $\sim$ 4563 ± 1 Ma. The age of fayalite is identical within errors to that in Mokoa and Kaba CV3 chondrites, which belong to the Bali-like oxidized subgroup. The identical age implies that aqueous alteration occurred at the same time in parent asteroids of Bali-like subgroup materials. These fayalite-bearing materials may have been derived from a single CV3 asteroid or from separate CV3 asteroids where aqueous alteration simultaneously occurred.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

CV3 carbonaceous chondrites are subdivided into the reduced (CV$_{3\text{Red}}$) and two oxidized subgroups, Allende-like (CV$_{3\text{Ox}}$) and Bali-like (CV$_{3\text{Bli}}$) (McSween, 1977; Weisberg et al., 1997). These subgroups are considered to be affected by different degrees of aqueous alteration and subsequent metamorphism, which resulted in different secondary mineralization (Lee et al., 1996; Krot et al., 1995, 1998a, 1998b, 2004). For example, olivine in the CV$_{3\text{Red}}$ and CV$_{3\text{Ox}}$ chondrites is Fa$_{10-60}$, but that of CV$_{3\text{Bli}}$ Chondrite is Fa$_{10-100}$ (Weisberg et al., 1997; Krot et al., 2004). Generally, only CV$_{3\text{Ox}}$ chondrites contain near-pure fayalite (Fa$_{90}$) (Hua and Buseck, 1995; Krot et al., 1995, 1998a, 1998b, 2000, 2004; Weisberg et al., 1997; Hutcheon et al., 1998; Choi et al., 2000; Hua et al., 2005).

The near-pure fayalite in the CV$_{3\text{Ox}}$ chondrites occurs as discrete grains (up to 600 µm in size) or as a component of veins. The fayalite commonly associates with troilite and/or magnetite, and exists in chondrules and in matrix. Several formation models of the CV$_{3\text{Ox}}$ fayalite have been proposed (Nagahara et al., 1988, 1994; Hua and Buseck, 1995; Krot et al., 1998a, 1998b, 2000, 2004; Choi et al., 2000; Ohnishi and Tomeoka, 2002; Krot et al., 2004; Hua et al., 2005; Zolotov et al., 2006; Jogo et al., 2008). According to the asteroidal models, fayalite may have formed through aqueous alteration (e.g., Krot et al., 1998a, 1998b, 2000, 2004; Choi et al., 2000; Jogo et al., 2008), or dehydration of Fe-rich phyllosilicates (e.g., Krot et al., 1995; Ohnishi and Tomeoka, 2002). According to the nebular model, fayalite may have formed by condensation of a gas (e.g., Nagahara et al., 1988, 1994), or by reaction of SiO gas and magnetite (e.g., Hua and Buseck, 2000, 2004).
The asteroidal origin of fayalite is consistent with the oxygen isotopic data for fayalite and magnetite (Choi et al., 2000; Hua et al., 2005; Jogo et al., 2008). Thermodynamic analysis of fayalite stability is also consistent with asteroidal formation at temperatures below 300–350 °C (Krot et al., 1998a,b; Zolotov et al., 2006).

Mn–Cr dating were performed on the large fayalite grains (100 to 600 µm in size) in the CV3\textsubscript{red} Mokoia and Koba meteorites. The fayalite grains in both meteorites show excesses of \(^{53}\text{Cr}\) corresponding to the initial \(^{57}\text{Mn}/^{55}\text{Mn}\) radio of \((2.22 \pm 0.18) \times 10^{-6}\) (Mokoia, Hutcheon et al., 1998) and of \((2.07 \pm 0.17) \times 10^{-6}\) (Kaba, Hua et al., 2005). These ratios indicate that both of the Mokoia and Koba fayalite have formed at the same time of 4562–4563 Ma, which is calculated using the angrite NWA 4801 as a time marker; Pb–Pb age of this angrite is 4558.0 ± 13 Ma (Amelin and Irving, 2007) and the corresponding \(^{52}\text{Mn}/^{55}\text{Mn}\) ratio is \(0.96 \pm 0.04 \times 10^{-6}\) (Shukolyukov et al., 2009).

Although Vigarano meteorite is classified to the CV3\textsubscript{red} subgroup, it also contains fayalite (Fa=80) (Krot and Todd, 1998; Meibom and Krot, 1998; Tomeoka and Tanimura, 2000; Krot et al., 2000; Noguchi et al., 2003). The fayalite has similar occurrence to the CV3\textsubscript{red} fayalite. It coexists with troilite and/or magnetite, and occurs as discrete grains (up to 50 µm in size) or as a component of veins. The Vigarano fayalite coexists with troilite and/or magnetite, and occurs as discrete grains in both meteorites show excesses of \(^{53}\text{Cr}\) corresponding to the initial \(^{57}\text{Mn}/^{55}\text{Mn}\) ratio of \((35.0 \pm 0.04) \times 10^{-6}\) (Shukolyukov et al., 2009).

Although Vigarano meteorite is classified to the CV3\textsubscript{red} subgroup, it also contains fayalite (Fa=80) (Krot and Todd, 1998; Meibom and Krot, 1998; Tomeoka and Tanimura, 2000; Krot et al., 2000; Noguchi et al., 2003). The fayalite has similar occurrence to the CV3\textsubscript{red} fayalite. It coexists with troilite and/or magnetite, and occurs as discrete grains (up to 50 µm in size) or as a component of veins. The Vigarano fayalite coexists with troilite and/or magnetite, and occurs as discrete grains in both meteorites show excesses of \(^{53}\text{Cr}\) corresponding to the initial \(^{57}\text{Mn}/^{55}\text{Mn}\) ratio of \((35.0 \pm 0.04) \times 10^{-6}\) (Shukolyukov et al., 2009).

2. Methods

2.1. Mineralogical characterization

We examined two polished thin sections of CV3\textsubscript{red} Vigarano with areas of ~2 cm\(^2\) and ~3 cm\(^2\) using an optical microscope, a scanning electron microscope (SEM), and an electron probe micro analyzer (EPMA). Carbon thin film (25 nm) was applied on the surface prior to SEM, FE-SEM and EPMA analyses in order to eliminate the electrostatic charge. The Mn–Cr analyses were performed using a focused \(\text{O}^+\) beam ~10 µm in diameter and with the current of 0.2–0.9 nA. The primary \(\text{O}^+\) ions were accelerated with +12 keV to sputter the sample surface. Positive secondary ions were accelerated with ~4.5 keV and sampled with a 100 eV energy window. The mass resolving power \((M/\Delta M)\) is ~3000, that was sufficient to resolve \(\text{Mg}^2\text{Si}^2+\) to \(\text{Cr}^+, \text{Mg}^2\text{Si}^+\) and \(\text{Mg}^2\text{Al}^+\) to \(\text{Cr}^+, \text{Mg}^2\text{Al}^+\) to \(\text{Mn}^+\), but was not sufficient to resolve \(\text{CrH}^+\) from \(\text{Cr}^+\) and \(\text{FeH}^+\) from \(\text{Mn}^+\). Hutcheon et al. (1998) and Hua et al. (2005) showed that the contributions of the hydride to \(\text{Cr}^+\) was confirmed to be <1% and the hydrides of \(^{53}\text{Mn}\) totaled less than 1%, and consequently hydrides could be neglected. Secondary ion mass fractionation was also consistent with asteroidal formation at temperatures below 300–350 °C (Krot et al., 1998a,b; Zolotov et al., 2006).

2.2. \(^{53}\text{Mn}/^{52}\text{Cr}\) dating using ion probe

The \(^{53}\text{Mn}/^{52}\text{Cr}\) isotopic measurements were carried out using a secondary ion mass spectrometer (SIMS: CAMECA ims-6f at Kyushu University). We analyzed only large fayalites, which have high Mn/Cr ratios and are bigger than SIMS beam size. A polished thin section containing the fayalites was coated with gold of 30 nm thickness to eliminate the electrostatic charging on the sample surface. The Mn–Cr analyses were performed using a focused \(\text{O}^+\) beam ~10 µm in diameter and with the current of 0.2–0.9 nA. The primary \(\text{O}^+\) ions were accelerated with +12 keV to sputter the sample surface. Positive secondary ions were accelerated with ~4.5 keV and sampled with a 100 eV energy window. The mass resolving power \((M/\Delta M)\) is ~3000, that was sufficient to resolve \(\text{Mg}^2\text{Si}^2+\) to \(\text{Cr}^+, \text{Mg}^2\text{Si}^+\) and \(\text{Mg}^2\text{Al}^+\) to \(\text{Cr}^+, \text{Mg}^2\text{Al}^+\) to \(\text{Mn}^+\), but was not sufficient to resolve \(\text{CrH}^+\) from \(\text{Cr}^+\) and \(\text{FeH}^+\) from \(\text{Mn}^+\). Hutcheon et al. (1998) and Hua et al. (2005) showed that the contributions of the hydride to \(\text{Cr}^+\) was confirmed to be <1% and the hydrides of \(^{53}\text{Mn}\) totaled less than 1%, and consequently hydrides could be neglected. Secondary ion mass fractionation was also consistent with asteroidal formation at temperatures below 300–350 °C (Krot et al., 1998a,b; Zolotov et al., 2006).
322


intensities of $^{53}\text{Cr}$ were further corrected for background (measured on mass 52.9) and dead time of electron multiplier (24 ns). One analysis consists of 10 to 20 cycles of the measurement set in which $^{47}\text{Ti}^+, ^{49}\text{Ti}^+, ^{50}\text{Cr}^+, ^{52}\text{Cr}^+, ^{53}\text{Cr}^+$ and $^{55}\text{Mn}^+$ were counted for 5 s, 5 s, 10 s, 100 s, 200 s and 10 s, respectively. Each run was started after stabilization of the secondary ion beam intensity following pre-sputtering. Under these conditions, $^{50}\text{Ti}^+$ is irresolvable isobaric interferences at mass/charge $^{52}\text{Cr}^+$. In order to estimate $^{50}\text{Ti}^+$ contributions on $^{50}\text{Cr}^+$, we used the following calculations. $^{50}\text{Ti}^+/^{52}\text{Cr}^+$ ratios are obtained by $(^{50}\text{Ti}^+/^{47}\text{Ti}^+) \times (^{47}\text{Ti}^+/^{52}\text{Cr}^+)$. Because we can measure $^{47}\text{Ti}^+/^{52}\text{Cr}^+$ ratios but not $^{50}\text{Ti}^+/^{47}\text{Ti}^+$ ratios, we got $^{50}\text{Ti}^+/^{47}\text{Ti}^+$ ratios in order to check whether instrumental mass fractionation on Ti isotopes occurred. Measured $^{47}\text{Ti}^+/^{47}\text{Ti}^+$ ratios were consistent within errors to the reference value (Papanastassiou, 1986), thus we used reference value of $^{50}\text{Ti}^+/^{47}\text{Ti}^+$ ratios for these calculations.

The San Carlos olivine (Fo89) was used as a standard for calibrating $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{55}\text{Mn}/^{52}\text{Cr}$ ratios of fayalites. The $^{53}\text{Cr}/^{52}\text{Cr}$ ratios were corrected for instrumental mass fractionation by a linear fractionation law normalized to the reference values for Cr isotopic ratios. Equation for this calculation is shown as follows:

$$\frac{(^{53}\text{Cr})_{\text{REF}}}{(^{52}\text{Cr})_{\text{REF}}} = A \times \left(\frac{(^{53}\text{Cr})_{\text{SIMS}}}{(^{52}\text{Cr})_{\text{SIMS}}}\right)$$

Here $(^{53}\text{Cr}/^{52}\text{Cr})_{\text{REF}} = 0.113459$ (Papanastassiou, 1986), and $(^{53}\text{Cr}+/^{52}\text{Cr}+)_{\text{SIMS}}$ are the ratios of secondary ion intensities between $^{53}\text{Cr}$ and $^{52}\text{Cr}$ of San Carlos olivine. In this study, values of $A$ were $1.00 \pm 0.02$ (1σ), and thus instrumental mass fractionation between Cr isotopes could be neglected.

The true $^{55}\text{Mn}/^{52}\text{Cr}$ ratios were calculated using the sensitivity factor, which was determined from San Carlos olivine. The Mn/Cr ratio of the San Carlos olivine was analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES: Seiko Instruments, SPS-1200AR at Kyushu University). Differences in ionization efficiency between Mn and Cr were taken into account by comparing the measured $^{55}\text{Mn}^-/^{52}\text{Cr}^+$ ratio to the $^{53}\text{Mn}/^{52}\text{Cr}$ ratio for San Carlos olivine standard by the following equation.

$$\frac{(^{53}\text{Mn})_{\text{ICP-AES}}}{(^{52}\text{Cr})_{\text{ICP-AES}}} = B \times \left(\frac{(^{53}\text{Mn})_{\text{SIMS}}}{(^{52}\text{Cr})_{\text{SIMS}}}\right)$$

Here $(^{53}\text{Mn}/^{52}\text{Cr})_{\text{ICP-AES}}$ is the ratio that was determined by ICP-AES, and $(^{53}\text{Mn}+/^{52}\text{Cr}+)_{\text{SIMS}}$ is the ratio of secondary ion intensities between $^{53}\text{Mn}$ and $^{52}\text{Cr}$. $B$ is the Mn/Cr relative sensitivity factor. In this study, values of $B$ were found to be $1.57 \pm 0.09$ (1σ) for the San Carlos olivine standard. We correct the SIMS $^{55}\text{Mn}/^{52}\text{Cr}$ data using the RSF to compensate the instrumental elemental fractionation.

We used San Carlos olivine (Fo89) as standard, not fayalite, for age determination of fayalite crystals. Thus the obtained ages may include potential errors. However, the sequence of timing for fayalite formation may not be changed, because previous data reported by Hutcheon et al. (1998) and Hua et al. (2005) were used the San Carlos olivine standard and may suffer a similar degree of instrumental fractionation.

After SIMS measurements, the samples were checked again with SEM to verify that the ion probe hit the right spots. For this SEM analyses, we polished the thin section with diamond paste to remove carbon and gold films, then coated it with carbon film again.

2.3. Equilibrium calculations in water–chondrite system

Physical–chemical conditions of formation for fayalite and other secondary minerals in observed clasts were evaluated through calculations of thermochemical chemical equilibria. Equilibrium mineral compositions in the closed water–chondrite system O–H–Mg–Fe–Ca–Si–Al–C–P–S–Cr–Na–K–Cl–Mn–Co–Ni were calculated for a range of temperatures ($T = 0–350 ^\circ\text{C}$), pressures ($P = 1–260$ bar) and water/rock mass ratios ($W/R = 0.01–1$). The range of parameters is chosen to overlap conditions of fayalite formation obtained in Zolotov et al. (2006). The system includes 123 one-component minerals, 21 mineral solid solutions, a non-ideal gas ($\text{H}_2\text{O}, \text{H}_2, \text{CO}_2, \text{CO}, \text{H}_2\text{S}, \text{SO}_2$) and a non-ideal aqueous solution (98 species). Formation of CH$_4$ was suppressed due to the inhibition of its formation at low temperatures. The bulk water-free composition of the Bali CV3$_{Deb}$ chondrite (Jarosewich, 1990) represented the initial rock. Calculated data include amount and compositions of solid, gas, and aqueous phases. The calculations were performed with the GEOCHEQ code that considers non-ideal gas, aqueous, and solid solutions (Mironenko et al., 2008). Details of the calculations and data sources are presented in Zolotov et al. (2006).

3. Results

3.1. Mineralogy and petrology

In both of CV3 Vigarano sections, areal ratios of coarse-grained objects (chondrules and chondrule fragments) to fine-grained matrix are about 1. In total, 23 chondrules were identified. They range in diameter from 0.3 to 1 mm and have porphyritic textures; among them 9 porphyritic olivine pyroxene chondrules (POP), 11 porphyritic olivine chondrules (PO), and 3 porphyritic pyroxene chondrules (PP) can be recognized. Metal and minor iron sulfides are present in the interiors of chondrules. In contrast, iron sulfides and oxides, and minor metal grains are present at chondrule boundaries.

Most of chondrules are surrounded by fine-grained materials, which are in <100 µm thick (Fig. 1). A chondrule and a fine-grained material constitute a typical building block of Vigarano. Hereafter, we define the building block as a ‘clast’. Clasts are embedded in the host matrix or have direct contact with adjacent clasts. The boundaries of clasts are well-defined and distinguished by SEM and FE-SEM, if an enclosing chondrule is round. In contrast, the boundaries are blurred and difficult to be distinguished from host matrix, if an enclosing chondrule is broken.

Fig. 1. A backscattered electron (BSE) image of representative CV3$_{Deb}$ Vigarano breccia. Clast boundaries are shown by arrows. One clast contains a fayalite (fa)-bearing vein.
We found 4 clasts with fayalite (e.g., Figs. 1, 2, 4) out of 23 clasts from investigation of chondrules and those surrounding fine-grained materials. The major secondary minerals in those clasts include fayalite, magnetite, troilite, low-Ca and high-Ca pyroxene and minor Fe–Ni metal. These features are similar to mineralogy of CV3OxB chondrites reported by Krot et al. (1995, 2000). Rest of the clasts and host matrix is fayalite-free and contain magnetite, troilite, Fe-Ni metal ferrous olivine, high-Ca pyroxene and plagioclase, which are similar to mineralogy of CV3Red chondrite reported by Krot et al. (1995).

Among the 4 clasts with fayalite, one clast contains a subhedral fayalite-bearing grain (Fig. 2b) and other 3 clasts contain 4 fayalite-bearing veins (e.g., Figs. 2, 4). Two veins are in the same clast (Fig. 2) and other two locate in different clasts (e.g., Fig. 4). The veins are typically up to 20×100 µm in size and extend from magnetite–sulfide nodules at chondrules into surrounding olivine (Fa40–60) rich fine-grained materials (e.g., Figs. 2, 4). All veins crosscut the fine-grained materials and, terminate at or within the boundaries of clasts (e.g., Fig. 2ab). In the veins, fayalite commonly coexists with troilite and/or magnetite. The troilite and magnetite in the veins are compositionally pure, whereas those in the nodules contain high Cr, Ni etc. These petrologic features are consistent with those reported by Hurcheon et al. (1998), Krot et al. (2000) and Hua et al. (2005). These fayalite-bearing veins are very similar in morphology to fayalite-free troilite–magnetite veins found in the other areas of Vigarano (Fig. 3 in this paper; Noguchi, 1997, 1998, 1999; Noguchi and Nakamura, 2000; Noguchi et al., 2003).

The composition of the fayalite is typically from Fa99 to Fa80, occasionally down to Fa70. Fayalite grains commonly reveal Fe–Mg zoning with lowering Fa number toward the rim (e.g., fayalite (A) in Fig. 2b). On the other hand, olivine-rich fine-grained materials adjacent to the fayalite seem to have homogeneous Fe/Mg ratios (Fa40–60). Some of Mg-rich olivines (typically <Fa20), which occur as isolated fragments in the fine-grained materials do not show Fe–Mg zoning.

In the following sections, we describe details of representative 3 fayalite-bearing veins in 2 clasts. In addition, we also describe mineralogy of the fayalite-bearing grain and the troilite–magnetite veins. Hereafter, we define clasts as follows: clast 1 contains two fayalite-bearing veins (~10×100 µm in size) (Fig. 2). In the veins, subhedral to anhedral fayalite grains coexist between troilite and/or magnetite. The troilite and magnetite in the veins are compositionally pure, whereas those in the nodules contain high Cr, Ni etc. These petrologic features are consistent with those reported by Hurcheon et al. (1998), Krot et al. (2000) and Hua et al. (2005). These fayalite-bearing veins are very similar in morphology to fayalite-free troilite–magnetite veins found in the other areas of Vigarano (Fig. 3 in this paper; Noguchi, 1997, 1998, 1999; Noguchi and Nakamura, 2000; Noguchi et al., 2003).

The composition of the fayalite is typically from Fa99 to Fa80, occasionally down to Fa70. Fayalite grains commonly reveal Fe–Mg zoning with lowering Fa number toward the rim (e.g., fayalite (A) in Fig. 2b). On the other hand, olivine-rich fine-grained materials adjacent to the fayalite seem to have homogeneous Fe/Mg ratios (Fa40–60). Some of Mg-rich olivines (typically <Fa20), which occur as isolated fragments in the fine-grained materials do not show Fe–Mg zoning.

In the following sections, we describe details of representative 3 fayalite-bearing veins in 2 clasts. In addition, we also describe mineralogy of the fayalite-bearing grain and the troilite–magnetite veins. Hereafter, we define clasts as follows: clast 1 contains two fayalite-bearing veins (Fig. 2); clast 2 contains a subhedral fayalite grain (Fig. 2b); clast 3 contains several magnetite–troilite veins (Fig. 3); clast 4 contains a fayalite-bearing vein (Fig. 4), as summarized in Table 2.

Clast 1 contains two fayalite–troilite–magnetite veins (~10×100 µm in size) (Fig. 2). In the veins, subhedral to anhedral fayalite grains coexist between troilite and magnetite grains or occur in peripheral parts of the vein (Fig. 2bc). In Fig. 2d, irregularly-shaped magnetite grains are embedded in an assemblage of small fayalite grains. This texture implies that fayalite formed at the expense of magnetite, but the replacement was not complete. The Fe/Mg ratio varies among fayalites (Fig. 2b), and an individual fayalite grain commonly shows Fe–Mg zoning (e.g., subhedral fayalite (A) in Fig. 2b shows Fe–Mg zoning Fa84–97). Fayalite grains in Fig. 2d are too small (~1 µm in size) to detect variations in Fe/Mg ratios within each grain.

Clast 2 contains an isolated subhedral fayalite grain (~10×10 µm in size) (fayalite (B) in Fig. 2b) that coexists with a small amount of troilite. Although this grain is adjacent to the vein in the clast 1, it has a

uniform composition (Fa₉₉). This suggests that clasts 1 and 2 had not been altered after formation of Vigarano breccia.

Some of mineralogical and petrographic characterizations of clast 3 have been reported in previous studies (Noguchi, 1997; Noguchi et al., 2003). In brief, clast 3 contains several magnetite–troilite veins without fayalite (~20×100 µm in size) (Fig. 3). All veins terminate at or within the clast boundary. They extend from magnetite–sulfide–kamacite nodules with a carbon-bearing amorphous material at a chondrule boundary into saponite-rich fine-grained materials. Some veins penetrate the nodules. Saponite in the fine-grained materials of this clast was identified by X-ray diffraction (Noguchi et al., 2003). Veins shown in Fig. 3 (clast 3) and Fig. 2cd (clast 1) have similar morphology but different mineralogy. Therefore, magnetite–troilite veins and fayalite-bearing veins could have genetic relations.

Clast 4 contains a fayalite–troilite vein (~20×100 µm in size) (Fig. 4). The compositions of these fayalites show systematic pattern from a position near nodule (Fa₀₇₉) to near chondrule (Fa₁₀₀). Individual fayalite grains at the edge of the vein show Fe-Mg zoning (e.g., Fa₈₉ at the center and Fa₉₇ at the surface). They are larger than SIMS beam size (10 µm) and typically have high MnO 0.6–0.8 wt.% and low Cr₂O₃ <0.05 wt.% contents (Table 1). Thus, these fayalite grains are suitable for Mn–Cr isotopic analysis by SIMS.

3.2. ⁵³Mn–⁵⁵Cr dating of fayalite

We performed Mn–Cr isotopic measurement on two large fayalite grains in the vein in clast 4 (circles in Fig. 4). We found clear evidence of extinct ⁵³Mn in fayalites having the high Mn/Cr ratio = −5000–24000 (Fig. 5 and Table 3). We measured one large fayalite for three times (FA-2 to FA-4). These data showed different ⁵⁵Mn/⁵³MnCr ratios with depth, but their ⁵³Cr/⁵²Cr ratios lie on the same regression line within an error (Fig. 5). All data for fayalites lie within analytical errors on a straight line with inferred initial ⁵³Mn/⁵⁵Mn ratio of (2.3 ± 0.5)×10⁻⁶ (2σm). An initial ⁵³Cr/⁵²Cr ratio is 0.11185 ± 0.00003 (2σm). Errors of ⁵³Mn/⁵⁵Mn and ⁵³Cr/⁵²Cr ratios are 1 standard deviations of the mean (Table 3). Data FO-1 and PX-1 were analyzed on the adjacent forsterite and low-Ca pyroxene grains in the same clast 4 (Fig. 4).

3.3. Equilibrium calculations

Equilibrium calculations in the water–chondrite system show that fayalite forms at narrow conditions: $T = −60–200 ^\circ$C, $W/R = 0.07–0.18$, $f_{H_2}/f_{H_2}O = −30–4000$, and $P$ that exceeds that of water saturation (Fig. 6). The excess of $P$ is attributed to $H_2$ gas formed through mineral (e.g., kamacite, schreibersite) oxidation by water. Increase in $P$ (effectively, $H_2$) leads to increase of lower and upper boundaries of temperature stability of fayalite. Although fayalite can

![Fig. 3. BSE images of the clast 3. (a) Several troilite–magnetite veins occur in saponite-rich fine-grained materials (sap-rich FGM) around a chondrule. A boundary of the clast is shown by arrows. (b) A part of (a). A magnetite–troilite vein extends from an opaque nodule. The nodule has complex layers of kamacite, a carbon(C)-bearing amorphous material, troilite and magnetite. We adopt Fig. 3 from Noguchi (1997).](image)

![Fig. 4. A BSE image of clast 4. A vein consisting of fayalite and troilite extends from a magnetite–sulfide nodule. Circles in fayalite, olivine and pyroxene grains show SIMS measurement spots. Fayalites in the vein have a different composition.](image)

<table>
<thead>
<tr>
<th>Clast</th>
<th>Fig.</th>
<th>Vein</th>
<th>Fayalite</th>
<th>Nodule</th>
<th>Fine-grained material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minerals</td>
<td>Size (µm)</td>
<td>Morphology</td>
<td>Size (µm)</td>
<td>Fa#</td>
</tr>
<tr>
<td>1</td>
<td>fa, tr, mt</td>
<td>10 × 100</td>
<td>Anhedral</td>
<td>Up to 10 × 10</td>
<td>88–97</td>
</tr>
<tr>
<td>2</td>
<td>fa, tr, mt</td>
<td>10 × 100</td>
<td>Subhedral</td>
<td>10 × 10</td>
<td>84–97</td>
</tr>
<tr>
<td>3</td>
<td>fa, tr</td>
<td>20 × 100</td>
<td>Anhedral</td>
<td>Up to 10</td>
<td>69–75</td>
</tr>
<tr>
<td>4</td>
<td>fa, tr</td>
<td>20 × 100</td>
<td>Subhedral</td>
<td>10 × 20</td>
<td>87–97</td>
</tr>
</tbody>
</table>

Fa = fayalite, tr = troilite, sif = sulfide, mt = magnetite, kam = kamacite, C-material = carbon-bearing amorphous material; sap = saporite, ol = olivine.

* Isolated grain.
form at temperatures up to 300–350 °C, for typical asteroidal pressure (~100 bar, Grimm and McSween, 1989; Wilson et al., 1999), the upper temperature boundary of fayalite stability is ~180 °C (cf. Zolotov et al., 2006). At higher W/R ratio, fayalite can be stable at slightly higher temperatures. Pure fayalite (Fa_{100}) forms at lower temperatures, and Fa number decreases with temperature (Fig. 6).

In contrast to fayalite, magnetite, troilite, saponite and other modeled secondary phases form at wider range of conditions (Fig. 6). In our calculations, fayalite coexists with troilite and often coexists with magnetite. However, at reducing conditions (lower W/R and higher $f_{H_2}/f_{H_2O}$ ratios), magnetite is absent from fayalite-bearing assemblages. Equilibrium calculations imply that fayalite can form as rare and transient mineral during aqueous to metamorphic transition in parent asteroids.

Because mineralogy of our fayalite-bearing clasts is similar to that of CV3$_{dob}$ chondrites, equilibrium calculations for Bali CV3$_{dob}$ composition could be applied to the CV3$_{dob}$ clasts in the Vigarano. Previous calculations (Zolotov et al., 2006) show only a minor effect of bulk chondritic composition on the stability fields of fayalite and other phases.

4. Discussions

Observed clastic structures of Vigarano CV3$_{Red}$ chondrite (Figs. 1–4) are similar to previous studies (Noguchi, 1997, 1998, 1999; Noguchi and Nakamura, 2000; Krot et al., 2000; Tomeoka and Tanimura, 2000; Noguchi et al., 2003). Occurrences of secondary minerals in the 4 clasts containing fayalites indicate that mineralogy of the clasts is similar to that of CV3$_{dob}$ chondrites (Weisberg et al., 1997). Thus, the 4 clasts would be CV3$_{dob}$ Clasts that formed via similar mechanism in which CV3$_{dob}$ chondrites formed.

4.1. Asteroidal origin of fayalite-bearing veins

Several formation models for CV3 fayalite were proposed in previous studies and main difference between them is the location where fayalite formed: asteroids or nebula. Our observation indicates that the fayalite-bearing veins have very complex structures and are connected each other in the fine-grained materials (e.g., Figs. 2, 4). Troilite–magnetite vein runs through magnetite nodules in the fine-grained materials (Fig. 3). It would be implausible that such complex veins have formed in the solar nebula and later embedded in the present locations without giving heavy damages to the structure. Therefore, we concluded that the vein formation occurred in asteroids rather than in the nebula and support the proposition given by Krot et al. (1998a, 2004).

The observed termination of veins at chondrule’s boundaries indicate that initially fayalite-bearing veins would have extended from nodules at chondrule boundaries to matrix for longer distance as reported in Krot et al. (2000). Later, clasts containing parts of the veins would be separated and accrete to present locations of the CV3$_{Red}$ Vigarano. The vein formation might have occurred in different asteroids or in different locations of the same asteroid from which CV3$_{Red}$ Vigarano derived.

4.2. Formation mechanisms of fayalite-bearing veins

The fayalite-bearing veins (or their precursors) could have formed in asteroids by impact shock heating (e.g., Chen et al., 1996) or aqueous alteration (e.g., Krot et al., 1998a). High-intensity impact would have resulted in formation of opaque melt veins (e.g., Chen et al., 1996) and compaction of fine-grained materials (e.g., Stöffler et al., 1988). However the fine-grained materials in the CV3$_{dob}$ clasts in this study do not show compaction (Figs. 2–4). Olivine and pyroxene chondrule phenocrysts adjacent to the veins do not show remarkable wavy extinction and high-density microcracks that were expected to have formed by impact (e.g., Stöffler et al., 1988). These observations suggest that fayalite-bearing veins have not been formed by the impact shock.

During aqueous alteration, fayalite-bearing veins could form by the following mechanisms. (1) Precursor veined minerals (e.g., magnetite) were replaced by fayalite. In this mechanism, SiO$_2$ and magnetite should have a genetic relationship. Similar relationships with either magnetite or troilite. No direct textual and mineralogical evidence of their relationships has been obtained, but thermochemical calculations (Fig. 6) indicate that replacement of magnetite by fayalite (or vice versa) can occur by changes in temperature, W/R ratio and $f_{H_2}/f_{H_2O}$ ratio. In addition, troilite is more stable than magnetite in the stability field of fayalite. Therefore, fayalite and magnetite (not troilite) should have a genetic relationship. Similar

---

**Table 3**

Mn–Cr isotopic data of fayalites.

<table>
<thead>
<tr>
<th>Spot</th>
<th>$^{55}$Mn/$^{52}$Cr</th>
<th>$^{53}$Cr/$^{52}$Cr</th>
<th>$^{51}$Cr/$^{52}$Cr</th>
<th>$^{50}$Cr/$^{52}$Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA1-1</td>
<td>5647</td>
<td>829</td>
<td>1.0124</td>
<td>1.0104</td>
</tr>
<tr>
<td>FA1-2</td>
<td>6906</td>
<td>549</td>
<td>1.0123</td>
<td>0.0045</td>
</tr>
<tr>
<td>FA1-3</td>
<td>9079</td>
<td>551</td>
<td>1.0134</td>
<td>0.0051</td>
</tr>
<tr>
<td>FA1-4</td>
<td>23503</td>
<td>2084</td>
<td>1.0166</td>
<td>0.0049</td>
</tr>
<tr>
<td>FO-1</td>
<td>0.2913</td>
<td>0.173</td>
<td>0.1118</td>
<td>0.0088</td>
</tr>
<tr>
<td>PX-1</td>
<td>0.8304</td>
<td>0.0457</td>
<td>0.1119</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

All listed errors are 1 standard deviation of the mean.
relationship is argued by Krot et al. (1998a, 2004) and Choi et al. (2000).

Based on the above discussion, we estimated formation pathways of fayalite-bearing mineral assemblages (CV30xB clasts 1 and 4) as shown in Fig. 6a. At the early stage of asteroidal evolution, aqueous alteration should have occurred at low $T$, high $W/R$ ratio and low $f_{\text{H}_2}/f_{\text{H}_2\text{O}}$ ratio due to melting of ice by the decay heat of short-lived radioluclides (Grimm and McSween, 1989; Zolotov et al., 2006). Primary and secondary troilite and newly-formed magnetite are stable at these conditions (upper-left corners in Fig. 6a and b). This suggests that troilite–magnetite veins formed in aqueous conditions. At the same time, phyllosilicates (e.g., serpentine, saponite) might have formed in the fine-grained matrix. If increasing $T$, decreasing $W/R$ ratio and/or increasing $f_{\text{H}_2}/f_{\text{H}_2\text{O}}$ ratio have occurred, some magnetite in the veins was replaced by fayalite, fayalite–troilite veins formed ("clasts 4" down-arrow). Further increase in $T$ may have led to Mg-enriched olivines. Some olivines may have formed through dehydration of phyllosilicates in the matrix (Mg-enriched olivine is stable to the right of the fayalite stability field in Fig. 6a). Fayalite forms at moderately reduced conditions that are characterized by an excess of $H_2$ in the system (at $f_{\text{H}_2}/f_{\text{H}_2\text{O}}$ from 30 to 4000).

This formation pathway of increasing $T$ and decreasing $W/R$ ratio is supported by Fe–Mg zoning within the fayalite grains. Because pure fayalite is more stable at lower $T$ and higher $W/R$ ratio (Fig. 6a), such zoning (Fa numbers decrease toward rims) requires increasing temperature and may also reflect decreasing $W/R$ ratio. After replacement of magnetite by pure fayalite, fayalite with lower Fe content could have formed and overgrew on the pure fayalite cores. Formation of the zoning through Fe–Mg diffusion between the pure fayalite and surrounding olivine-rich fine-grained materials is unlikely, because not all Mg-rich olivine grains adjacent to the fayalites show Fe–Mg zoning. If the zoning in fayalites formed by diffusion, all olivines should have Fe–Mg zoning.

Formation pathway of clasts 3 with fayalite-free troilite–magnetite veins remains unclear: it might be pre- or post-material of clasts with fayalite-bearing veins. Initial formation of magnetite–troilite veins would have required aqueous conditions at $W/R$ > ~0.18. Further
evolution pathways may have fayalite as an intermediate phase. For example, increase in $T$ (see continuation of pathways clasts 1 and 4 in Fig. 6a) could lead to fayalite oxidation to magnetite and the formation of magnetite–troilite assemblage ($W/R = -0.06$–0.18 and $T > 140$–200 °C). Although we do not observe signs of fayalite replacement by magnetite, the simple texture of troilite–magnetite veins may imply that clasts 3 are precursor of clasts 1 and 4. This notion is supported by the presence of saponite in the fine-grained materials, which indicates that clasts 3 did not experience high temperature enough to decompose saponite. Note, however, that evolution in the T-W/R field (Fig. 6a) may have never crossed the stability field of fayalite. In such a case, early formed magnetite–troilite veins remained unaltered during the aqueous to metamorphic alteration.

4.3. $^{53}$Mn/$^{55}$Cr dating of fayalite

The slope of the isochron gives an initial $^{53}$Mn/$^{55}$Mn ratio of $(2.3 \pm 0.5) \times 10^{-6}$ (Fig. 5). This ratio indicates that Vigarano’s fayalite formed 5 ± 1 Ma before the timing when the Mn-Cr isotopic system was closed in angrite NWA 4801 ($^{53}$Mn/$^{55}$Mn = $(0.96 \pm 0.04) \times 10^{-6}$; Shukolyukov et al., 2009). This corresponds to an absolute age of 4563 ± 1 Ma, which is calculated using Pb-Pb age of this angrite (4558.0 ± 0.13 Ma; Amelin and Irving, 2007). To determine the relative age, we compared the initial $^{53}$Mn/$^{55}$Mn ratio of fayalite with that of CAIs. We used two CAIs data, because initial $^{53}$Mn/$^{55}$Mn ratio of CAIs is uncertain. If we compare the inferred ratio with $^{53}$Mn/$^{55}$Mn = 4.4 × 10$^{-5}$ of Allende CAI (Birck and Allègre, 1988), Vigarano fayalite formed about 16 Ma after formation of it. If we compare inferred ratio with $^{53}$Mn/$^{55}$Mn = 9.1 × 10$^{-6}$ of Allende CAI (Birck and Allègre, 1988), Vigarano fayalite formed about 7 Ma after formation of it. This corresponds to an absolute age of ~4561 Ma, which is calculated using the estimated absolute age of these CAIs (4568.2 ± 0.5 Ma; Nyquist et al., 2009). The latter age of 7 Ma after CAI formation is more consistent with our observations than 16 Ma after CAI formation (Birck and Allègre, 1988). In fact, based on thermodynamics, Fe–Mg zoning in the fayalite requires elevated temperatures, which occurred at earlier stage (i.e., shorter time after CAI formation) of asteroidal evolution.

The inferred initial $^{53}$Mn/$^{55}$Mn ratio of the fayalite in the CV3OxB clasts is identical within errors to that of CV3OxB Mokoia (Hutcheon et al., 1998) and Kaba (Hua et al., 2004). This match indicates that aqueous alteration and fayalite formation could have occurred at the same time in a parent body of CV3OxB materials (CV3OxB clasts in the Vigarano, and CV3OxA chondrite Kaba and Mokoia). Therefore, they may have been derived from a single CV3 asteroid. This model is also argued by Krot et al. (2000, 2004). The authors reveal that CV3OxB, CV3OxA, and CV3Red chondrites have similar components and metamorphic sequence indicating possible formation of these chondrites on one asteroid that experienced complex alteration history. However, we cannot rule out the possibility that they could have originated from separate CV3 asteroids where aqueous alteration simultaneously occurred. In that case, the fayalite formation age indicates the upper limit for the formation age of Vigarano parent asteroid, because it had accreted after the formation of fayalite.

4.4. Formation of Vigarano breccia

Our formation model for the Vigarano breccia is illustrated in Fig. 7. First (stage A), chondrules, fine-grained dust and some water...
ice accreted to form CV3 asteroid(s). Radioactive decay of short-lived radionuclides (e.g., $^{26}$Al, $^{60}$Fe) caused ice melting and aqueous alteration of some solids. Neither fayalite nor veins formed at the deficiency of water (lithology of CV3red clasts). However, the troilite–magnetite veins formed in the presence of aqueous solutions. Some magnetite grains in initially formed troilite–magnetite veins have been replaced by fayalite (solid down-arrow in stage B). The fayalite in veins and individual fayalite grains formed at the transition between aqueous and metamorphic conditions (cf. Zolotov et al., 2006). In some cases, further thermal evolution could have caused fayalite conversion to other minerals (e.g., Mg-enriched olivine, magnetite: dashed up-arrow in stage B). After formation of vein minerals, impacts excavated materials from CV3 asteroid(s) or led to their significant fragmentation (stage C). Then, fragments of CV3 asteroids were accreted (or re-accreted) into the present structure of Vigarano. As a result, the CV3red-clasts with fayalite, the CV3red-like-clasts with troilite–magnetite veins, and the CV3red-clasts constitute the Vigarano breccia (stage D). Our model is consistent with the Vigarano breccia model proposed by Tomeoka and Tanimura (2000) and Krot et al. (2000).

5. Summary

We found four CV3red clasts containing fayalite in the CV3red chondrite Vigarano. Mineralogical observations indicate that these clasts represent Bali-type CV3red chondritic material formed in a CV3 asteroid(s) prior to formation of the Vigarano breccia. The identical formation age of fayalites in these CV3 red clasts and in the CV3red asteroids prior to formation of the Vigarano breccia: evidence for complex formation of CV3 asteroids. Lunar Planet. Sci. Conf. 39, #1576 (absr.).


References


