Petrology and shock history of the first depleted-like poikilitic shergottite Asuka 12325

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(Received 02 March 2023; revision accepted 15 August 2023)

Abstract—Asuka (A) 12325 is the first poikilitic shergottite having a depleted pattern in light rare earth elements (REE). Compared with known poikilitic shergottites, A 12325 has smaller but more abundant pyroxene oikocrysts with remarkable Fe-rich pigeonite rims, indicating that A 12325 cooled relatively faster at a shallower part of the crust. The redox condition (log O₂ = IW + 0.6-IW + 1.7) and Fe-rich chemical compositions of each mineral in A 12325 are close to enriched shergottites. The intermediate shergottites could not form by a simple mixing between parent magmas of A 12325 and enriched shergottites. Although A 12325 contains various high-pressure minerals such as majorite and ringwoodite, plagioclase is only partly maskelynitized. Therefore, the maximum shock pressure may be within 17–22 GPa. Thermal conduction and ringwoodite growth calculation around a shock vein revealed that the shock dwell time of A 12325 is at least 40 ms. The weaker shock pressure and longer shock dwell time in A 12325 may be attained by an impact event similar to those of nakhlites and Northwest Africa (NWA) 8159. Such a weak shock ejection event may be as common on Mars as a severe shock event recorded in shergottites. Alteration of sulfide observed in A 12325 may imply the presence of magmatic fluid in its reservoir on Mars. A 12325 expands a chemical variety of Martian rocks and has a unique shock history among poikilitic shergottites while A 12325 also implies that poikilitic shergottites are common rocks on Mars regardless of their sources.

INTRODUCTION

Shergottites constitute the largest subgroup of Martian meteorites and provide critical information about igneous processes that operated on Mars (McSween, 1994; McSween et al., 2009; Papke et al., 2009; Udry et al., 2020). Shergottites are generally subdivided into three petrological types: basaltic (diabasic), olivine–phyric, and poikilitic, while gabbroic shergottites have recently been added to the fourth subgroup. They are also classified into three chemical types from depleted to enriched, via an intermediate type based on rare earth element (REE) patterns, incompatible trace elements, and isotopic systems (e.g., Rb/Sr and Lu/Hf). Although all three chemical types have been identified among the diabasic and olivine–phyric shergottites, poikilitic shergottites with depleted REE patterns have not so far been reported. Recently, Debaille et al. (2019) and Takenouchi et al. (2019b) provided preliminary studies of a newly found shergottite Asuka (A) 12325 (Yamaguchi et al., 2018) and reported that it might be the first “depleted-like” poikilitic shergottite. Note that A 12325 is termed “depleted-like” because its REE pattern
does not entirely match that of other “depleted” samples in respect of the heavy REEs (see Figure 2 in Debaille et al., 2019). Precise geochemical analysis of A 12325 is ongoing. The finding of this “missing” chemical type improves our understandings of Martian igneous bodies and provides an essential constraint on the formation of Martian geochemical diversity.

Furthermore, we can gain clues about the distinct source regions of Martian meteorites by studying the shock history of A 12325. Here, we present the results of a petrological and mineralogical study of A 12325 with the aim of understanding its cooling and shock histories. We also compare A 12325 to other poikilitic shergottites to provide new insights into volcanic activity and impact events on Mars.

SAMPLE AND ANALYTICAL METHODS

A 12325 was collected in the 2012–2013 season by the Belgium–Japan joint Antarctic meteorite search expedition (JARE-54 and BELARE 2012–2013) (Imae et al., 2015). This is the first Martian meteorite from the Nansen Ice field in the south of the Sor Rondane Mountains. Its original mass was 28.022 g (Yamaguchi et al., 2018). A polished thin section (PTS) prepared at the National Institute of Polar research, Japan (NIPR), was studied both by optical microscopy and field emission scanning electron microscopy (FE-SEM), with electron-dispersive x-ray spectroscopy (EDS) at NIPR (JEOL JSM-7100F). Electron backscattered diffraction (EBSD) analysis was undertaken for phase identification by using Kikuchi patterns induced by diffraction from the crystal surface. Crystal orientation analysis was carried out using an AZtec EBSD system (Oxford Instruments). Micro-Raman spectroscopy (JASCO NRS-1000) was also used for phase identification using a 532.12 nm green laser with a laser power of ~2.5 mW. Quantitative chemical composition analysis for each of the main mineral phases present in A 12325 was performed using an electron microprobe at NIPR (JEOL JXA-8200) with an accelerating voltage of 15 kV. Beam current was 6 nA for plagioclase and glass and 30 nA for olivine, pyroxene, and oxides. The electron beam was focused (spot analysis) for the compositional analysis of most minerals, while it was defocused to 5 µm during the analysis of plagioclase and glass. Peak counting times were 20 s for Na and K; 30 s for Al, Mg, Si, Fe, Ti, Ca, Ni, Cr, V; and 60 s for Mn. Standards we used for calculation were as follows: olivine (Mg, Si), jadeite (Na), albite (Na), orthoclase (K), wollastonite (Ca), chromite (Cr), spessartine (Mn), and oxides (Ti, Al, Ni, V). Data reduction was performed by the ZAF correction method. All FeO data obtained from spinel were recalculated as FeO and Fe₂O₃ by constraining the sum of cations to be 3 when oxygen is 4 (stoichiometry). Typical detection limits were <0.02 wt% for Fe and Mn and <0.01 wt% for others. Iron valences in plagioclase (maskelynite) were analyzed by synchrotron x-ray absorption near-edge structure (SR-XANES) at beamline BL-4A, Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The obtained Fe Kα pre-edge peaks were deconvoluted to calculate the centroid peak positions using the methods described in Takenouchi et al. (2017). These centroid peak positions were used to obtain the quantitative Fe³⁺/ΣFe total ratios using the regression curve reported in Wilke et al. (2001) after normalization by the centroid peak positions of standard kaersutite crystals from Iki, Nagasaki, Japan (Fe³⁺ = 1%) and from Qaersut, Umanq District, Greenland (Fe³⁺ = 93%) (Monkawa et al., 2006). Oxygen isotope analysis was performed by infrared laser-assisted fluorination (Greenwood et al., 2017). Analyses were undertaken on aliquots of ~2 mg of whole-rock powder, drawn from a larger reservoir produced by crushing and homogenizing a clean interior chip weighing ~100 mg.

RESULTS

Petrological Observation and Chemical Analysis

Oxygen isotope analyses (N = 2) yielded mean δ¹⁷O, δ¹⁸O, and linearized Δ¹⁷O values of 2.59 ± 0.03, 4.38 ± 0.08, and 0.28 ± 0.02 (2σ), respectively. The value of δ¹⁷O is defined as (R¹⁷sample/R¹⁷SMOW−1)/1000, where R¹⁷ = ¹⁷O/¹⁶O, and SMOW is the standard mean ocean water. The value of δ¹⁸O is defined similarly using the ¹⁸O/¹⁶O ratios. The linearized value for Δ¹⁷O was calculated using the method of Miller (2002) with a slope factor 0.528. Our analysis of A 12325 plots close to the average Δ¹⁷O value for literature-derived Martian oxygen isotope values, thus confirming that A 12325 is of Martian origin (Figure 1).

Observation by optical microscopy has revealed that A 12325 is a poikilitic shergottite and that the polished section examined in this study contains an opaque shock vein crosscutting the PTS (Figure 2). Shock features are described in a later section, and igneous textures are addressed in this section. Quantitative chemical compositions of each mineral are summarized in Table 1. ImageJ analysis (binarization and pixel count) of x-ray chemical maps reveals that A 12325 is comprised of the following mineral phases: olivine (57 vol%), pyroxene (28 vol%), plagioclase (11 vol%). Accessory phases are Ca phosphate, chromite–ulvöspinel, Fe-sulfide, and ilmenite. Amphibole was not observed in the polished section studied.

Olivine chadacrysts that are completely enclosed by pyroxene oikocrysts, in poikilitic areas are smaller (~20-
Pyroxene oikocrysts in A 12325 are up to 2 mm in size. Most of them are less than 1.5 mm, which may be the smallest among poikilitic shergottites (e.g., ~5 mm in Yamato (Y) 000027 Mikouchi and Kurihara (2008); ~6 mm in Northwest Africa (NWA) 7397 Howarth et al. (2014)). The number of oikocrysts is significant, and we recognized at least 20 oikocrysts in our polished section. In a similar way to olivine, pyroxene oikocrysts include feldspathic glass as melt inclusions. As is the case with oikocrysts in other poikilitic shergottites, the oikocrysts have low-Ca pyroxene (pigeonite) cores (En$_{73.0}$Fs$_{23.4}$Wo$_{3.6}$-En$_{84.3}$Fs$_{15.6}$Wo$_{10.1}$) and high-Ca pyroxene (augite) mantles (En$_{52.2}$Fs$_{20.0}$Wo$_{27.3}$-En$_{42.8}$Fs$_{16.4}$Wo$_{40.6}$). A characteristic feature of the oikocrysts in A 12325 is the anhedral pigeonite rims (~En$_{60}$Fs$_{30}$Wo$_{10}$) overgrowing high-Ca pyroxene (Figure 5). EBSD analysis revealed that these pyroxenes display the same crystal orientation from core to rim implying they are a single crystal (Figure 5b,c). The low-Ca pyroxene rims are enriched in Fe and Ca (En$_{60}$Fs$_{30}$Wo$_{10}$) compared to the cores (Figure 5d). Pyroxene in non-poikilitic areas displays anhedral to subhedral morphologies (Figure 2c). The Ca-poor and Ca-rich areas have almost identical chemical compositions to pigeonite rim and augite mantle in the pyroxene oikocrysts, respectively (Figure 6a). The Al$_2$O$_3$ (0.28–2.85 wt%) and TiO$_2$ (0.06–0.66 wt%) contents show a clear correlation in low-Ca pyroxene oikocrysts and high-Ca pyroxene, although they are not correlated in the rim of oikocrysts and non-poikilitic low-Ca pyroxene (Figure 6b). The Fe–Mn ratio of low-Ca pyroxene in A 12325 is within the range for Martian meteorites (Figure 6c) (Papike et al., 2009).

Plagioclase is anhedral and euhedral when it is located next to olivine and pyroxene, respectively (Figure 3c). Some plagioclase grains include anhedral pyroxene grains and are sometimes associated with Ca phosphate. Each grain is chemically zoned, and its chemical composition ranges from An$_{40.5}$Ab$_{56.5}$Or$_{3.0}$ to An$_{58.0}$Ab$_{40.4}$Or$_{1.6}$, which is within the range of plagioclase compositions in the other poikilitic shergottites (Figure 7a). We obtained four SR-XANES spectra from plagioclase with a smooth surface (maskelynite, described later). Pre-edge spectra were deconvoluted into two Gaussians after baseline subtraction and yielded the centroid peak positions from 7112.46 to 7112.61 eV by an area-weighted average of two Gaussian peaks (Cottrell et al., 2009) (Table 2). Assuming an exponential correlation between a centroid peak position and Fe$^{3+}$ contents, as reported by Wilke et al. (2001), these centroid peak positions indicate that about 12%–15% of Fe in plagioclase is trivalent (Figure 7b).

Spinel (chromite–ulvöspinel–spinel) grains are scattered throughout the thin section in various sizes from <10 to ~160 µm (Figure 3d,e). Spinel in olivine chadacrysts, pyroxene oikocrysts, and non-poikilitic olivine are relatively small (~80 µm) compared within the interstices of non-poikilitic areas. Spinel in A 12325 shows a wide range of chemical compositions (Figure 8). In olivine chadacrysts, spinel is relatively enriched in Cr and shows smaller compositional variation than spinel in other areas (Ch$_{78.3}$Ul$_{3.0}$Sp$_{13.2}$-Ch$_{72.7}$Ul$_{4.6}$Sp$_{22.6}$). Spinel next to magmatic glass in olivine chadacrysts

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**FIGURE 1.** Oxygen isotope plot of Asuka 12325. All $\Delta^{17}$O values were calculated using the method of Miller (2002) using a slope value of 0.528. Our analysis of A 12325 plots close to the average $\Delta^{17}$O value for a literature compilation of Martian oxygen isotope values, confirming that A 12325 is of Martian origin. MFL, Martian fractionation Line; TFL, terrestrial fractionation line.
showed chemical zoning and becomes Al-rich and Cr-poor in the rims (Figure 3b). Pyroxene oikocrysts contain spinel with a variety of Cr-Ti contents (Chr84.9Ulv2.7Sp12.3-Chr46.5Ulv38.4Sp15.1). Spinel within the rims of pyroxene oikocrysts is richer in Ti than those inside the oikocrysts. Individual spinel grains display chemical zoning, with Ti increasing toward the rims of the oikocrysts. The chemical composition of spinel in the non-poikilitic areas ranges from Cr-rich to Ti-rich (Chr85.1Ulv2.6Sp12.4-Chr37.2Ulv51.9Sp10.9), and the chemical composition changes continuously (Figure 8a). Cr-rich spinel occurs in non-poikilitic olivine grains, while the Ti-rich type was found as an isolated grain at the edge of the non-poikilitic area. The Cr# (=molar Cr/(Cr + Al)) and the Mg# (=molar Mg/(Mg + Fe)) of interstitial spinel and spinel in non-poikilitic olivine are positively correlated at Mg# > 14. In contrast, they are negatively correlated at Mg# < 14 (Figure 8b). The Cr# and the Mg# in the other spinel show no correlations. Some Cr-rich spinel grains in contact with olivine are accompanied by a thin pyroxene rim. In non-poikilitic areas, the Ti-rich spinel shows exsolution lamellae of ilmenite (darker lamellae) and lamellae of unknown phase developed parallel to three directions (Figure 3d). The latter lamellae is brighter in the backscattered electron (BSE) images and has an identical composition to the host spinel. These lamellae are not observed in Cr-rich spinel in poikilitic areas. Although we conducted EBSD analysis and observation by transmission electron microscopy of these lamellae, the lamellar phase is not confirmed so far and will report in another paper. Anhedral ilmenite and iron sulfide sometimes coexist with the Ti-rich spinel (Figure 3e). Pyrrhotite sometimes contains spinel and/or pentlandite (Figure 3f). All pyrrhotite grains are partly altered, resulting in partial replacement by Fe-S-rich materials, which showed
no clear EBSD patterns. Its chemical composition is \( \text{FeO}_{\text{Total}} = 61.2 \), \( \text{SO}_3 = 14.0 \), \( \text{SiO}_2 = 2.9 \), and \( \text{MgO} = 0.8 \text{ wt}\% \) and the total mass is about 79.6 wt\% in average \((N = 11)\). The altered material shows Raman peaks at 210, 270, and 384 cm\(^{-1}\), similar but slightly different from the Raman peaks of tochilinite \((235, 298, \text{ and } 357 \text{ cm}^{-1})\). The alteration product shows abundant cracks radiating from the central pyrrhotite and has a layered schlieren structure. Moreover, the altered assemblage in A 12325 is accompanied by a small amount of Fe-rich olivine at the boundary with pyroxene (Figure 3f). Although this alteration material is apparently similar to magnetite veins in sulfide in Grove Mountain (GRV) 020090 (Lin et al., 2013), they are distinct because of differences in sulfur content and the layered structure.

**Shock Metamorphism**

Optical microscopic observations revealed that olivine and pyroxene in A 12325 have planar fractures and their extinction is relatively sharp, with kinks rather than undulatory. While plagioclase around the shock melt vein is entirely vitrified, most plagioclase grains are only partly maskelynitized and still show birefringence with wavy extinction. We detected no chemical compositional differences between crystalline plagioclase and maskelynite. The shock melt vein is straight rather than curvy, and its maximum width is \(~300 \mu\m\).

In BSE images, crystalline plagioclase and maskelynite are distinguishable by the presence/absence of cracks (Figure 9a). Plagioclase has abundant cracks, while maskelynite has a smooth surface. This trend is also seen in the EBSD phase maps in which the area displaying cracks clearly shows Kikuchi patterns (Figure 10a). The shock melt vein is highly heterogeneous and composed of small grains, relict mineral fragments and clasts, and a glassy matrix (Figure 9b). Although the vein was highly fractured, we found no vugs, which commonly occur in shock veins in severely shocked \(~55 \text{ GPa}\) Martian meteorites with brown olivine (Takenouchi et al., 2018). We found various high-pressure phases within and around the shock melt vein by EBSD phase analysis and micro-Raman analysis (Figures 10 and 11). Granular minerals in the shock vein are majorite–pyrope garnet, the most abundant high-pressure phase in this meteorite (Figures 9c, 10b and 11). The largest garnet grain is about 3 \(\mu\m\) in diameter and shows oscillatory contrast in BSE images (Figure 9c). Our EDS line analysis showed that the band area with brighter contrast seems to be enriched in Fe and Ca, and the core is Mg-rich compared with its rim. However, we cannot obtain a clear relationship between chemical compositions and the BSE contrast due to weak intensity...
and a low spatial resolution of EDS. The interstitial area between garnet consists of materials with darker and brighter BSE contrasts (Figure 9c) enriched in Fe, Ca, Na, and P. While the darker area is glass, the brighter area may be Fe-metal or oxide.

Ringwoodite is also common in this meteorite and is found in the vein as individual grains (<1 μm) (Figure 9d) or parts of relict fragments replacing olivine. Outside of the vein, the olivine rim in contact with the shock melt vein is also transformed to ringwoodite (Figures 9e and 10b). This ringwoodite rim is composed of homogeneous microcrystals at the near side of the vein and lamellae at the far side (Figure 9e), a common ringwoodite occurrence in Martian meteorites (e.g., Greshake et al., 2013; Walton et al., 2014). Around the 110 μm-thick shock melt veins, the homogeneous ringwoodite rim and lamellar area have up to 25–35 μm thickness. The width of individual ringwoodite lamella is about 0.5–0.8 μm. We also found wadsleyite by EBSD analysis (Figure 10), although wadsleyite is relatively rare compared with ringwoodite.

The other high-pressure minerals we found in the shock vein of A 12325 are jadeite and tuite. Jadeite occurred as dendritic- or radial-shaped microcrystals in the glassy area in the shock melt vein (Figure 9f).
identified by EBSD (Figure 10). Tuite, identified by Raman analysis (Figure 11), replaces a Ca phosphate fragment in the shock vein-forming polycrystals. These high-pressure minerals are present everywhere in the vein, even in the center of the thickest area.

**DISCUSSION**

**Crystallization Sequence**

We can estimate the crystallization sequence of A 12325 based on its igneous textures and mineral compositions in the same way as other poikilitic shergottites (e.g., Combs et al., 2019; Howarth et al., 2014; Ikeda, 1997; Kizovski et al., 2019; Lin et al., 2005, 2013; Mikouchi, 2005; Mikouchi & Kurihara, 2008; Rahib et al., 2019; Takenouchi, 2018; Usui et al., 2010; Walton & Herd, 2007). Since olivine chadacrysts and pyroxene oikocrysts have a composition that is more Mg-rich than those in non-poikilitic areas (Figures 4 and 6), the poikilitic areas should have formed prior to the non-poikilitic areas. In the poikilitic area, the inclusion relations of each mineral indicate that Cr-rich spinel was the first mineral to crystallize and then olivine crystallized to include the Cr-rich spinel grains (Figure 3a).

During Cr-rich spinel and olivine growth, low-Ca pyroxene started crystallizing and enclosed parts of Cr-rich spinel and olivine. Mg-rich olivine chadacrysts, which may be included by pyroxene oikocrysts, tend to be more rounded compared with later enclosed Fe-rich ones, as reported in other poikilitic shergottites (e.g., Howarth et al., 2014; Usui et al., 2010). Some spinel and olivine grains were not enclosed by pyroxene and grew larger than those in poikilitic areas. The Cr-rich spinel grains in non-poikilitic areas should have started crystallizing simultaneously with Cr-rich spinel in poikilitic areas because their compositions are identical to each other (Figure 8). While such Cr-rich spinel can retain its original chemical composition, olivine and spinel not enclosed by pyroxene were in equilibrium with residual melt, and their compositions became Fe-rich and Ti-rich gradually during cooling, respectively. Such equilibration is enough to erase Mg-Fe chemical zoning in the olivine, while Ca zoning was retained due to its slower diffusion rate (Figure 4d).

After the growth of pigeonite oikocrysts, augite formed around the oikocrysts with the same crystal...
orientation. Two pyroxene thermometers (Lindsley, 1983) indicate their equilibration temperature as ~1150°C. The smaller size but the larger number of oikocrysts in A 12325 may imply that the cooling to 1150°C was relatively fast compared to other poikilitic shergottites. When plagioclase started crystallizing from the melt, oikocrysts (pigeonite core and augite mantle) may have stopped growing. Instead, Fe-rich pigeonite formed around augite after/during crystallization of plagioclase. This crystallization sequence is inferred from the mineral distribution in oikocrysts: plagioclase penetrates only into pigeonite rims but not into augite areas (Figure 5). This mineral distribution is slightly different from RBT 04261, in which augite includes plagioclase grains indicating continuous augite crystallization after plagioclase formation (Usui et al., 2010). This sequential difference may have been induced by differences in whole-rock compositions because RBT 04261 is enriched in plagioclase (15.9–20.2 vol%), but deficient in olivine (39.4–42.1 vol%) compared with A 12325 (plagioclase: ~10.7 vol%; olivine: 57.1 vol%).

The zoned structure of the pyroxene oikocrysts (pigeonite core + augite mantle + Fe-rich pigeonite rim) has not previously been reported in poikilitic shergottites, although NWA 7397 (Howarth et al., 2014) seems to show pigeonite rims as evidenced in chemical x-ray maps. In contrast, other types of shergottites, such as diabasic shergottite Queen Alexandra Range (QUE) 94201 (Mikouchi et al., 1998) and olivine-phyric shergottite Larkman Nunatak 06319 (Peslier et al., 2010), do show similar zoned structures in rapidly crystallized pyroxene. Based on these studies, suppression of plagioclase crystallization by rapid cooling causes Ca partitioning into pyroxene to form augite until the onset of plagioclase formation. Although the cooling rate of A 12325 may not have been as fast as that of QUE 94201 or LAR 06319, non-equilibrium crystallization should cause this characteristic pyroxene structure.

Since the pigeonite rims in A 12325 have an almost identical composition to that of pigeonite in the non-poikilitic area (Figure 6a), the pigeonite rim may have crystallized simultaneously with the non-poikilitic areas.
Two-pyroxene thermometry (Lindsley, 1983) indicates an equilibrated temperature in the non-poikilitic area of 1100 °C. With a further temperature drop, Ca-phosphate and Fe-sulfide crystallized interstitially, and ilmenite formed as exsolution lamellae in ulvospinel. Although A12325 formed in a distinct igneous body from that of the other poikilitic shergottites, their crystallizing sequence is almost identical. This result implies that the poikilitic rock commonly forms on Mars regardless of its source magma.

Cooling Rate and Re-Equilibration

The re-equilibration of A12325 erased Mg-Fe chemical zoning in individual olivine chadacrysts but could not homogenize compositional differences between each grain. The positive and negative correlations between Cr# and Mg# in spinel represent a typical magmatic trend and a re-equilibration trend between olivine and spinel, respectively (e.g., Barnes & Roeder, 2001; Usui et al., 2010). In A12325 spinel, the weak negative trend in Mg# < 14 and the strong positive trend in Mg# > 14 (Figure 8) indicate that spinel preserves the igneous trend and the degree of re-equilibration is limited. Moreover, since the oxygen fugacity of A12325 is below the quartz–fayalite–magnetite (QFM) buffer (see the next section), the spinel crystallization should have stopped during pyroxene crystallization in equilibrium, which results in chemical compositional gaps in the Cr-Ti-Al diagram (Figure 8) as reported by previous studies (e.g., Goodrich et al., 2003; Lin et al., 2013). However, the spinel composition in A12325 is continuous from chromite to ulvospinel, indicating that the non-poikilitic areas have solidified under the disequilibrium condition to crystallize spinel continuously from a parental melt. Al-rich chromite in olivine chadacrysts may have formed by re-equilibration of coexisting trapped melt inclusions. To summarize the above discussion, both the poikilitic and the non-poikilitic areas formed continuously under the disequilibrium condition.

The Al/Ti ratios of low-Ca pyroxene in mare basalt and alkali basalt increase as a pressure at which
crystallization took place rises (Akella & Boyd, 1973; Nekvasil et al., 2004). The Al/Ti ratios of pyroxene are thus used as a function of pressure in Martian basalt (e.g., Filiberto et al., 2010; Howarth et al., 2014; Lin et al., 2005, 2013; Mikouchi, 2005; Mikouchi & Kurihara, 2008; Mikouchi & Miyamoto, 2000; Rahib et al., 2019; Usui et al., 2010). Lin et al. (2013) discussed that pyroxene oikocrysts in GRV 020090 show higher Al/Ti ratios with smaller deviation than non-poikilitic pyroxene, indicating that the oikocrysts and non-poikilitic pyroxene crystallized at deeper and shallower levels, respectively. The constant Al/Ti ratios in pyroxene oikocrysts in A 12325 infer that the oikocrysts crystallized at a specific pressure. According to the above studies, the estimated pressure for crystallization of pyroxene oikocrysts in A 12325 is about 10 kbar (∼85 km depth in the Martian crust and possibly a crust–mantle boundary), while the reliability of the qualitative depth is uncertain due to the small amount of both Ti and Al in A 12325. However, since the Al/Ti ratios of the oikocrysts in A 12325 are similar to those in other poikilitic shergottites (e.g., Howarth et al., 2014; Mikouchi & Miyamoto, 2000), pyroxene oikocrysts in most poikilitic shergottites possibly formed at similar depth in the Martian crust. The correlation between Al/Ti ratios and the pressure is disturbed by plagioclase crystallization (Howarth et al., 2014), and it is difficult to estimate the quantitative depth at which the non-poikilitic area crystallized.

Focusing on Ca zoning in non-poikilitic olivine, we can roughly estimate the cooling rate using its diffusion rate in a similar manner to Mikouchi et al. (1998) and Miyamoto et al. (1986). We adopt a homogenous Ca composition using the core composition as an initial condition and assume an outflow of Ca from olivine by diffusion. When we postulate a cooling from 1200 to 800°C, the zoning profile is well reproduced by cooling rates of 50–100°C year⁻¹ using Ca diffusion rate reported in Jurewicz and Watson (1988) (Figure 12). Although this method is not optimized for Martian meteorites and we have ignored crystal growth, which could yield different initial conditions from our assumption, the order of cooling rate for A 12325 may not be further from our estimation, as demonstrated by Miyamoto et al. (2009). The chemical compositional zoning in olivine is rarely reported in other poikilitic olivine; therefore, it would seem that cooling rates of A 12325 were faster than the other poikilitic shergottites.

To summarize, although pyroxene oikocrysts in A 12325 formed at a similar depth to those in other poikilitic shergottites, A 12325 may have cooled at a

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**TABLE 2. XANES.**

<table>
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<th>Name</th>
<th>Measured centroid peak positions (eV)</th>
<th>Normalized centroid positions (eV)</th>
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*Note: Kst-std: Kaersutite from Qaersut, Umanq District, Greenland. Iki-std: Kaersutite from Iki, Nagasaki Japan.*

*Monkawa et al. (2006).*
faster rate after/during the pyroxene oikocryst formation, which was supported by similar spinel composition, small-sized pyroxene oikocrysts, and Ca chemical compositional zoning in olivine. Therefore, this rapid cooling may imply that A 12325 cooled at a relatively shallower depth and so was derived from near the surface of the Martian crust compared with other enriched and intermediate poikilitic shergottites.

Estimation of Oxygen Fugacity

We have estimated the oxygen fugacity (fO2) of A 12325 based on olivine–spinel–orthopyroxene equilibrium and Fe-Ti oxides equilibrium using the MELTS-related calculator (Ghiorso & Evans, 2008; Sack & Ghiorso, 1989, 1991a, 1991b, 1994a, 1994b, 1994c). For the calculation based on olivine–spinel–orthopyroxene equilibrium, we selected the most Mg-rich olivine and pyroxene and the most Cr-rich spinel in the poikilitic areas, as described in Goodrich et al. (2003), because these minerals are the least modified by re-equilibrium and tend to retain the original equilibrium compositions. Moreover, the average compositions of five grains from the highest Mg or Cr compositions were also used for the oxygen fugacity calculation. The chemical compositions we used are summarized in Table 3, and these compositions yield the redox state of 0.6–0.7 log units above the iron–wüstite buffer (IW + 0.6–0.7) at 1238–1256°C. Our compositional data provide the Mg-Fe distribution coefficients between olivine and pyroxene (KD_{Fe/Mg[ol/px]} = 1.29, which indicates they are out of equilibrium because the value of KD_{Fe/Mg[ol/px]} should be 1.2 if they are in equilibrium (Goodrich et al., 2003). However, since these compositions are the least modified, the calculated value may be acceptable. We also calculated oxygen fugacity in the non-poikilitic areas using the chemical composition of coexisting Cr-rich spinels and low-Ca pyroxenes with Fe-rich olivine and obtained more oxidized values IW + 1.8–2.5 at a lower temperature (995–1133°C) within KD_{Fe/Mg[ol/px]} = 1.2 ± 0.2. The Fe-Ti oxide geothermobarometer using coexisting ulvospinel and ilmenite (Table 3) again yields reduced values IW + 0.4–1.7 at the lowest temperature (810–873°C). The obtained redox states at each temperature are summarized in Figure 13.

The Martian mantle may have the oxygen fugacity of logfO2 = IW-IW + 1, and the oxygen fugacity has been considered to correlate with REE patterns because Martian magma may become enriched in REE by assimilation of oxidized crust (e.g., Herd, 2003; Herd et al., 2002; Wadhwa, 2001). The intermediate poikilitic shergottite Allan Hills (ALH) 77005 is reported to have QFM-2.6 (QFM: quartz–fayalite–magnetite buffer), which is close to the mantle value (Goodrich et al., 2003). Enriched poikilitic shergottite RBT 04261/2 shows a relatively oxidized value QFM-1.6 (Usui et al., 2010). Since A 12325 has the depleted light-REE pattern (Debaille et al., 2019), the relatively reduced condition of A 12325 (IW + 0.6–IW + 0.7 = QFM-2.7–QFM-2.8 at 1238–1256°C) is consistent with the previous REE/fO2 trend. Previous studies propose the presence of an enriched source mantle instead of crustal assimilation to explain the enriched magma source (e.g., Borg & Draper, 2003; Combs et al., 2019; Howarth et al., 2014; Udry et al., 2020), and therefore, the redox state is not necessarily related to the REE patterns.
Some enriched and intermediate shergottites are oxidized during progressive crystallization resulting in more oxidized oxygen fugacity at a lower temperature (NWA 7397: from QFM-2 to QFM-0.3, Howarth et al. (2014); LAR 06319: from QFM-2 to QFM + 0.3, Peslier et al. (2010), NWAs in Rahib et al. (2019)). While A 12325 does not show such a simple crystallization-oxidation change by cooling, the meteorite exhibits a slightly different trend: once oxidized from IW + 0.6-IW + 0.7 to IW + 1.8-IW + 2.5 and then re-reduced to IW + 0.4-IW + 1.7 (Figure 13). However, this trend may be incorrect and reflect an inappropriate oxygen buffer calculation in the non-poikilitic areas. Although we selected near-equilibrated neighboring olivine and pyroxene for the calculation, the calculation result highly depends on Mg contents in spinel, and variable spinel composition in the non-poikilitic area makes the calculation results uncertain. Since plagioclase contains little Fe$^{3+}$ ($\text{Fe}^{3+}/\Sigma\text{Fe} = 12\%-15\%$) similar to those in reduced and intermediate shergottites (Satake et al., 2014), the redox state during the crystallization of non-poikilitic areas may be similar to those shergottites. A 12325 may have experienced no redox change or a slight oxidation during its crystallization from IW + 0.6-IW + 0.7 to IW + 0.4-IW + 1.7. Therefore, the unique light-REE depleted poikilitic shergottite A 12325 has a...
redox history similar to enriched poikilitic shergottites rather than intermediate ones.

Comparison of Mineral Chemistries with Other Poikilitic Shergottites

Comparing mineral compositions between A 12325 and other poikilitic shergottites, the olivine compositional range of A 12325 is close to those in enriched poikilitic shergottites (Figure 4b). Some intermediate poikilitic shergottites have Mg-richer composition compared with olivine in A 12325. In particular, olivine with the lowest Fo# in poikilitic areas of NWA 1950 is still Mg richer than any olivines in A 12325. Pyroxene and spinel compositional ranges of A 12325 also overlap with those of enriched shergottites rather than intermediate ones.
A compositional range of plagioclase (maskelynite) looks close to that of intermediate shergottites because plagioclase in enriched shergottites shows more Na richer composition (Figure 7a), while NWA 10618 and NWA 4468 (enriched) have almost identical composition to A 12325. The features of mineral composition and redox states signify that a simple mixing process between magmas of enriched shergottites and A 12325 could not generate that of intermediate shergottites. Therefore, in order to form poikilitic shergottites with the above three chemical compositional subgroups, we need at least three distinct parent magmas. There may be an unrevealed primitive depleted source or an independent intermediate source in Mars; otherwise, there are some mechanisms to change the magma composition. Although their compositions are different, they have similar petrogenesis and crystallization processes: for example, Al/Ti ratios indicate that the oikocrysts form at almost identical depths, possibly a crust–mantle boundary. The oikocrysts are moved to shallower parts, and non-poikilitic areas are crystallized as an intrusion (e.g., Howarth et al., 2014; Rahib et al., 2019). Then, the scale of intrusions may control the cooling rate of non-poikilitic areas. A 12325 implies that there are various-sized intrusions with a variety of chemical compositions in the Martian crust.

**Shock History**

Two types of “crystalline” plagioclase are known in shergottites. One is once maskelynitized (or partly melted) and then recrystallized, examples being those in GRV 99027 and NWA 6342 (Kizovski et al., 2019; Lin et al., 2005; Wang & Chen, 2006). This type of recrystallized plagioclase is generally polycrystalline, retaining the original shape of igneous plagioclase. The other type is igneous plagioclase escaping maskelynitization during shock metamorphism. Such igneous crystalline plagioclase is very rare in shergottites and has only been reported in four samples: NWA 8159, NWA 4480, NWA 10416, and NWA 12241 (Irving et al., 2016; Piercy et al., 2020; Sharp et al., 2019; Udry et al., 2021). The crystalline plagioclase in A 12325 is most likely of igneous origin because these grains are single crystals, in contrast to recrystallized plagioclase. Complete maskelynitization was only observed around the shock melt vein is ascribed to a decrease of maskelynitization pressure by high temperature (e.g., Fritz et al., 2019; Kudo et al., 2010). Although the maskelynitization pressure depends on Ca-contents in plagioclase (e.g., Fritz et al., 2019; Fritz, Artemieva, et al., 2005; Stöffler et al., 1986), partial maskelynitization throughout the meteorite may be induced by local high pressure or high temperature induced at a shock wave front because no compositional differences are detected between maskelynite and plagioclase. Since the expected shock pressure considering the plagioclase composition in A 12325 is about 30 GPa for complete maskelynitization (Fritz et al., 2019) and 17–22 GPa for partial maskelynitization (Hu et al., 2023), the estimated shock pressure of A 12325 should be at least <30 GPa and possibly 17–22 GPa.
If the high-pressure minerals are present throughout the vein, the high-pressure minerals yield lower limits of shock pressure for the shock vein solidification: The transformation of olivine (Fo60-70) to ringwoodite occurs about 13–23 GPa at 1600°C according to an equilibrated phase diagram (e.g., Presnall, 1995; Tomioka & Miyahara, 2017). While the transformation pressure for majorite–pyrope solid solution from pyroxene depends on Al2O3 contents, pyroxene in A 12325 contains little Al2O3 (~2 wt%). Therefore, the complete transformation of pyroxene to the garnet structure in the shock vein of A 12325 infers the lower limit for shock pressure above 17 GPa (e.g., Tomioka & Miyahara, 2017), which is consistent with the partial maskelynitization pressure (17–22 GPa, Hu et al., 2023). Jadeite could be stable above ~3 GPa (Ozawa et al., 2014), and tuite forms at 12–23 GPa (Murayama et al., 1986; Xie et al., 2003). Therefore, the shock pressure for shock melt vein solidification in A 12325 is about 17–22 GPa.

The shock dwell times of Martian meteorites are widely estimated to describe impact events on Mars (e.g., Beck et al., 2005; Fritz & Greshake, 2009; Sharp et al., 2019; Walton et al., 2014). We also estimate the shock dwell time of A 12325 in the same way that Ohtani

### TABLE 3. Results of calculated oxygen fugacity and temperature, and chemical compositions used for the calculation.

<table>
<thead>
<tr>
<th>Poikilitic</th>
<th>Mg-richest olivine</th>
<th>5-point average</th>
<th>Non-poikilitic</th>
<th>Mg-richest olivine</th>
<th>5-point average</th>
</tr>
</thead>
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<tr>
<td></td>
<td>ol sp px</td>
<td>ol sp px</td>
<td>ol sp px</td>
<td>ol sp px</td>
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<td>SiO2</td>
<td>38.0 0.12 54.7</td>
<td>37.7 0.11 54.6</td>
<td>36.4 0.05 52.9</td>
<td>36.0 0.05 52.8</td>
<td>36.3 0.05 52.2</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.01 0.99 0.07</td>
<td>0.02 1.11 0.08</td>
<td>0.04 6.62 0.50</td>
<td>0.03 7.54 0.64</td>
<td>0.06 4.75 0.58</td>
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<td>Al2O3</td>
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<td>0.02 6.12 0.34</td>
<td>n.d. 7.65 0.76</td>
<td>n.d. 7.48 0.69</td>
<td>0.03 6.60 0.90</td>
</tr>
<tr>
<td>FeO</td>
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<td>n.m. 3.12 n.m.</td>
<td>n.m. 6.79 n.m.</td>
<td>n.m. 8.14 n.m.</td>
<td>n.m. 5.22 n.m.</td>
</tr>
<tr>
<td>Cr2O3</td>
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<td>0.08 56.3 0.59</td>
<td>0.04 39.3 0.25</td>
<td>0.08 35.6 0.20</td>
<td>0.09 45.6 0.47</td>
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<tr>
<td>FeO</td>
<td>26.4 26.9 14.9</td>
<td>26.7 26.7 15.4</td>
<td>32.3 35.0 18.7</td>
<td>32.8 37.5 19.0</td>
<td>32.0 34.2 17.3</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.54 0.51 0.51</td>
<td>0.69 0.59 0.64</td>
<td>0.67 0.61 0.65</td>
<td>0.64 0.59 0.61</td>
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<td>MgO</td>
<td>35.9 5.54 26.2</td>
<td>35.3 5.56 26.3</td>
<td>30.2 4.46 21.6</td>
<td>30.6 3.70 21.1</td>
<td>30.1 3.46 20.4</td>
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<tr>
<td>NiO</td>
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<td>0.06 0.02 0.02</td>
<td>0.03 0.03 0.02</td>
<td>0.04 0.02 0.03</td>
<td>0.06 0.03 0.02</td>
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<td>CaO</td>
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<td>0.13 0.02 1.85</td>
<td>0.22 0.11 4.23</td>
<td>0.16 0.06 5.14</td>
<td>0.19 0.04 6.71</td>
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<td>Na2O</td>
<td>0.01 0.03</td>
<td>0.01 0.03</td>
<td>0.01 0.07</td>
<td>0.07 0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>Total</td>
<td>101.1 100.9 99.3</td>
<td>100.5 100.1 99.7</td>
<td>99.80 101.03 99.78</td>
<td>100.5 101.3 100.2</td>
<td>99.5 101.0 99.2</td>
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<tr>
<td>T (°C)</td>
<td>1238</td>
<td>1256</td>
<td>1133</td>
<td>996</td>
<td>1003</td>
</tr>
<tr>
<td>log fO2/C0</td>
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<td>−10.5</td>
<td>−10.7</td>
<td>−12.2</td>
<td>−12.8</td>
</tr>
<tr>
<td>IW</td>
<td>0.72</td>
<td>0.63</td>
<td>1.95</td>
<td>2.48</td>
<td>1.79</td>
</tr>
<tr>
<td>QFM</td>
<td>−2.68</td>
<td>−2.75</td>
<td>−1.57</td>
<td>−1.22</td>
<td>−1.90</td>
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### Fe-Ti oxides

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<tr>
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<th>sp ilm</th>
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</tr>
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<tbody>
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<td>SiO2</td>
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<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
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<td>5.13</td>
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<td>FeO</td>
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<td>1.01</td>
<td>8.21</td>
<td>0.56</td>
<td>8.60</td>
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<td>V2O5</td>
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<td>0.00</td>
<td>0.29</td>
<td>0.00</td>
<td>0.25</td>
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<tr>
<td>Cr2O3</td>
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<td>0.72</td>
<td>23.0</td>
<td>0.99</td>
<td>22.4</td>
</tr>
<tr>
<td>FeO</td>
<td>45.0</td>
<td>39.7</td>
<td>45.9</td>
<td>41.0</td>
<td>47.0</td>
</tr>
<tr>
<td>MnO</td>
<td>0.61</td>
<td>0.72</td>
<td>0.68</td>
<td>0.85</td>
<td>0.70</td>
</tr>
<tr>
<td>MgO</td>
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<td>4.49</td>
<td>2.81</td>
<td>3.54</td>
<td>2.82</td>
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<tr>
<td>CaO</td>
<td>0.03</td>
<td>0.17</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>Total</td>
<td>101.8</td>
<td>100.0</td>
<td>101.6</td>
<td>100.1</td>
<td>103.0</td>
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<tr>
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<td>810</td>
<td>873</td>
<td>812</td>
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</tr>
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<td>log fO2/C0</td>
<td>−16.1</td>
<td>−18.0</td>
<td>−15.3</td>
<td>−17.8</td>
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</tr>
<tr>
<td>IW</td>
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<td>0.35</td>
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<tr>
<td>QFM</td>
<td>−2.72</td>
<td>−3.68</td>
<td>−2.26</td>
<td>−3.59</td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: ilm, ilmenite; ol, olivine; px, pyroxene; sp, spinel.
et al. (2004) described. They calculated the shock dwell time by considering shock vein cooling and ringwoodite lamellar growth around the shock vein based on one-dimensional thermal conduction (Carlsow & Jaeger, 1959) and an interface-controlled growth (Kerschhofer et al., 2000; Mosenfelder et al., 2001), respectively. In A 12325, the 110 μm wide vein has a 35 μm-wide ringwoodite rim, and the width of ringwoodite lamellae at 25–35 μm away from the vein was about 0.5–0.8 μm (Figure 14a). We adopt a similar geometry to that of Ohtani et al. (2004) and simulate the ringwoodite lamellae growth at the points at 25 and 35 μm away from the vein assuming the 110 μm-wide vein’s temperature as 2300°C and the surrounding temperature as 800, 1000, and 1200°C (Figure 14b). The vein temperature of 2300°C is the same as the liquidus temperature of the KLBI peridotite and was also employed in Ohtani et al. (2004). Numeric constants for the vein cooling and ringwoodite growth calculations are the same as those in Ohtani et al. (2004), aside from thermal diffusivity. In this study, the thermal diffusivity was calculated from the heat capacity (1000 J kg \(^{-1}\) K \(^{-1}\)), thermal conductivity (1.8 W m K \(^{-1}\)), and density (3000 kg m \(^{-3}\)) of basalt used for calculation of Martian basalts’ cooling by Shaw and Walton (2013). Since the 300 μm wide vein is wholly filled by ringwoodite and majorite, we assume that the 110 μm wide vein should have been completely cooled before the decompression. Therefore, ringwoodite growth should not be interrupted by decompression but instead by a temperature drop. In other words, the ringwoodite should grow up to its maximum size in our calculation. Figure 14c shows the measured ringwoodites width of 0.5 μm in about 40 ms.

FIGURE 14. (a) Backscattered electron image of the shock vein and surrounding ringwoodite in A 12325. The width of the shock vein is about 110 μm. Ringwoodite has 25 μm wide homogeneous rim and 15 μm wide lamella-rich area. (b) A geometry for the calculation of vein cooling and ringwoodite growth (see text in detail). (c) The calculated ringwoodite lamellar width assuming the host-rock temperature as 800, 1000, and 1200°C. The host-rock temperature of 1000°C well reproduces the measured ringwoodites width of 0.5 μm in about 40 ms.
results of our calculations for ringwoodite lamellar growth. For the calculation assuming the host rock temperature as 1200°C, the ringwoodite lamellae grow up to 6–8 μm in width, about 10 times wider than those observed in A 12325. If the host rock is about 800°C, the ringwoodite hardly grows at 25–35 μm away from the vein. The calculation postulating the host rock temperature as 1000°C could reproduce the ringwoodite lamellae corresponding width (~0.5 μm) to those in A 12325. Therefore, the host rock temperature as 1000°C at 25–35 μm away from the vein should be the best assumption for the ringwoodite growth in A 12325. In this case, it takes about 40 ms for the lamellae to grow up to 0.5 μm in width, and this could be a minimum estimate for the shock dwell time of A 12325. Compared with other shergottites, a little shorter shock dwell time (10–20 ms) is estimated for Tissint (Walton et al., 2014). Since Tissint has a little narrower ringwoodite rim (15–20 μm) compared with A 12325 and the shock veins with equivalent width (100–110 μm), the shock dwell time of 40 ms for A 12325 may be a reasonable estimate. Commonly, a short dwell time of about 1–20 ms has been suggested for A 12325 because A 12325 may be ejected from the Martian surface as also discussed in the next section.

**Comparison of Shock Histories with Other Poikilitic Shergottites**

There are several textural indicators for severe shock metamorphism, such as the presence/absence of high-pressure minerals, widespread maskelynite or normal (non-diaplectic) feldspar glass (vesiculated glass), brown olivine, and recrystallization of olivine and feldspar as discussed in Fritz et al. (2017) and Stöffler et al. (2018). Table 4 summarizes the characteristic shock features observed in poikilitic shergottites (Boonsue & Spray, 2012; Combs et al., 2019; Fritz, Artemieva, et al., 2005; Fritz, Greshake, & Stöffler, 2005; Kizovski et al., 2019; Lin et al., 2005; Mikouchi & Kurihara, 2008; Takenouchi et al., 2018, 2019; Van de Moorté et al., 2007; Wang & Chen, 2006).

Both A 12325 and the enriched poikilitic shergottites contain high-pressure minerals, while only A 12325 retains the crystalline plagioclase, indicating its weaker shock pressure than the enriched shergottites. The intermediate poikilitic shergottites rarely contain high-pressure minerals. Meteorites with high-pressure minerals seem to have experienced more severe shock metamorphism than other samples because high-pressure minerals have been used as the indicator of intense shock metamorphism (e.g., Bischoff & Stöffler, 1992; Stöffler et al., 1991). However, the presence/absence of high-pressure minerals generally depends on local shock pressure–temperature histories (P–T–t paths) as discussed in various studies (e.g., DeCarli

**TABLE 4. Characteristic shock features of poikilitic shergottites.**

<table>
<thead>
<tr>
<th>REE type</th>
<th>Name</th>
<th>Olivine–pyroxene high-pressure phases</th>
<th>Widespread maskelynite</th>
<th>Brown olivine</th>
<th>Normal feldspar glass</th>
<th>Recrystallization of olivine</th>
<th>Recrystallization of feldspar</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depleted-like</td>
<td>A 12325</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>This study</td>
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<tr>
<td>Enriched</td>
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<td></td>
<td></td>
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<tr>
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<td>NWA 4468</td>
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<td>Intermediate</td>
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<td>○</td>
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<td></td>
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For example, high-pressure minerals can be backtransformed to non-high-pressure minerals if the ambient temperature is high enough after decompression (e.g., Fritz et al., 2017; Hu & Sharp, 2017; Takenouchi et al., 2018; Walton, 2013). Alternatively, high-pressure phases only rarely form under short shock dwell time conditions, such as shock recovery experiments, even if the shock pressure and temperature reach the stability fields of high-pressure minerals (e.g., Hu & Sharp, 2022). On the basis of the above discussion, careful analysis, in particular combining information provided by various shock features, is needed to interpret the shock histories of meteorites with/without high-pressure minerals. The intermediate poikilitic shergottites in Table 4 should have experienced higher post-shock temperature than A 12325 because the other features, such as olivine darkening and recrystallization of both olivine and plagioclase, indicate the severe thermal metamorphism after decompression (e.g., Bläß et al., 2010; Kizovski et al., 2019; Lin et al., 2005; Takenouchi et al., 2018; Treiman et al., 2007; Van de Moortele et al., 2007; Wang & Chen, 2006). Therefore, since the post-shock temperature is related to shock pressure (= shock energy), the shock pressure of the intermediate poikilitic shergottites should be higher (> ~ 40 GPa, Fritz, Artemieva, et al. (2005); Fritz, Greshake, et al. (2005)) than that of A 12325. In contrast, the shock pressure of A 12325 is significantly weaker than other poikilitic shergottites despite abundant high-pressure minerals.

Differences in shock metamorphic degrees among the poikilitic shergottites possibly reflect the relative distance from the impact site because a shock metamorphic degree (P–T–t paths) changes depending on the relative location within the impact site in a single impact event (Bowling et al., 2020; Sharp et al., 2019). However, their geochemical features such as REE patterns, crystallization ages, and cosmic ray exposure ages imply that they were ejected from dissimilar igneous bodies by several distinct impact events (e.g., Christen et al., 2005; Fritz, Artemieva, et al., 2005; Nyquist et al., 2001). Therefore, the unique geochemical features of A 12325 suggest that the impact event which launched A 12325 is distinct from those that launched the other poikilitic shergottites.

Poikilitic shergottites with similar sources, such as intermediate ones in Table 4, tend to show similar shock metamorphic degrees. This result indicates that a single impact event, which must induce a variety of shock metamorphisms on the rocks around the impact site, can eject rocks only from significantly restricted areas with almost identical shock metamorphism. Furthermore, rocks from deeper parts in the Martian crust (poikilitic shergottites) may have experienced more severe shock metamorphism compared with surface rocks such as basaltic shergottites and nakhlites (e.g., Fritz, Artemieva, et al., 2005; Takenouchi et al., 2018). In the case of A 12325, since it may have originated from a shallower region compared with the other poikilitic shergottites, this may explain why A 12325 avoided such a severe degree of shock metamorphism. This is similar to the situation of NWA 8159 and the nakhlites (Fritz, Artemieva, et al., 2005; Sharp et al., 2019). While NWA 10416 may possibly be derived from the same parental igneous body due to its geochemical similarity (Piercy et al., 2020; Váci et al., 2020), the source region of A 12325 is probably different from most of the other weakly shocked Martian meteorites such as nakhlites, NWA 8159 and NWA 4480 because they have different igneous textures, redox states, and/or REE patterns. Therefore, there is likely to have been several ejection events that induced only weak shock metamorphism, and such ejection mechanism may be relatively common rather than unique.

Possible Alteration Record on Mars?

Another remarkable feature of A 12325 is the sulfide alteration forming the Fe-S-rich material and small Fe-rich olivine at the boundaries between pyroxene and sulfide (Figure 3e,f). The Fe-S-rich material may be a mixture of Fe-sulfide and Fe-hydroxide judged from its schlieren structure and non-stoichiometric microprobe data.

Two possibilities may be suggested for the origin of these alteration materials. One possibility is that they are weathering products on the Earth. All meteorites found on the Earth are weathered to some extent, and sulfides are more susceptible to alteration than silicates. Martian meteorites found in hot deserts certainly contain similar Fe-(oxy)hydroxides as terrestrial weathering products of sulfides (Lorand et al., 2005). However, there is no Fe-rich olivine around the weathering products, and the weathering affects are restricted to relatively limited areas, which is different from the widespread olivine-associated alteration in A 12325. Although A 12325 shows weak terrestrial weathering at the rim of the thin section showing olivine staining to yellowish color (Figure 2), the degree of sulfide alteration does not correlate with its location within the thin section. Moreover, no other weathering products are found in A 12325, such as crack-filling iron hydroxide. Therefore, we consider that the altered materials may not be terrestrial origin but from Mars.

If the alteration did occur on Mars, the altered material should have experienced shock metamorphism. Although we observed no obvious shock features such as melting of the altered materials, the cracks radiating from the sulfide may be one of the shock features similar to those around inclusions in shocked olivine (e.g., Monkawa et al., 2005; Treiman, 1995). The Fe-rich
olivine around the altered material is similar to those in eucrites which forms via metasomatism on their parent body. However, the alteration in A 12325 may have occurred in a closed system because of the highly restricted distribution of alteration products. While nakhlites record an aqueous alteration on Mars (e.g., Bunch & Reid, 1975; Daly et al., 2019; Lee et al., 2018; Reid & Bunch, 1975; Treiman, 2005), the evidence for such alteration in shergottites is still rare. Olivine in the olivine–phylitic shergottite NWA 10416 shows the evidence of aqueous alteration to form laihunite during a magmatic process (Váci et al., 2020), while there are also terrestrial weathering products (Piercy et al., 2020). Sulfide in A 12325 is possibly affected by such magmatic fluid just after the solidification to form Fe-S-rich materials and Fe-rich olivine from sulfide and pyroxene. The evidence of alteration in these meteorites may indicate that such alteration processes are relatively common near the Martian surface.

CONCLUSIONS

We studied a newly found poikilitic shergottite Asuka 12325. A 12325 widens a diversity of Martian meteorites collections and it indicates that poikilitic textures are common in Martian rocks regardless of its sources. Detailed conclusions obtained in this study are below:

1. A 12325 is the first poikilitic shergottite with geochemically depleted features in light REEs. While the crystallization sequence of A 12325 is similar to that of the other poikilitic shergottites, A 12325 cooled relatively faster at a shallower level compared to the other poikilitic shergottites as indicated by small pyroxene oikocrysts and its Fe-rich pigeonite rim.
2. The oxygen fugacity of A 12325 on the basis of olivine–spinel–orthopyroxene and Fe-Ti oxides equilibrium is about \( \log(O_2) = IW + 0.6-IW + 1.7 \). The redox conditions experienced by A 12325 are close to that of the enriched shergottites rather than the intermediate ones.
3. Observations of shock features present in A 12325 indicate that the shock pressure it experienced should be at least \(<30\) GPa and probably \(17–22\) GPa, and the shock vein it contains should have also solidified within \(17–22\) GPa. Thermal conduction and ringwoodite growth calculation based on Ohtani et al. (2004) revealed that the shock dwell time of A 12325 is at least 40 ms.
4. Although A 12325 contains abundant high-pressure minerals, its shock metamorphism is the weakest among poikilitic shergottites because high-pressure minerals are likely to backtransform in severely shocked shergottites due to high post-shock heating.
5. A 12325 was ejected from the near Martian surface by an impact event that was similar to that which ejected the nakhlites and NWA 8159 from Mars. Such a weak shock ejection event may not be a rare event on Mars.
6. All Fe sulfide in A 12325 is altered to form Fe-S-rich-altered materials and Fe-rich olivine, indicating a presence of magmatic fluid alteration on Mars.

Acknowledgments—We would like to thank NIPR for lending us the thin section of A 12325. We are grateful to the associate editor Dr. J. Spray for handling our manuscript. Drs. C. D. K. Herd and A. Udry provided us constructive comments, which significantly improved our manuscript. This work was supported by JSPS Fellowship to A.T. (19J00954), by JSPS KAKENHI grants to A.Y. (JP19H01959) and to T.M. (JP19H00726 and JP21K18645), by NIPR, Research Project Funds KP-307 and General Collaboration Project no. 28-30, and Astrobiology Center of National Institutes of Natural Sciences (NINS) to T.M. (Grant Numbers AB311022 and AB041010). The XANES work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal Nos. 2018G558, 2020G611 and 2022G564).

Data Availability Statement—Data available on request from the authors.

Editorial Handling—Dr. John G. Spray

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