The sulfurization recorded in tridymite in the monomict eucrite
Northwest Africa 11591

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Abstract–Some of the tridymite in the monomict Northwest Africa (NWA) 11591 eucrite are found to have sulfide-rich replacement textures (SRTs) to varying degrees. The SRTs of tridymite in NWA 11591 are characterized by the distribution of loose porous regions with aggregates of quartz and minor troilite grains along the rims and fractures of the tridymite, and we propose a new mechanism for the origin of this texture. According to the volume and density conversion relationship, the quartz in the SRT of tridymite with a hackle fracture pattern was transformed from tridymite. We suggest that the primary tridymite grains are affected by the S-rich vapors along the rims and fractures, leading to the transformation of tridymite into quartz. In addition, the S-rich vapors reacted with Fe2+, which was transported from the relict tridymite and/or the adjacent Fe-rich minerals, and/or the S-rich vapors react with the exotic metallic Fe to form troilite grains. The sulfurization in NWA 11591 most likely occurred during the prolonged subsolidus thermal metamorphism in the shallow crust of Vesta and might be an open, relatively high temperature (>800 °C) process. Sulfur would be an important component of the metasomatic fluid on Vesta.

INTRODUCTION

Eucrites, which are members of the howardites–eucrites–diogenites (HED) meteorite group, are cumulate-gabbroic to basaltic rocks and are a typical type of magma-derived achondrites. According to the infrared spectroscopy and oxygen isotope studies of the HED and the data from the Dawn Mission, it is generally agreed that most of the eucrite originated from asteroid 4 Vesta (e.g., McCord et al. 1970; Binzel and Xu 1993; Scott et al. 2009; McSween et al. 2013; Greenwood et al. 2014; McCoy et al. 2015), although other viewpoints about the parent body of the HED meteorites also exist (e.g., Yamaguchi et al. 2002; Wiechert et al. 2004; Scott et al. 2009; Schiller et al. 2011; Wasson 2013; Greenwood et al. 2014).

Historically, the HEDs were thought to have been formed on a volatile-depleted asteroid and volatile fluids were not considered to be involved in the magma crystallization, melting, or subsolidus thermal metamorphism (Mittlefehldt 2015). However, in recent years, the remote-sensing data from the Dawn Mission and the study of apatite in the HED meteorites have indicated that there is a high probability of the presence of H or H2O-bearing volatiles inside or on the surface of Vesta (Hasegawa et al. 2003; Denevi et al. 2012; Prettyman et al. 2012; Reddy et al. 2012; Russell et al. 2013; Sarafian et al. 2013, 2014; Guan et al. 2015; Barrett et al. 2016, 2018). Evidence pointing toward fluid-derived secondary alteration has been found in a significant subset of HED meteorites.

Vein-like minerals are currently the most common type of secondary alteration reported in the HED meteorites. These minerals are widely distributed in different types of lithic fragments, such as the fayalite-olivine veinlets, which are found in isolated clasts in polymict brecciated eucrites (Takeda et al. 1983; Buchanan et al. 2000), a few individual monomict
Eucrites (Warren 2002; Rosjar et al. 2011), unequilibrated eucrites (Barrat et al. 2011), and equilibrated eucrites (Warren et al. 2014). The fluids associated with the genesis of these vein-like minerals are considered to bear H2O and are the main fluidic associated with the genesis of these vein-like minerals equilibrated eucrites (Warren et al. 2014). The fluids unequilibrated eucrites (Barrat et al. 2011), and Vesta in addition to the H2O-bearing fluid. It is worth noting that the sulfurization recorded in a few polymict brecciated eucrites, mentioned by Zhang et al. (2013, 2018) and Wang et al. (2019), has not been found in any monomict eucrites. Additionally, no other minerals are found to have been reduced by fluid metasomatism except for the main rock-forming minerals (e.g., olivine, pyroxene, and plagioclase) in the literature.

In this work, some of the tridymite in the monomict NWA 11591 eucrite are found to have sulfide-rich replacement textures (SRTs) to varying degrees. The SRTs of tridymite in NWA 11591, which may show an increased occurrence of sulfurization of minerals in the HED meteorites, were first proposed in the study of eucrite. NWA 11591 is a type 7 eucrite which is unusual among eucrites that record sulfurization. The sulfurized tridymite in the monomict source of NWA 11591 may place constraints on the distribution and potential physical conditions of sulfurization in Vesta. Therefore, we observe and analyze the detailed petrographic and mineralogical features of the potential SRTs of the tridymite in NWA 11591. We also discuss the sulfurization process of tridymite as well as constrain the possible formation environment. This work will add new information and evidence to the study of fluid metasomatism on Vesta.

SAMPLE AND ANALYTICAL METHODS

NWA 11591 is a eucrite and has a total mass of 1.55 kg. The meteorite is porous, and cracks have developed on it. One side of the meteorite’s surface is covered with a thin, shiny black fusion crust that covers approximately a third of the surface of the meteorite. The fusion crust has been largely weathered from the surface of the sample. NWA 11591 is approximately 6.8 × 8.6 × 3.8 cm. The NWA 11591 sample used in this study was purchased by Bing-an Miao in 2016 from Morocco.

The NWA 11591 sample used in this study is a conventional polished thin section. The petrography and mineralogy of the NWA 11591 sample were studied using the Nikon Eclipse 50I polarizing microscope and the Zeiss SIGMA field emission scanning electron microscope (FE-SEM) in the backscattered electron (BSE) mode at Guilin University of Technology, China. The BSE images were mainly obtained with an accelerating voltage of 15 kV. The quantitative chemical compositions of the minerals were determined by using the JEOL JXA-8230 electron probe microanalyzer (EMPA) at Guilin University of Technology. The operating conditions were as follows: for most minerals, an accelerating voltage of 15 kV, a beam current of 20 nA, a focused beam for most minerals, and a defocused beam for plagioclase (2–3 μm in diameter) were used. Sulfide minerals were analyzed with an accelerating voltage of 20 kV and a beam current of 20 nA. Both natural and synthetic standards were used. The typical detection limits for oxides of most elements are better than 0.02 wt%. All data were processed with the ZAF correction procedure supplied by the JEOL microprobe.

X-ray element mapping with wavelength dispersive X-ray spectroscopy (WDS) attached on the EMPA was performed on a few pyroxene samples to determine the distribution of a few elements like Ca, Fe, and Mg. The operating conditions for the X-ray mapping were an accelerating voltage of 15 kV and a beam current of 20 nA. The cathodoluminescence (CL) images were recorded using the CL system in the JEOL JXA-8230 EMPA.

In order to identify the silica and pyroxene phases, the electron backscatter diffraction (EBSD) patterns and Raman spectra were obtained by the FE-SEM and laser Raman spectrometry, respectively. EBSD analysis was performed using a Zeiss SIGMA FE-SEM equipped with an EBSD detector (Aztec Energy; Oxford Instruments). The analyses were conducted at an accelerating voltage of 20 kV, a beam current of 10 nA, and a 19 mm working distance. Kikuchi patterns were fitted for phase identification using AZtec 4.0, developed by Oxford Instruments. The laser Raman spectroscopy analysis was conducted using an inVia Raman System (Renishaw) at Guilin University of
Technology. A microscope was used to focus the excitation laser beam (514 nm lines of a Spectra Physics Ar$^+$ laser) to a 1 µm spot and to collect the Raman signal in the backscattered direction. The laser power was restricted to 5–20 mW to avoid deterioration of the samples. Phase modal abundances were determined using an image analysis of the BSE mosaics and X-ray maps to essentially count all the pixels of each phase. The counts were then divided by the total number of pixels (background subtracted) to obtain the fraction in a given area, which we took to be proportional to the volume fraction.

**NWA 11591 Eucrite**

NWA 11591 is a monomict basaltic eucrite. The dominant minerals (and their modal abundances) are pyroxene (46.2 vol%); plagioclase (43.3 vol%); silica (9.0 vol%); opaque minerals including ilmenite, chromite, and troilite (1.1 vol%); and traces of merrillite and apatite (0.4 vol%); NWA 11591 is slightly brecciated, and the lithic clast has a subophitic-ophitic texture with subequal amounts of euhedral lath-shaped plagioclase (30 × 150 µm ~ 300 × 700 µm in size) and coarse-grained pyroxene (600 × 700 µm in size on average, up to 1 mm). The exsolution of pyroxene in clasts is very common, mainly in low-Ca pyroxene containing exsolved high-Ca pyroxene lamellae of up to 5 µm in width. Most of the high-Ca pyroxene lamellae are uniformly distributed from the core to the rim in the pyroxene crystals, but some coarse pyroxene crystals are composed of cores with widely spaced, thick augite lamellae (3 µm; Ca-poor core) and rims with closely spaced thin augite lamellae (<1 µm; Ca-rich rim), which indicate a partial preservation of the original igneous Ca-zoning in pyroxene (Fig. 1a; Takeda and Graham 1991). Pyroxene in NWA 11591 generally exhibits a cloudy appearance, mainly caused by the precipitation of sub-micrometer scale opaque minerals located along the healed cracks in pyroxene (Takeda and Graham 1991; Yamaguchi et al. 1996). The fine-grained mesostasis materials, which are composed of quartz, high-Ca pyroxene, troilite, and a small amount of ilmenite, are scattered in matrices (Figs. 1b and 1c). This assemblage is interstitial to the surrounding major minerals (Fig. 1b) and it sometimes appears in matrices as an irregular assemblage (Fig. 1c). Medium- to large-grained ilmenite and merrillite also appeared in the matrix (Fig. 1b). Medium- to large-grained ilmenite and merrillite also appeared in the matrix.

The low-Ca pyroxene in lithic clasts in NWA11591 includes low-Ca pigeonite and orthopyroxene with Wo below 5 (Wo$_{1.82}$Fs$_{64.5}$En$_{33.7}$, Mg$^\#$ = 34.3, Fe/Mn = 29.8, on average; Fig. 2). Most of the low-Ca pyroxene in NWA 11591 has pigeonite calculated EBSD patterns (Figs. 3a and 3b), but a few of them show orthopyroxene calculated EBSD patterns (Figs. 3c and 3d). The EBSD patterns of the low-Ca pyroxene in NWA 11591 confirm that pigeonite is partially inverted to orthopyroxene. The very low Wo content (e.g., Wo$_{1.7}$) of the low-Ca pyroxene is also consistent with the presence of inverted orthopyroxene (Fig. 2). The average composition of the high-Ca pyroxene lamellae in lithic clasts is Wo$_{44.5}$Fs$_{28.2}$En$_{27.3}$, Mg$^\#$ = 49.2, Fe/Mn = 29.3. The composition ranges of fine-grained low-Ca pyroxene (Wo$_{1.64}$Fs$_{64.3}$En$_{34.1}$, Mg$^\#$ = 34.7, Fe/Mn = 29.5, on average) and high-Ca pyroxene (Wo$_{44.7}$Fs$_{28.2}$En$_{27.1}$, Mg$^\#$ = 48.9, Fe/Mn = 30.8, on average) in the matrix are almost the same as that of pyroxene in lithic clasts, which fall within the range of those in known basaltic eucritic meteorites (Fig. 2; Mittlefehldt 2015). The compositional variations of plagioclase within single fragments from the core to the rim (An$_{68.7}$Ab$_{27.5}$Or$_{3.8}$-An$_{92.2}$Ab$_{7.6}$Or$_{0.2}$) indicate a partial preservation of the original igneous zoning in plagioclase, which fall within the range of those in known eucritic meteorites (Fig. 4; Mittlefehldt 2015). Representative electron microprobe analyses (wt%) of the typical primary minerals in NWA 11591 are given in Tables 1 and 2.

Some pyroxenes in NWA 11591 have high-Ca pyroxene rims (Wo$_{44.3}$Fs$_{28.2}$En$_{27.6}$, Fe/Mn = 30.9, on average; Fig. 2) that contain vermicular quartz, troilite, traces of ilmenite, plagioclase, low-Ca pyroxene, apatites, and a very small amount of Fe-metal inclusions (Figs. 1e and 1f). The high-Ca pyroxene rim and the low-Ca pyroxene core are optically continuous and have the same extinction behavior. The high-Ca pyroxene rim contains exsolved low-Ca pyroxene lamellae with a width of approximately 1–2 µm, and the low-Ca pyroxene core also contains exsolution lamellae of high-Ca pyroxene. The direction of the exsolution lamellae in both the low-Ca pyroxene core and the high-Ca pyroxene rim is consistent (Fig. 1f). Some of these pyroxenes retained the original igneous Ca-zoning (Fig. 1e and red arrow in Fig. 5). The X-ray elemental mapping results of this pyroxene show that the Ca components in the high-Ca pyroxene rim increase abruptly, while the Fe components plummet as compared to the low-Ca pyroxene core, and the Mg component is almost equilibrated (Fig. 5).

There are no shock melt veins or pockets, no deformation features (e.g., weak mosaicism or planar fractures) of rock-forming minerals, and no maskelynite and high-pressure minerals (e.g., majorite, coesite, or stishovite) observed in the chip of NWA 11591 meteorite (Table 3).

**Sulfide-rich Replacement Textures in Tridymite**

In addition to the fine-grained quartz in the mesostasis and the quartz inclusions in the high-Ca...
pyroxene rims (~3.8 vol%), there is a high abundance (~6.4 vol%) of lath-shaped or irregular granular tridymites in NWA 11591 (Fig. 6). Tridymites appear in both clasts and matrices, usually intergrown with plagioclase in a lath shape (average size ~100 x 700 μm, up to 200 μm in width; Figs. 7a, 7b, and 7c), or appear as irregular granular and isolated grains in broken matrices (Fig. 7d).

Most of the tridymites in NWA 11591 exhibit potential SRTs except for the small part of unaltered tridymites (Fig. 7a). Tridymite with SRTs is dispersed in clasts and matrices without local enrichment (Fig. 6). The SRTs of tridymite are characterized by loose porous regions with aggregates of quartz and minor troilite grains, which are distributed along the rims and fractures of the tridymite (Figs. 7b, 7c, and 7d). The relict tridymite core associated with the SRTs is retained. The interior of the relict tridymite core (unaltered regions) is relatively clean and contains almost no inclusions except a few submicrometer scale

Fig. 1. Backscattered electron (BSE) images of the petrographic characteristics of NWA 11591. a) Low-Ca pyroxene with exsolved augite lamellae. Note the thin and dense augite lamellae (the upper left corner) in the rim and the thicker lamellae in the core (the lower right corner). b) The fine-grained mesostasis is interstitial to the surrounding major minerals. c) The fine-grained mesostasis appears in the matrix as an irregular assemblage. d) Ilmenite and merrillite in the matrix. e) The pyroxene with high-Ca pyroxene rim. f) Close-up image of the area indicated by the rectangle in (e). The high-Ca pyroxene rims contain vermicular quartz, troilite, traces of ilmenite, plagioclase, low-Ca pyroxene, and a very small amount of Fe-metal inclusions. Note the direction of the exsolution lamellae in both the low-Ca pyroxene core and the high-Ca pyroxene rim is consistent. L-py = low-Ca pyroxene; H-py = high-Ca pyroxene; Q = quartz; Ilm = ilmenite; Tro = troilite; Pl = plagioclase; Mer: merrillite; L-py* = low-Ca pyroxene inclusion in the high-Ca pyroxene rim; M = Fe-metal.
Fe-rich particles (Fig. 8a). There is an embayed metasomatism boundary between the SRT regions and the unaltered regions of tridymite under the polarizing microscope (Figs. 7e and 8d). The unaltered regions of tridymite have a gray-white interference color of grade I, while the potential SRT regions of tridymite have a patchy appearance and a yellow-white interference color of grade I (Figs. 7e and 8d). The CL images of these two regions in tridymite also show different characteristics. The CL (strong light of red-yellow) of the unaltered region is stronger than that of the potential SRT regions (dark light of yellow-green; Fig. 7f).

Fig. 2. Compositions of pyroxene in NWA 11591. Note the chemical equilibration of pyroxenes in clasts and matrices. There may be an electron beam overlap with the adjacent high-Ca pyroxene components in the composition analysis of the low-Ca pyroxene exsolution lamellae in the high-Ca pyroxene rim. The composition range of basaltic eucrite, cumulate eucrite, and diogenite taken from Mittlefehldt (2015). L-py = low-Ca pyroxene; H-py = high-Ca pyroxene. (Color figure can be viewed at wileyonlinelibrary.com.)

Fig. 3. a) Observed EBSD pattern of monoclinic pigeonite in NWA 11591. b) Calculated EBSD pattern of monoclinic pigeonite, matching with the observed pattern of (a). c) Observed EBSD pattern of orthopyroxene in NWA 11591. d) Calculated EBSD pattern of orthopyroxene, matching with the observed pattern of (c). (Color figure can be viewed at wileyonlinelibrary.com.)
Fig. 4. Compositions of plagioclase in NWA 11591. Data are taken from Mittlefehldt (2015) and this work. (Color figure can be viewed at wileyonlinelibrary.com.)

Table 1. Representative chemical compositions (wt%) of pyroxene in NWA 11591.

| Notes | Typical primary pyroxene in clasts | Typical primary pyroxene in matrices | Relict pyroxene core | High-Ca pyroxene rim |
|-------|-----------------------------------|-------------------------------------|----------------------|----------------------|
|       | Low-Ca pyroxene av. of 29         | High-Ca pyroxene lamellae av. of 23 | Low-Ca pyroxene av. of 18 | High-Ca pyroxene av. of 15 | Low-Ca pyroxene av. of 7 | High-Ca pyroxene lamellae av. of 11 | High-Ca pyroxene av. of 8 | Low-Ca pyroxene lamellae* av. of 6 | Low-Ca pyroxene inclusion av. of 10 |
| SiO₂  | 48.9                              | 50.4                                | 48.7                 | 49.9                 | 48.2                 | 49.9                 | 50.9                 | 48.8                 | 49.3                 |
| TiO₂  | 0.19                              | 0.30                                | 0.11                 | 0.35                 | 0.18                 | 0.05                 | 0.43                 | 0.23                 | 0.10                 |
| Al₂O₃ | 0.20                              | 0.66                                | 0.23                 | 0.63                 | 0.17                 | 0.63                 | 0.79                 | 0.32                 | 0.18                 |
| Cr₂O₃ | 0.14                              | 0.21                                | 0.07                 | 0.20                 | 0.04                 | 0.22                 | 0.26                 | 0.17                 | 0.09                 |
| FeO   | 37.3                              | 17.2                                | 37.2                 | 17.2                 | 38.3                 | 17.3                 | 17.2                 | 35.8                 | 38.3                 |
| MnO   | 1.23                              | 0.58                                | 1.25                 | 0.55                 | 1.28                 | 0.57                 | 0.55                 | 1.18                 | 1.21                 |
| MgO   | 10.9                              | 9.32                                | 11.1                 | 9.23                 | 10.5                 | 9.44                 | 9.43                 | 10.0                 | 10.3                 |
| CaO   | 0.82                              | 21.1                                | 0.74                 | 21.3                 | 0.69                 | 20.6                 | 21.1                 | 4.17                 | 0.80                 |
| Na₂O  | bd                                | 0.06                                | 0.03                 | 0.05                 | bd                   | 0.06                 | 0.03                 | bd                   | bd                   |
| K₂O   | bd                                | bd                                  | bd                   | bd                   | bd                   | bd                   | bd                   | bd                   | bd                   |
| Total | 99.7                              | 99.8                                | 99.4                 | 99.4                 | 99.4                 | 98.8                 | 100.7                | 100.7                | 100.3                |
| Mg²⁺  | 34.3                              | 49.2                                | 34.7                 | 48.9                 | 32.9                 | 49.3                 | 49.4                 | 33.3                 | 32.5                 |
| Fe/Mn | 29.8                              | 29.3                                | 29.5                 | 30.8                 | 29.6                 | 30.2                 | 30.9                 | 29.8                 | 31.2                 |
| En    | 33.7                              | 27.3                                | 34.1                 | 27.1                 | 32.4                 | 27.8                 | 27.6                 | 30.3                 | 31.9                 |
| Fs    | 64.5                              | 28.2                                | 64.3                 | 28.2                 | 66.1                 | 28.6                 | 28.2                 | 60.7                 | 66.4                 |
| Wo    | 1.82                              | 44.5                                | 1.64                 | 44.7                 | 1.53                 | 43.6                 | 44.2                 | 9.06                 | 1.77                 |

Mg²⁺ = 100 × Mg/(Mg + Fe) in mole; bd = below detection limit.
En = 100 × Mg/(Mg + Fe + Ca); Fs = 100 × Fe/(Mg + Fe + Ca); Wo = 100 × Ca/(Mg + Fe + Ca).
*There may be an electron beam overlap with adjacent high-Ca pyroxene components.
The EBSD patterns and Raman spectra of the SRT regions and unaltered regions of the tridymite show distinct characteristics, indicating that they are two different silica phases. The EBSD patterns and Raman spectra confirm that the unaltered regions of tridymite are monoclinic tridymite (Figs. 9a, 9b, and 9e), while the potential SRT regions have a typical Raman quartz peak, and their EBSD patterns show that these silica crystals are quartz too (Figs. 9c, 9d, and 9e). It is worth noting that the quartz in the potential SRT regions of tridymite all has peaks that have shifted to lower positions (462.4 cm\(^{-1}\)) as compared to the typical quartz peak of the standard Raman spectrum (466.1 cm\(^{-1}\); Fig. 9e and Table 4). It can be seen from the close-up SEM images that the hackle fracture pattern (HFP) appears at the edge of the quartz in the potential SRT regions (Fig. 8a), which is characterized by densely distributed crinkled fractures and small vesicles (Fig. 8b; Seddio et al. 2015). Strip-like quartz crystals often appear at the edge of the potential SRT regions, while troilite often appears at the end of the strip quartz crystals in a fine-grained square shape (red arrow in Fig. 8c). Most of the troilite grains in the potential SRT regions in tridymite are 1–2 \(\mu m\), some of them have a size of up to 5 \(\mu m\) (Figs. 8a, 8b, and 8c).

NWA 11591 showed differences in the content of minor elements between the SRT regions and unaltered regions of tridymite. The unaltered regions contained a relatively large number of Al\(_2\)O\(_3\) (0.36–0.50 wt%), K\(_2\)O (0.20–0.29 wt%), CaO (0.04–0.16 wt%), and Ti\(_2\)O (0.04–0.19 wt%) components, while the SRT region contained relatively a lower number of Al\(_2\)O\(_3\) (0.0–0.20 wt%), K\(_2\)O (0.0–0.11 wt%), CaO (0.0–0.07 wt%), and Ti\(_2\)O (0.0–0.08 wt%) components. The components in the SRT region are generally poorer than those in the unaltered region of tridymite in terms of lithophile elements such as Al, K, Ca, and Ti (Fig. 10 and Table 2). However, the content of FeO (0.12–0.82 wt%) in the potential SRT region of tridymite is slightly higher than that in the unaltered region (FeO: 0.03–0.29 wt%). There is no significant difference in the other elements (Table 2). Representative compositions of the minerals related to the potential SRTs of tridymite are given in Tables 1 and 2.

**DISCUSSION**

**A Type 7 Eucrite**

The cloudy appearance of pyroxene, the exsolution of high-Ca pyroxene lamellae generally wider than...
The vestiges of the basaltic texture and remnant Ca-zoning of pyroxenes in NWA 11591 indicate that the NWA 11591 is a type 7 eucrite (Yamaguchi et al. 1996). The type 7 eucrite NWA 11591 has both the thermal metamorphism features of type 4 (the presence of remnant Ca-zoning in pyroxene) and type 6 (partial inversion of pigeonite) eucrite, which suggest that NWA 11591 eucrites could have experienced a slower cooling process at low temperature than the other thermal metamorphic grade eucrites (Yamaguchi et al. 1996). We have estimated the equilibration temperatures of the clasts and matrices in NWA 11591 using the two-pyroxene geothermometer of Kretz (1982), which has an estimated uncertainty of 60 °C. The estimated equilibration temperatures of the low-Ca pyroxene host and the high-Ca pyroxene lamellae pairs in clasts vary from 673 to 735 °C. The equilibration temperatures of fine-grained low-Ca pyroxene and high-Ca pyroxene in matrices (726 °C on average) are not much different from that in clasts. The relatively low equilibration temperatures indicate that the type 7 eucrite NWA 11591 would have experienced prolonged thermal metamorphism at relatively low temperatures so that it could have both the thermal metamorphism features of remnant Ca-zoning in pyroxene and partial inversion of pigeonite. Schwartz and McCallum (2005) suggested that the formation of type 7 eucrite is not just the product of a simple

Table 3. Representative chemical compositions (wt%) of troilite and Fe-metal in NWA 11591.

| Troilite in mesostasis av. of 6 | Troilite in SRT of tridymite av. of 10 | Fe-metal av. of 6 |
|--------------------------------|----------------------------------------|-----------------|
| S                               | 36.0                                   | 36.3            |
| Si                              | 0.72                                   | 1.35            |
| Fe                              | 62.7                                   | 61.3            |
| Co                              | 0.10                                   | 0.08            |
| Ni                              | 0.04                                   | bd              |
| Total                           | 99.6                                   | 99.0            |

SRT = sulfide-rich replacement texture; bd = below detection limit.

1 μm, the presence of the remnant Ca-zoning, and the inversion of pigeonite in NWA 11591 indicate that the NWA 11591 is a type 7 eucrite (Yamaguchi et al. 1996).

The vestiges of the basaltic texture and remnant Ca-zoning of pyroxenes in NWA 11591 indicate that the NWA 11591 eucrite crystallized rapidly in lava flows or shallow intrusions (e.g., Yamaguchi et al. 2009). If the primary pigeonites of the noncumulate eucrites cooled very slowly in the subsolidus regime, they would be converted into orthopyroxene in a complex way (Yamaguchi et al. 1996). The type 7 eucrite NWA 11591 has both the thermal metamorphism features of type 4 (the presence of remnant Ca-zoning in pyroxene) and type 6 (partial inversion of pigeonite) eucrite, which suggest that NWA 11591 eucrites could have experienced a slower cooling process at low temperature than the other thermal metamorphic grade eucrites (Yamaguchi et al. 1996). We have estimated the equilibration temperatures of the clasts and matrices in NWA 11591 using the two-pyroxene geothermometer of Kretz (1982), which has an estimated uncertainty of 60 °C. The estimated equilibration temperatures of the low-Ca pyroxene host and the high-Ca pyroxene lamellae pairs in clasts vary from 673 to 735 °C. The equilibration temperatures of fine-grained low-Ca pyroxene and high-Ca pyroxene in matrices (726 °C on average) are not much different from that in clasts. The relatively low equilibration temperatures indicate that the type 7 eucrite NWA 11591 would have experienced prolonged thermal metamorphism at relatively low temperatures so that it could have both the thermal metamorphism features of remnant Ca-zoning in pyroxene and partial inversion of pigeonite. Schwartz and McCallum (2005) suggested that the formation of type 7 eucrite is not just the product of a simple
prolonged burial thermal metamorphism but also the superimposition of reheating events (impact events or magma intrusion events) on the crust-wide prolonged burial thermal metamorphism. We suggest that these superimposed reheating events during the prolonged burial thermal metamorphism may be closely related to the genesis of some anomalous petrological phenomena in NWA11591, such as the high-Ca pyroxene rim in some pyroxenes and the SRT of tridymite. For the genesis of the high-Ca pyroxene rim of some pyroxenes in NWA11591, Ca enrichment can also be observed at the edge of the original igneous zoning of pyroxene. However, the Ca component gradually increases from the core to the rim in the primary chemical-zoning pyroxene (red arrow in Fig. 5) and does not have sharply changing boundaries of the Ca and Fe components. Therefore, the original igneous Ca-zoning of pyroxene, or the Ca-zoning partially preserved from the prolonged burial thermal metamorphism, can be excluded as the origin of the high-Ca pyroxene rim of some pyroxenes in NWA11591. Instead, their texture and mineralogy characteristics tend to indicate that the high-Ca pyroxene rim might be an overgrowth rim on early crystallized pigeonite grains. The low-Ca pyroxene core (pigeonite) and the high-Ca pyroxene rim might be crystallization products at different stages, as they have an abruptly changing boundary of the Ca and Fe components (Fig. 5). Because of the structural similarity between low-Ca pyroxene core and high-Ca pyroxene rim, they both share the same extinction behavior. We suggest that the high-Ca pyroxene rim is likely to be a pyroxene overgrowth rim due to the influence of reheating event during the prolonged burial thermal metamorphism, which may cause partial melting. Perhaps the degree of melting is very small, which is only distributed along grain boundaries and fractures and subsequently crystallized the high-Ca pyroxene overgrowth rim. During crystallization of the high-Ca pyroxene rim, fine-grained mesostasis minerals such as quartz, troilite, ilmenite, plagioclase, low-Ca pyroxene, and apatite were included. During later thermal metamorphism, exsolution took place in both the low-Ca pyroxene core and the high-Ca pyroxene rim, resulting in the similar orientations of the exsolution lamellae in both.

Transformation of Tridymite into Quartz

In NWA 11591, the mineral phase and optical characteristics of the SRT regions in tridymite are different as compared to the unaltered regions (Figs. 7–9), indicating that the physicochemical conditions changed when the SRTs are formed. The rims of quartz in the SRT show an HFP to varying degrees, and similar quartz with an HFP has also been reported in the lunar granitic samples (Seddio et al. 2015) and cumulate eucrite Y 980433 (Ono et al. 2019). Seddio et al. (2015) calculated that the HFP of quartz in lunar granitic samples is formed by a molar volume contraction caused by a lower density polymorph (tridymite, 2.18–2.28 g cm$^{-3}$; Kihara 1978) changing to a higher density polymorph (quartz, 2.65 g cm$^{-3}$; Kihara 1978) using the volume and density conversion relationship. Ono et al. (2019) also considered that the quartz in cumulate eucrite Y 980433 is transformed from monoclinic tridymite by a shock event. Therefore, we consider that the quartz in the SRT of tridymite in NWA 11591 meteorite may have been converted from tridymite due to the change in the physicochemical conditions. To investigate whether the quartz with an HFP in the SRT of tridymite is formed by the transformation from low-density tridymite, we calculate the percentage of the surface area in the fracture area ($A_{Frac}$) and quartz area ($A_{Qtz}$) based on a secondary electron scanning electron microscope image (SEM) and assume that they represent their volume percentages ($V_{Frac}$ and $V_{Qtz}$, respectively). The density of silica
polymorph that originally crystallized in the SRT of tridymite can be calculated by the following method (Seddio et al. 2015):

\[ \rho_{\text{HighT}} = \rho_{\text{Qtz}} \frac{V_{\text{Qtz}}}{V_{\text{HighT}}} = \rho_{\text{Qtz}} \frac{A_{\text{Qtz}}}{A_{\text{HighT}}} = \rho_{\text{Qtz}} \frac{A_{\text{Qtz}}}{A_{\text{Qtz}} + A_{\text{Frac}}} \]

We tested several quartz regions with an HFP, and the results showed that the density of the original silica polymorphs in the SRT of tridymite is all within the range of tridymite (2.18–2.28 g cm\(^{-3}\); Kihara 1978) and not within the range of cristobalite (2.32–2.36 g cm\(^{-3}\); Schmahl et al. 1992; Table 5). The volume of quartz and the fracture space are consistent with a molar volume contraction from tridymite. This hypothesis is also supported by the coexistence of quartz and tridymite within the same grain, which indicates that the quartz is partially transformed from a single monoclinic tridymite grain.

In addition, the characteristic peak value of quartz with an HFP in tridymite is shifted slightly to a lower position (462.4 cm\(^{-1}\)) from the typical quartz peak of the standard Raman spectrum (466.1 cm\(^{-1}\); Fig. 9 and Table 4). This slight left shift (shift to small wave number) is the result of the stress release within the SiO\(_2\) structure framework, which is suggested to be caused by impact metamorphism (McMillan et al. 1992;...
Ling et al. 2011). The experimental results of McMillan et al. (1992) show that the magnitude of the peak shift in the Raman spectrum of the quartz is directly related to the magnitude of the impact pressure experienced by the sample. According to the peak shift magnitude of quartz (462.4 \text{ cm}^{-1}) in the SRTs of tridymite in NWA 11591, the impact pressure would be greater than 21.7 GPa (McMillan et al. 1992). However, the lack of deformation features (e.g., weak mosaicisms or planar fractures) of rock-forming minerals and the absence of glass and high-pressure minerals (e.g., majorite, coesite, or stishovite) in NWA 11591 indicate that the impact pressure of the NWA 11591 meteorite might not be greater than 21.7 GPa (e.g., Fritz et al. 2017). Therefore, the left shift of the characteristic peak of quartz (462.4 \text{ cm}^{-1}) in the SRTs of tridymite in NWA 11591 might not be caused by impact metamorphism. In addition to impact metamorphism, the release of tensile stress caused by the crystal density transformation can also lead to a distortion of the SiO$_2$ structural framework and thus, shift the Raman peak position (McMillan et al. 1992). Seddio et al. (2015) also suggested that the left shift of Raman spectrum in quartz with an HFP in the lunar granitic samples is caused by the fact that fracturing of the quartz crystal does not completely relieve the stress within the silica after inversion to a higher density phase. Perhaps this remnant stress may also be responsible for the slight left shift of the peak in the Raman spectrum of quartz with an HFP in NWA 11591. This further suggests that the quartz with an HFP in NWA 11591 would be transformed from tridymite.

Therefore, quartz with an HFP in the SRT of tridymite in NWA 11591 could be a local product formed by a solid-state transformation from monoclinic tridymite.

**Sulfurization of Tridymite**

Unlike the quartz, with an HFP, which appears in lunar granitic sample (Seddie et al. 2015) and cumulate eucrite Y 980433 (Ono et al. 2019), the quartz in the SRT of NWA11591 is also accompanied by tiny troilite grains. There may be two scenarios between the formation of troilite and the transformation of tridymite into quartz. (1) Troilite is formed before or after the transformation of tridymite. (2) The formation of troilite and the transformation of tridymite occurred simultaneously. From the occurrence of troilite in the SRTs, it is obvious that model (1) is not supported, but model (2) is more favored. If troilite is formed before the formation of quartz, it would not have a close occurrence relationship with quartz (troilite often...
appears with a fine-grained square shape at the end of the strip-like quartz crystals; red arrow in Figs. 8a and 8c). The troilite grains do not fill the gap between the quartz grains, indicating that the formation of troilite might not occur after the formation of quartz. In addition, the troilite grains are also unlikely to be the mesostasis inclusions that are wrapped in quartz during the formation of quartz, because the mesostasis usually contains ilmenite, high-Ca pyroxene, and other phases in addition to silica and troilite. Therefore, the origin of troilite is closely related to the formation of quartz, which would be formed at the same stage as quartz.

The SRT of tridymite in NWA 11591 has obvious metasomatic characteristics in mineralogy. (1) Unlike the random distribution of quartz with an HFP in the

| The occurrence of silica | Phase                | Peaks used for identification (cm⁻¹) |
|-------------------------|----------------------|-------------------------------------|
| Silica in mesostasis (M-Q) | Quartz              | 463.6 353.6                         |
| The unaltered regions of tridymite (Tri) | Monoclinic tridymite | 432.7 350.0 305.3                   |
| Silica in the SRTs of tridymite (SRT-Q) | Quartz              | 462.4 353.6                         |
| Reference spectra*      | Quartz              | 466.1 357.6                         |
|                         | Monoclinic tridymite | 432.9 349.5 304.2                   |

*Standard Raman spectra of quartz and monoclinic tridymite for comparison from the RRUFF database.
lunar granitic sample (Seddio et al. 2015) and the cumulate eucrite Y 980433 (Ono et al. 2019), the distribution of quartz (SRT regions) in NWA1591 is not random but is distributed along the rims and fractures of the primary tridymite grains (Figs. 7 and 8). This is indicative of the genetic mechanism of metasomatism along the rim and fracture. (2) The SRT regions have an embayed metasomatic boundary with the unaltered regions of tridymite. (3) The relict tridymite core associated with the SRT regions is retained (Fig. 7). Therefore, combined with the fact that all the SRT regions of tridymite contain fine-grained troilite, we suggest that the transformation from tridymite to quartz could be related to the sulfurization of tridymite, which possibly accounts for the formation of troilite and would be a metasomatism process. The transformation from monoclinic tridymite to quartz occurred when NWA 11591 experienced a sulfurization process, which involves the addition of S-rich vapors (Zhang et al. 2013).

Fig. 10. Distribution of minor elements in tridymite with SRTs in NWA 11591. Tri = the unaltered regions of monoclinic tridymite; SRT-Q = quartz in the SRTs of tridymite. (Color figure can be viewed at wileyonlinelibrary.com.)

Table 5. Initial density calculation for quartz with hackle fracture pattern.

| The test area | \(A_{Qz}\) | \(A_{Frac}\) | \(\rho_Q\) | \(\rho_I\) | \(P_I\) | \(\rho_{tri}\) | \(\rho_{cri}\) |
|--------------|----------|-----------|--------|-------|-------|----------|----------|
| FHP-Q1       | 83.0%    | 17.0%     | 2.65   | 2.20  | Tridymite |
| FHP-Q2       | 82.6%    | 17.4%     | 2.65   | 2.19  | Tridymite |
| FHP-Q3       | 83.4%    | 16.6%     | 2.65   | 2.21  | Tridymite |

\(\rho_Q\) = The assumed density of quartz used in the calculation. \(\rho_I\) = The calculated initial density for the silica. \(\rho_{tri}\) = Density of tridymite (Kihara 1978) is given for comparison. \(\rho_{cri}\) = Density of cristobalite (Schmahl et al. 1992) is given for comparison. All values are in g cm\(^{-3}\).

The sulfurization in monomict eucrite 1453.
where metallic Fe is present (Dohmen et al. 1998), the Fe in troilite in the SRTs may also be exotic metallic Fe, and the following reaction occurred:

\[
2\text{FeO}^0(g) + \text{S}_2(g) = 2\text{FeS}
\]  

(3)

There are very few reports on the analog SRTs of tridymite in the present studies of eucrite (Ono et al. 2016, 2017). For example, the quartz in the porous regions of the lath-shaped silica containing tiny sulfide grains and vesicles has been mentioned in the Millbillillie meteorite, but this is not proposed as SRT (Ono et al. 2017). The sulfurization genesis of the SRT of tridymite was first proposed in the study of noncumulate eucrites.

**Conditions for the Sulfurization of Tridymite**

For an analogous SRT of olivine in lunar basalt samples, as discussed by Bell et al. (2015), the oxygen fugacity of the sulfurization reaction 2 is consistent with the normal-eucritic \( f_{O_2} \) (approximately \( \Delta IW-1 \)), and the sulfur fugacity (\( \log f_{S_2} \)) value of the reaction 2 occurring in the sulfide-saturated lunar mare basalt is approximately \(-4.15 \) at \( 1125 \) °C. However, the different degrees of the SRTs in NWA 11591 suggest that the oxygen fugacity and sulfur fugacity may not be constant throughout the evolution process that occurs later. In reactions 2 and 3, the diminution of oxygen fugacity or an increase in sulfur fugacity will tend to promote the reduction of \( \text{FeO}/\text{Fe}^0 \) and the formation of FeS, but the sulfur fugacity would be lower than that of reaction \( \text{FeS} + 1/2\text{S}_2 = \text{FeS}_2 \), since the pyrite or pyrrhotite that would be formed when the sulfur fugacity in the system is large enough (Toulmin and Barton 1964).

In a pure silica system on Earth, the inversion of tridymite into quartz at \( 867 \) °C is a reconstructive phase transition, requiring the reconfiguration of Si–O bonds. The process is extremely slow and thus, cannot be observed in the laboratory time-frame unless a flux (e.g., NaWO\(_4\)) is used to accelerate its transformation (e.g., Lakshitanov et al. 2007). The transformation from tridymite to quartz is difficult to form by simple cooling in terrestrial rocks, and it takes place over a long period of time at relatively low temperature (<863 °C; e.g., Yamaguchi et al. 1996). However, our observations indicate that the transformation from tridymite to quartz in NWA 11591 could occur when the S-rich vapor was added. The transformation and sulfurization of tridymite in NWA 11591 would occur simultaneously. The rate of the transformation from tridymite to quartz driven by sulfurization (S-rich vapor may act as a catalyst) can be much faster than the mineral phase transition driven solely by thermodynamics. Zhang et al. (2013) suggested that the sulfurization of pyroxene in polymict brecciated NWA 2339 eucrite is a relatively high temperature (>800 °C) and rapid reaction process (lasted only 2 weeks). Therefore, the sulfurization of tridymite in NWA 11591 might be a relatively high temperature (>800 °C) and open thermal process, and its reaction rate would be faster than the rate of the transformation from tridymite to quartz driven solely by thermodynamics.

**Implications for Sulfurization of Vesta**

The SRT of tridymite commonly found in NWA 11591 indicates that S would be an important component of metasomatism fluid on Vesta. The origin of the sulfide-rich replacement texture of olivine in some lunar samples is also considered to be related to the sulfurization of the primary rock by S-rich vapor (Shearer et al. 2012; Bell et al. 2015). The hypotheses for the origin of the SRTs on the Moon have three models. (1) It occurred in the impact crater near the lunar surface. Sulfur, the heat source of the reaction, and other volatiles (e.g., P and chalcophile metals) were all derived by the impactor (Haskin and Warren 1991). (2) It occurred in an ejecta blanket. Both the heat source and the sulfur were generated by the impactor, and then, the volatiles in the primary rock were degassed (Haskin and Warren 1991). (3) It occurred in the shallow crust of the moon. Sulfur, the heat source of the reaction, and other volatiles were all derived from the degassed intrusive magmas, which penetrated into the shallow crust of the moon, resulting in sulfurization of the adjacent country rocks (Norman et al. 1995).

The possibility of the aforementioned sulfuridization models occurring on Vesta can be preliminarily evaluated. Model (1): As discussed in the previous section, we suggest the impact metamorphism of NWA 11591 is not so serious. Although too intense an impact metamorphism may erase the shock features, the remnant igneous basaltic texture, the slightly brecciated structures, and the lack of shock melting of plagioclase indicate that the NWA 11591 meteorite has not undergone intense impact metamorphism (e.g., Fritz et al. 2017). Hence, the sulfurization of NWA 11591 might not be a thermal event that occurred in the impact crater on Vesta caused by the impact events directly. Models (2) and (3): Either the contact heating of the ejecta blanket or the heating events occurring in the shallow crust of Vesta can cause high temperature (e.g., >800 °C) to the NWA 11591 eucrite, but the former tends to make the NWA 11591 eucrite form polymict brecciated rocks. Since the NWA 11591 meteorite is a monomict basaltic eucrite, and its degree of brecciation is slight, we suggest that the sulfurization of NWA 11591 is more likely to have occurred in the shallow crust of...
Vesta. The sulfurization would be a relatively high temperature process (>800 °C; Zhang et al. 2013), which is inconsistent with the relatively low equilibration temperatures of two-pyroxene pairs in clasts in NWA 11591. Thus, we suggest that the sulfurization would be a high temperature reheating event superimposed on the prolonged burial thermal metamorphism.

Schwarz and McCallum (2005) and Yamaguchi et al. (2009) suggested that the long duration of the global crustal metamorphism can be interspersed with short durations of reheating events that are caused by the impact or intrusions of hot magmas in different degrees and periods. The magma intrusion or indirect impact events during burial metamorphism can increase the ambient temperatures rapidly, and then slowly or rapidly (excavating the rock out to the surface) cool down. Therefore, we speculate that the heat source of sulfurization in NWA 11591 and the source of the S-rich vapors may have two explanations. (1) The protolith of NWA 11591 was buried in the shallow crust by the repeated eruption and rapid accumulation of lava flow, and it has been reheated by the intrusion of degassed magma during this period. The S-rich vapors then evaporated from the degassed intrusive magma, and subsequently sulfurized some tridymite grains in the protolith of NWA 11591. (2) During the period of prolonged burial thermal metamorphism, the S-rich material (e.g., carbonaceous chondrite; Reddy et al. 2012; McSween et al. 2013; Russell et al. 2013), that was accreted beforehand near the NWA 11591 protolith, was subjected to an indirect reheating impact event and released the S-rich vapors, which subsequently sulfurized some tridymite grains in the protolith of NWA 11591. If the hypothesis mentioned in (1) is correct, the sulfurization by S-rich vapors may be a ubiquitous phenomenon during the evolution of the Vesta crust. However, the environmental conditions under which the sulfurization of NWA 11591 occurred and the source of the S-rich vapors need to be demonstrated.

The sulfurized pyroxenes in NWA 2339 and NWA 1109 have distinctly lower Fe/Mn values than those of normal pyroxenes in HEDs, so the sulfurization recorded in NWA 2339 and NWA 1109 has been suggested to have occurred on or near the surface of Vesta and is not an indigenous process of Vesta (Zhang et al. 2013; Wang et al. 2019). However, this may be quite different in the case of sulfurization of tridymite’ in NWA 11591. The sulfurized tridymites, intergrowth with the primary lath-shaped plagioclase grains in NWA 11591 indicates that the sulfurized tridymites is a native mineral of NWA 11591 rather than an exotic one. Thus, combined with the above discussion, we suggested that the sulfurization recorded in NWA 11591 would be a thermal process occurring in the shallow crust of Vesta. This is consistent with the recent discovery of sulfurized olivine in the unbrecciated noritic diogenite, which is also suggested to have occurred in the interior of Vesta (Zhang et al. 2020). The tridymite with SRTs is dispersed in clasts and matrices of the monomict eucrite NWA 11591 without local enrichment. This indicates that the sulfurization would have occurred at least within the range of the protolith of NWA 11591, and that there may be localized S-rich fluid in the shallow crust of Vesta. Sulfur would be an important component of the metasomatic fluid on Vesta, in addition to the possibly H2O-bearing fluid (e.g., Treiman et al. 2004; Barrat et al. 2011; Warren et al. 2014).

**CONCLUSIONS**

1. The NWA 11591 meteorite is a non-cumulate monomict basaltic eucrite, and it is a type 7 eucrite.

2. The SRTs of tridymite in NWA 11591 are characterized by the distribution of loose porous regions with aggregates of quartz and minor troilite grains along the rims and fractures of tridymites. We suggest that the primary tridymite grains are affected by the S-rich vapors along the rims and fractures, leading to the transformation of tridymite into quartz. In addition, the S-rich vapors react with Fe2+, which is partially transported from the relict tridymite and/or the adjacent Fe-rich minerals, and/or the S-rich vapors react with the exotic metallic Fe to form troilite grains. Some lithophile elements (e.g., Al, K, Ca, and Ti) may be affected by the S-rich vapors and are lost or removed to various extents from the original tridymite system.

The sulfurization genesis of the SRT of tridymite was first proposed in the study of noncumulate eucrites (e.g., Ono et al. 2016, 2017).

3. We speculate that the sulfurization in NWA 11591 may be an open, relatively high temperature (>800 °C) process which superimposed on the prolonged subsolidus thermal metamorphism in the shallow crust of Vesta. Both the heat source of the sulfurization and the S-rich vapors may originate from the degassed hot intrusion magmas or from the reheating of S-rich material (e.g., carbonaceous chondrite).

4. The dispersed occurrence of the SRTs in the monomict source of NWA 11591 indicates that sulfurization would be at least an event occurring within the range of the NWA 11591 protolith. S-rich vapors may be locally present in the shallow crust of Vesta. Sulfur would be an important component of the metasomatic fluid on Vesta.

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