Record of S-rich vapors on asteroid 4 Vesta: Sulfurization in the Northwest Africa 2339 eucrite

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Abstract

In the Northwest Africa (NWA) 2339 eucrite, a few high-Fe pigeonite fragments were partially replaced by fine-grained troilite, Mg-rich augite, silica, with minor ilmenite and Mg-rich ferrosilite. The relict pigeonite has distinctly lower Fe/Mn values (17–18) than those (30) of augite and Mg-rich ferrosilite in the fine-grained replacement textures and other eucritic pyroxenes in NWA 2339. The few plagioclase grains associated with these Fe-rich pigeonite fragments contain high albite components (Ab 17–31). Similar replacement textures are also present in a lithic clast consisting of pyroxene and Na-rich plagioclase (Ab20–25). In this lithic clast, high-Fe subcalcic augite was replaced by troilite, Mg-rich hedenbergite, silica, and minor ilmenite whereas Mg-rich pigeonite remains intact. Troilite also occurs as tiny inclusions in porous regions of plagioclase. Moreover, the porous regions of plagioclase are enriched in Si and depleted in Al, Ca, and Na, compared to relict plagioclase. These textures indicate that the formation of troilite-rich mineral assemblages is related to the reaction between FeSiO$_3$ component in pyroxene and S-rich vapors; whereas, the formation of tiny troilite in porous regions of plagioclase is related to the reaction between Fe$^{2+}$ in plagioclase and S-rich vapors. X-ray mapping results reveal that during sulfurization of pyroxene and plagioclase, lithophile elements Mn, Al, Ca, Na, and Mg were removed to various extents, very likely by the S-rich vapors. Based on our observations, the S-rich vapors could be dry S–O–P vapors, which most likely have been formed by volatilization of pre-existing S,P-bearing materials due to impact heating on the surface of asteroid 4 Vesta.

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1. INTRODUCTION

Similar reflectance spectroscopic features between the surface of 4 Vesta and howardite–eucrite–diogenite (HED) meteorites imply that the former could be the parent body of HED meteorites (Binzel and Xu, 1993; McSween et al., 2011; Russell et al., 2012). Short-lived and long-lived radiometric ages of HED meteorites indicate that Vesta could have completed its accretion and differentiation, and even thermal metamorphism very early (~4.5 Ga ago; Coradini et al., 2011 and references therein). Thus, Vesta is considered to be a remnant intact protoplanet (Russell et al., 2012), and its early history is very important for constraining the internal evolution of protoplanets. However, to understand the early history of Vesta, we must identify possible effects of post-crystallization processes (especially exogenous processes) that could have taken place on Vesta, such as shock metamorphism and fluid-rock interaction.

Shock metamorphism could be the most important process modifying the surface morphology of Vesta (e.g., Marchi et al., 2012). This process also results in fragmentation and brecciation of rocks on the surface of Vesta. However, the modification by impact events of minerals and the chemistry of surface rocks (e.g., HED meteorites) on Vesta has not been studied in detail. The few descriptions about
shock metamorphism of HED meteorites in the literature include: transformation of anorthite into maskelynite in eucrite NWA 1000 (Warren, 2002), formation of glass veins in eucrite Yamato 82202 (Buchanan et al., 2005), and formation of Fe-rich olivine veins that filled pyroxene fractures in eucrites Yamato 75011 and NWA 1000 which were interpreted to be related to impact events (Takeda et al., 1994; Warren, 2002). Recently, Barrat et al. (2012a) studied impact melts in some HED polymict breccias and described Fe-enrichment along cracks in pyroxenes. They suggested that the Fe-enrichment in pyroxene might be the result of Fe-metasomatism accompanied by an impact event.

Investigations about possible fluid-rock interactions in the rocks from Vesta are very limited. So far, very few papers reported possible, indirect evidence that aqueous fluids or hydrogen might exist on Vesta (Hasegawa et al., 2003; Treiman et al., 2004; Barrat et al., 2011; Mittlefehldt et al., 2011; Denevi et al., 2012; Prettyman et al., 2012). Hasegawa et al. (2003) suggested that OH and/or H2O-bearing minerals are present on the surface of Vesta based on their ground based Infrared Telescope data. They considered that the sources of OH or H2O could be fragments of carbonaceous chondrite impactors or solar wind implantation. Treiman et al. (2004) observed a few quartz veinlets in the Serra de Magé eucrite. They proposed that the quartz in this meteorite was likely deposited from liquid water solutions. Mittlefehldt et al. (2011) suggested that varying Fe/Mn values of a few pyroxene fragments in howardite meteorites could be evidence of fluid-mediated alteration by a fluid phase, likely H2O. More recently, Barrat et al. (2011) observed in a few eucrites: (1) Fe-enrichment along the cracks that cross cut pyroxene crystals; (2) deposits of Fe-rich olivine, troilite, and plagioclase inside cracks; and (3) Fe-enrichment and Al-depletion of pyroxene. They suggested that these features could be products of interactions between aqueous fluids and preexisting rocks. Recently, the remote-sensing data from Dawn Mission (Denevi et al., 2011; Prettyman et al., 2012) revealed that volatile components including exogenic hydrogen might be present on the surface of Vesta. However, only based on remote-sensing data, we do not know how these volatile components interacted with materials on the surface of Vesta. All these investigations suggested that the fluid that existed on the surface of Vesta could be water-rich or hydrogen-rich. No fluids with other chemical compositions have been reported on the surface of Vesta or in HED meteorites in the literature.

Recently, in a brecciated eucrite, Northwest Africa (NWA) 2339, we observed a few pyroxene fragments and lithic clasts containing sulfide-rich replacement textures. It could be direct evidence of S-rich vapor on the eucrite parent body. Here, we report the petrography and mineralogy of these sulfide-rich replacement textures, discuss the possible reaction mechanism between S-rich vapor and rocks and element mobilization during this process, and constrain the possible formation environment.

2. ANALYTICAL METHODS

The petrography of NWA 2339 was studied by using the Hitachi 3400N II at Purple Mountain Observatory and the JEOl JSM-7000F field emission scanning electron microscopes (FE-SEM) at Hokkaido University in back-scattered electron (BSE) mode. Quantitative chemical compositions of minerals were determined by using the JEOl 8100 electron microprobe (EMP) at Nanjing University. The operating conditions are 15 kV accelerating voltage, 20 nA beam current, and a focused beam for most minerals and a defocused beam for plagioclase (2 μm in diameter). Natural and synthetic standards were used. The typical detection limits for oxides of most elements are better than 0.02 wt%. Data were reduced by the ZAF procedure for the FE-SEM. X-ray element mapping with energy dispersive spectrometer (EDS) attached on the FE-SEM at Hokkaido University was performed on a few sulfide-rich fragments and lithic clasts to determine distribution of a few elements (e.g., Si, Al, Ca, Mg, Mn, S, and Na). The operating conditions for X-ray mapping are 15 kV accelerating voltage and 5–10 nA beam current.

3. NWA 2339 EUCRITE

NWA 2339 is an 11.9-g eucrite, found in Morocco in 2004 (Connolly et al., 2007). It has a typical brecciated texture and is dominated by fragments of pigeonite and anorthite (Fig. 1). A few pigeonite grains contain exsolution lamellae of augite, whose width is up to 20 μm. Subophitic and granular lithic clasts were also observed in the thin section (Zhang et al., 2011). The EPMA results reveal that Fe/Mn values of most pyroxene grains vary around 30, consistent with the eucritic origin of this meteorite (Fig. 2; McSween et al., 2011). Most plagioclase grains in NWA 2339 are anorthite in composition, also consistent with the eucritic origin (Fig. 3; Mayne et al., 2009). Accessory minerals in NWA 2339 include ilmenite, chromite, silica, troilite, and phosphate minerals. Iron-rich olivine is also common in NWA 2339 and has diverse petrographic

Fig. 1. Back-scattered electron (BSE) image of the NWA 2339 thin section. Px: pyroxene; pl: plagioclase; ol: olivine; chr: chromite. The outlined regions are shown in Figs. 4 and 5.
The oxygen isotopic composition ($\delta^{17}$O = 1.65‰, $\delta^{18}$O = 3.66‰, $\Delta^{17}$O = −0.253‰) of this meteorite is generally similar to that of other eucritic meteorites (average $\Delta^{17}$O = −0.239 ± 0.007‰, Greenwood et al., 2005), also supporting that NWA 2339 is a eucrite (Connolly et al., 2007).

4. SULFIDE-RICH REPLACEMENT TEXTURES

In the 0.55-cm² thin section of NWA 2339 (Fig. 1), nine pyroxene fragments and one lithic clast show sulfide-rich replacement textures (Figs. 4 and 5). Most pyroxene grains do not show this reaction texture, although pyroxene and sulfide are present together in a few lithic clasts. The sulfide-rich replacement textures appear to be restricted to individual pyroxene fragments or lithic clasts and do not extend across boundaries with surrounding mineral fragments or clasts (Figs. 4 and 5). One sulfurized pyroxene occurs in a breccia clast (Fig. 4f).

All pyroxene fragments containing sulfide-rich replacement textures are Fe-rich pigeonite and vary from 40 to 230 μm in size with most fragments larger than 100 μm. These pyroxene fragments are composed of coarse-grained Fe-rich pigeonite and a fine-grained mineral assemblage of calcic augite, troilite, and silica that replaced the Fe-rich pigeonite (Fig. 4). The troilite grains are usually larger than 1 μm in size and up to 5 μm. In a few Fe-rich pigeonite fragments, ilmenite and Mg-rich ferrosilite are also present as minor phases in the fine-grained replacement textures (Fig. 4b, d and e). The Mg-rich ferrosilite grains mainly occur as irregular grains with smooth outlines. The relict Fe-rich pigeonite grains show no exsolution lamellae, even with high magnification under the FE-SEM. In two of nine fragments, a few subhedral plagioclase laths (<10 μm in width) are in contact with fine-grained sulfide-rich replacement textures (Fig. 4d).

All the relict, coarse pigeonite grains (En15.8–23.9Fs62.1–69.6Wo11.0–15.2) in sulfurized fragments are Fe-rich (Mg# = Mg/(Mg + Fe) = 0.19–0.27) and have a limited chemical variation (Fig. 6). They are Mn-rich and have a relatively low Fe/Mn value (17.3–19.6, Table 1 and Fig. 2). Plagioclase grains are more Na-rich (Table 1; Fig. 3) than most plagioclase grains in NWA 2339 and have a large chemical variation between different fragments (An65.7–82.0) and a limited variation within single fragments. These plagioclase grains contain 0.9–1.4 wt% FeO, consistent with most plagioclase grains in NWA 2339, although some plagioclase grains with low FeO contents were also observed. Augite (En24.2–27.5Fs29.4–38.7Wo37.1–43.0) in the sulfide-rich replacement textures has high Mg# values (0.38–0.48) compared to the relict pigeonite. Their Fe/Mn values (26.6–31.2) are higher than relict pigeonite and similar to those of other pyroxene grains in NWA 2339. The Mg-rich ferrosilite (En33.7–35.9Fs62.1–62.6Wo2.1–3.7, Mg# = 0.35–0.37) in the sulfide-rich replacement textures also has a high Fe/Mn value (30.1–31.2, Table 1), similar to that of the fine-grained augite. Silica in the sulfide-rich reaction texture contains 96–98 wt% SiO₂ and minor amounts of FeO (1.0–1.5 wt%). The X-ray mapping results of the coarse-grained pigeonite and adjacent fine-grained replacement texture (Fig. 7) are consistent with spot analyses of different mineral phases. It is noteworthy that the
fine-grained sulfide-rich regions show lower Mn concentrations than the relict pigeonite (Fig. 7f).

The lithic clast shown in Fig. 5a is about 700 μm in size and contains two parts although their boundary cannot be well defined. Both parts are composed of pyroxene and plagioclase, but have different proportions of pyroxene and plagioclase (Fig. 5a). In the left part of this lithic clast, the pyroxene is Fe-rich pigeonite to subcalcic augite without chemical zoning. High-magnification SEM observations show that these pigeonite grains contain very thin exsolution lamellae (submicron in thickness; Fig. 5d). Both pyroxene and plagioclase grains have been heavily replaced by fine-grained mineral assemblages (Fig. 5b and c). The Fe-rich subcalcic augite is replaced by fine-grained Mg-rich hedenbergite, troilite, and silica. The troilite grains vary in size from submicron to 5 μm. A few ilmenite grains are also present in the fine-grained mineral assemblage (Fig. 5c and d). The altered regions of plagioclase grains are porous and contain small troilite grains (Fig. 5b and c). The troilite grains in the altered regions of plagioclase are usually sub-micron in size. The X-ray mapping results (Fig. 8) show that the altered regions of plagioclase contain higher Si and lower Al, Ca, and Na than the unaltered regions. It is noteworthy that the Si-rich altered regions are not pure silica (Fig. 8b). An irregular merrillite grain is also observed at the boundary between the altered pigeonite and plagioclase grains (Fig. 8a). Pyroxene grains in the right part of the lithic clast contain a large Mg-rich pigeonite core and a Fe-rich, subcalcic augite rim (Figs. 5e and 9a). The X-ray mapping results (Fig. 9) show that the boundary between the pigeonite core and the subcalcic augite is sharp. A few plagioclase grains and the Fe-rich, subcalcic augite rim in the right part were also altered, similar to that in the left part; however, the Mg-rich pigeonite core remains intact (Fig. 5e). The Fe-rich, subcalcic augite in the right part also contains very thin exsolution lamellae (Fig. 5f).

All Fe-rich subcalcic augite grains (some spots are pigeonite, $\text{En}_{9.9-21.3}\text{Fs}_{54.2-70.9}\text{Wo}_{16.2-28.8}$, $\text{Mg#} = 0.12$–0.28) in this lithic clast have a Fe/Mn value of 31.4–34.0. The Mg-rich hedenbergite grains ($\text{En}_{18.5-24.7}\text{Fs}_{26.5-35.9}$
 Wo$_{45.6-47.3}$, Mg$\# = 0.34–0.46$) have slightly higher Fe/Mn values (34.5–35.9). The Mg-rich pigeonite core (En$_{43.3–57.1}$Fs$_{32.9–42.2}$Wo$_{10.0–15.5}$, Mg$\# = 0.51–0.63$) in the right part of the lithic clast has similar Fe/Mn values (32.4–39.9) to those of the Fe-rich, subcalcic augite. Plagioclase in this lithic clast not only contains higher Ab components (An$_{73.3–79.3}$Ab$_{19.5–25.1}$Or$_{1.3–1.6}$) than most plagioclase grains in NWA 2339 (Fig. 3), but has slightly higher FeO contents (1.5–1.8 wt%; Table 2) than most other plagioclase grains (<1.5 wt%) in NWA 2339.

5. DISCUSSION

5.1. Sulfurization of pyroxene in NWA 2339

The petrographic textures shown in Figs. 4 and 5 strongly indicate that the fine-grained mineral assemblage of high-Ca pyroxene, troilite, and silica replaced primary Fe-rich pyroxene (pigeonite and subcalcic augite). The evidence includes: (1) the fine-grained replacement textures do not change the morphology of primary pyroxene; (2) the presence of remnant pyroxene grains associated with the fine-grained replacement textures; (3) the fine-grained replacement textures mainly occur along the margin of primary pyroxene grains; and (4) in the sulfurized pyroxene fragments, primary and secondary pyroxenes show distinctly different Fe/Mn values (Fig. 2), indicating that they formed under different physicochemical conditions.

Some mesostasis in basaltic eucrites also contains fine-grained silica and troilite, but it differs from the sulfurized textures in this study in the following aspects. (1) Mesostasis in basaltic eucrites usually has sharp boundaries with surrounding coarse-grained minerals and its shape is also confined by those of the latter. However, unlike mesostasis, the fine-grained mineral assemblages of silica, troilite, and high-Ca pyroxene in NWA 2339 mainly occur within pyroxene grains and no sharp boundaries were observed between the fine-grained mineral assemblages and relict Fe-
Table 1

<table>
<thead>
<tr>
<th></th>
<th>Pigeonite</th>
<th>Ferrosilite</th>
<th>Augite</th>
<th>Plagioclase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.0</td>
<td>48.7</td>
<td>48.0</td>
<td>46.6</td>
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<tr>
<td>TiO₂</td>
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<td>0.39</td>
<td>0.31</td>
<td>0.61</td>
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<tr>
<td>Al₂O₃</td>
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<td>0.27</td>
<td>0.25</td>
<td>0.34</td>
</tr>
<tr>
<td>Cr₂O₃</td>
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<td>0.03</td>
<td>bd</td>
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<tr>
<td>FeO</td>
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<td>36.3</td>
<td>37.9</td>
<td>35.5</td>
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<tr>
<td>MnO</td>
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<td>1.99</td>
<td>2.09</td>
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<tr>
<td>MgO</td>
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<td>7.42</td>
<td>6.39</td>
<td>6.57</td>
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<td>CaO</td>
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<td>5.21</td>
<td>6.37</td>
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<tr>
<td>Na₂O</td>
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<td>bd</td>
<td>bd</td>
<td>bd</td>
</tr>
<tr>
<td>K₂O</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
</tr>
<tr>
<td>Total</td>
<td>99.5</td>
<td>99.9</td>
<td>100.2</td>
<td>99.4</td>
</tr>
</tbody>
</table>

| Si           | 1.990     | 1.993       | 1.980    | 1.979       |
| Ti           | 0.015     | 0.012       | 0.010    | 0.019       |
| Al           | 0.013     | 0.013       | 0.012    | 0.017       |
| Cr           | bd        | 0.001       | 0.001    | bd          |
| Fe           | 1.284     | 1.237       | 1.303    | 1.221       |
| Mn           | 0.072     | 0.069       | 0.073    | 0.070       |
| Mg           | 0.363     | 0.455       | 0.396    | 0.406       |
| Ca           | 0.252     | 0.208       | 0.230    | 0.281       |
| Na           | bd        | bd          | bd       | bd          |
| K            | bd        | bd          | bd       | bd          |
| Cations      | 3.990     | 3.988       | 4.004    | 3.994       |

|Mg# = Mg/(Mg + Fe) in mole. Bd: below detection limit.
Cations in pyroxene are calculated based on 6 oxygen atoms; cations in plagioclase are calculated based on 8 oxygen atoms.

rich pyroxene. (2) Mesostasis in basaltic eucrites is usually dominated by silica with minor troilite and other phases. However, the fine-grained replacement textures contain comparable amounts of silica, troilite, and high-Ca pyroxene. (3) Pyroxene in the mesostasis in basaltic eucrites should have similar or identical Fe/Mn values to surrounding coarse-grained pyroxene grains, because they crystallized from a common melt. However, the augite and Mg-rich ferrosilite in the fine-grained replacement textures shown in Fig. 4 have different Fe/Mn values from the coarse Fe-rich pigeonite grains, indicating that they formed in different physic-chemical settings. (4) In addition, the altered regions of plagioclase in the lithic clast shown in Fig. 5a are also different from the mesostasis in basaltic eucrites. Although the altered regions of plagioclase are Si-rich compared to unaltered plagioclase grains, they are not pure silica (Fig. 8). However, pure silica grains are usually present in mesostasis of basaltic eucrites. Some highly fractionated clasts in eucrites or howardites contain fine-grained silica, ferroaugite, and fayalite (Buchanan et al., 2000; Barrat et al., 2012b). However, these fine-grained mineral assemblages also differ from the fine-grained replacement textures. The reasons are: (1) Fayalite associated with silica and ferroaugite in the highly fractionated mineral assemblages is not present in the troilite-rich replacement textures from NWA 2339. (2) The ferroaugite in the highly fractionated mineral assemblages is highly Fe-rich; whereas the augite and hedenbergite in the troilite-rich replacement textures are Mg-rich. Thus, the troilite-rich replacement textures are different in texture, mineralogy, and origin from the mesostases of eucrites and highly fractionated mineral assemblages of silica, ferroaugite, and fayalite.

The similarity of primary minerals and replacement textures between the pyroxene fragments (Fig. 4) and the lithic clast (Fig. 5a) in NWA 2339 suggests that their reaction mechanisms could be similar. The major reaction mechanism could be replacement of high-Fe and low-Ca pyroxene by relatively low-Fe and high-Ca pyroxene, troilite, and silica. To date, no experimental or theoretical data of sulfuration of pyroxene with compositions similar to the primary low-Ca pyroxene in this study have been reported in the literature (Kullerud and Yoder, 1963, 1964; Colson, 1992). However, Kullerud and Yoder (1963, 1964) performed a series of experiments of reactions between CaFe₂Si₂O₆ and sulfur under various conditions. The reaction products contain iron sulfide, pyroxene, silica, and SO₂ (Kullerud and Yoder, 1963, 1964). They found that reac-
tion products vary depending on the various mole proportions between sulfur and hedenbergite. One of the experiments was performed at 800 °C and 2000 bars (Kullerud and Yoder, 1963):

$$2\text{CaFeSi}_2\text{O}_6 + 3\text{S}_2(g) \rightarrow 2\text{FeS} + 2\text{CaSiO}_3 + 2\text{SO}_2(g)$$

(1)

The reaction products of (1) are similar to the mineral assemblage observed in the fine-grained replacement textures in NWA 2339. The main difference between reaction products of (1) and the sulfide-rich mineral assemblage observed in NWA 2339 is the different compositions of pyroxene (or pyroxenoid); one is CaSiO$_3$ and the other is augite or hedenbergite. However, Kullerud and Yoder (1963) stated that during reaction between silicate minerals and sulfur vapor, Mg and Ca are still present in the original silicates. Therefore, if we consider the existence of MgSiO$_3$ component in natural pigeonite and subcalcic augite, then (1) could be extended to a general reaction depending on the initial composition of primary pyroxene:

- **Fe-rich pigeonite fragments:**
  $$\text{Fe-rich pigeonite} + \text{S}_2(g) \iff \text{FeS} + \text{Mg-rich augite} + \text{SiO}_2 + \text{SO}_2(g)$$
  (2)

- **Fe-rich, subcalcic augite in the lithic clast:**

$$\text{Fe-rich, subcalcic augite} + \text{S}_2(g) \iff \text{FeS} + \text{Mg-rich hedenbergite} + \text{SiO}_2 + \text{SO}_2(g)$$

(3)

**Table 2**

Representative chemical compositions (wt%) of pyroxene and plagioclase in the sulfurized lithic clast in NWA 2339.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Pigeonite and subcalcic augite</th>
<th>Hedenbergite</th>
<th>Plagioclase</th>
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<tr>
<td>SiO$_2$</td>
<td>50.3</td>
<td>45.3</td>
<td>45.6</td>
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<tr>
<td>TiO$_2$</td>
<td>0.37</td>
<td>0.52</td>
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</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.72</td>
<td>2.39</td>
<td>1.43</td>
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<tr>
<td>Cr$_2$O$_3$</td>
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<td>FeO</td>
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<td>MnO</td>
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<td>Na$_2$O</td>
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<tr>
<td>K$_2$O</td>
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</tr>
<tr>
<td>Total</td>
<td>100.1</td>
<td>100.5</td>
<td>99.18</td>
</tr>
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</table>

Si = 1.892, Ti = 0.010, Al = 0.120, Cr = 0.024, Fe = 0.643, Mn = 0.020, Mg = 1.117, Ca = 0.195, Na = 0.001, K = 0.003, Cations = 4.027.

Mg# = Mg/(Mg + Fe) in mole. Bd: below detection limit.

Cations in pyroxene are calculated based on 6 oxygen atoms; cations in plagioclase are calculated based on 8 oxygen atoms.

**Fig. 6.** Compositions of pyroxene related to sulfide-rich replacement textures in NWA 2339. The red squares denote pyroxene in sulfurized pyroxene fragments shown in Fig. 4. The blue circles denote pyroxene in the sulfurized lithic clast shown in Fig. 5. The compositional regions are adopted from Morimoto et al. (1988).
In these reactions, we use $S_2$ rather than $S$ because $S_2$ was considered as the predominant species in sulfur vapor although other sulfur species $S$, $S_2$, $S_6$, and $S_8$ also exist (Toulmin and Barton, 1964). At the same time, as noted in Kullerud and Yoder (1964), even when the Reaction (1) took place, CaSiO$_3$ may contain some iron in solid solution. Keeping this in mind, it seems reasonable that the augite and Mg-rich hedenbergite in the fine-grained replacement textures from NWA 2339 contain FeSiO$_3$ component, but less than that in the primary pigeonite and subcalcic augite, respectively. In summary, the reactions (2) and (3) can qualitatively represent the formation of sulfide-rich replacement texture in pyroxene fragments and in the lithic clast from NWA 2339, respectively.

In other experiments by Kullerud and Yoder (1964) whose conditions are different from those of reaction (1), for instance at 650°C and 2000 bars, the reaction products between hedenbergite and sulfur did not contain FeS, but FeS$_2$. This indicates that temperature could be a key factor in affecting the species of sulfide in the reaction products. Based on these experimental results, we infer that the sulfurization recorded in NWA 2339 probably took place at or above 800°C. Besides temperature, Colson (1992) demonstrated that the sulfide species in sulfurization of olivine also depends on fugacities of sulfur and oxygen. If we assume that the behavior of sulfide in sulfurization of pyroxene is similar to that in sulfurization of olivine, the fugacity of sulfur should also be lower than that of reaction $FeS + 1/2S_2 \leftrightarrow FeS_2$ and higher than that of reaction $FeS - \leftrightarrow Fe + 1/2S_2$.

Within a few sulfide-pyroxene replacement textures in NWA 2339, ilmenite was also observed. These ilmenite grains could be byproducts of the sulfurization of pigeonite. This interpretation is supported by the variations of TiO$_2$ from remnant low-Ca pyroxene to the fine-grained high-Ca pyroxene in the replacement textures (Tables 1 and 2). It is very likely, that during sulfurization of primary high-Fe and low-Ca pyroxene, some Ti released from primary low-Ca pyroxene was inherited by secondary high-Ca pyroxene and the rest combined with Fe and formed ilmenite.

The Mg-rich ferrosilite grains shown in Fig. 4d and e could also be related to the sulfurization of pigeonite. The evidence includes: (1) the Mg-rich ferrosilite grains are closely related to the fine-grained replacement textures; (2) the Mg-rich ferrosilite grains have almost the same Fe/Mn va-
blue as those of fine-grained augite in the replacement textures, indicating that they formed under same conditions. Several scenarios may be suggested to explain the formation of Mg-rich ferrosilite related to sulfide-rich replacement textures. First, the Mg-rich ferrosilite might be a relict mineral during sulfurization of pigeonite. However, because the Mg-rich ferrosilite has distinctly different Fe/Mn values from those of relict pigeonite, a relict origin of the Mg-rich ferrosilite is unlikely. If the Mg-rich ferrosilite is of relict origin, the Mg-rich ferrosilite and pigeonite should have similar Fe/Mn values. The second possibility is that the Mg-rich ferrosilite is a sulfurization product of preexisting silicate minerals. Norman et al. (1995) and Shearer et al. (2012) suggested that low-Ca pyroxene observed in a few Apollo breccias could be the sulfurization product of olivine. Although Fe-rich olivine was also observed in NWA 2339 (Zhang et al., 2011), these occurrences are distinctly different from the texture of pigeonite fragments that are associated with troilite-rich replacement textures. This makes the explanation unlikely. The third possibility is that the Mg-rich ferrosilite is an in situ precipitation mineral from a hot vapor. Because the sulfurization process is a high-temperature process, it is possible that some elements (Fe, Mg, and Si) were mobilized by this process and then in situ deposited. This interpretation is consistent with the smooth outlines of the Mg-rich ferrosilite in the sulfide-silicate replacement textures. Although this possibility cannot be further constrained based on the data in present study, it seems to be the best interpretation for the presence of the Mg-rich ferrosilite in the fine-grained mineral assemblages.

5.2. Sulfurization of plagioclase in NWA 2339

The fact that all the altered regions of plagioclase contain fine-grained troilite grains (Figs. 5b, c and 8a) implies that the alteration of plagioclase could also be related to sulfurization. No similar descriptions of sulfurization of anorthite have been previously reported in natural samples and experimental products. In this study, we will infer the possible mechanism of sulfurization of plagioclase mainly based on the texture and mineral chemistry of plagioclase.
Troilite in the altered regions of plagioclase could have been formed by sulfurization of iron in plagioclase. The first reason is that plagioclase in the sulfurized lithic clast does contain high FeO (1.5–1.8 wt%) with respect to other plagioclase grains (usually <1.5 wt%) in NWA 2339. Second, troilite grains in the altered regions of plagioclase are much smaller than those in the replacement textures of Fe-rich subcalcic augite (Fig. 5 c). Compared to Fe-rich subcalcic augite, the low FeO content in plagioclase is consistent with the suggestion that there was not enough Fe to form troilite as coarse-grained as those in the troilite-rich replacement textures of Fe-rich pyroxene. If both the sulfur and iron that combined to form the troilite grains in the altered regions of plagioclase were derived from outside the lithic clast, the troilite grains in the altered regions of plagioclase might be larger than those we observed. However, it seems that the sulfurization of plagioclase has nothing to do with the albite components in plagioclase because the few Na-rich plagioclase grains associated with sulfurized Fe-rich pigeonite were not sulfurized.

5.3. Transport of lithophile elements during sulfurization of silicates

Transport of elements has been discussed for sulfurization of olivine in a few Apollo samples (Shearer et al., 2012). Shearer et al. (2012) suggested that the S-rich vapor also transported some chalcophile–siderophile elements (Fe, Ni, Co, Se, Cu, Zn, and Sb). This is important to understand the mobility of elements by a gas/vapor agent during sulfurization (cf. Dohmen et al., 1998). The EPMA spot analyses and SEM-EDS mapping results in this study allow for qualitative evaluation of mobilization of lithophile elements during sulfurization of silicates (pyroxene and plagioclase).

Previous investigations suggested that iron could have been added to the sulfurization reaction with sulfur vapor (e.g., Shearer et al., 2012). However, addition of iron is not necessary for interpreting the sulfurization of silicates in NWA 2339. First, relict pyroxenes associated with fine-grained troilite-rich replacement textures in NWA 2339 are very Fe-rich; most of them contain high ferrosilite component (>65 mole%). Second, in the lithic clast shown in Fig. 5a, only the Fe-rich rim was sulfurized and the Mg-rich core was not sulfurized. If addition of iron accompanied the S-rich vapor, the Mg-rich core would also be sulfurized. Third, the small size of troilite grains in the altered regions of plagioclase could be another piece of evidence of lack of addition of iron. If addition of iron occurred during sulfurization, the sizes of the troilite grains in the altered regions of plagioclase would be larger and similar to those observed in the fine-grained replacement textures of pyroxenes.

Relict pigeonite shown in Fig. 4 has distinctly different Fe/Mn values from those of fine-grained pyroxene (augite and Mg-rich ferrosilite) in the troilite-rich replacement textures and other pyroxenes in NWA 2339 (Fig. 2). This feature has at least two important implications. One is that these high-Mn pigeonite grains have an exogenous origin compared to other pyroxenes in NWA 2339. It is possible that these fragments are derived from a different parent body or a region where the conditions are different from those of most HED materials indicated. This conclusion is supported by the high albite components of plagioclase, compared to those in other plagioclase grains from NWA 2339 (Fig. 3). The other implication is that some Mn was lost during sulfurization of the Fe-rich pigeonite, because...
not only the secondary augite and Mg-rich ferrosilite but also the whole replacement textures contain lower Mn than the remnant pigeonite (Fig. 7). At the same time, the Fe/Mn values of secondary augite and Mg-rich ferrosilite are similar to those of other pyroxenes in NWA 2339. This feature may indicate that the Fe/Mn values of secondary pyroxenes (augite and Mg-rich ferrosilite) were controlled by conditions (e.g., volatility) of the eucritic parent body. This conclusion is consistent with the interpretation that the sulfurization reaction took place between a solid and a vapor, where volatility could be an important factor affecting geochemical behaviors of elements.

Based on the qualitative interpretations from reactions (2) and (3), the Ca/Mg mole ratios of secondary pyroxenes during sulfurization should be the same as those of primary pyroxenes. However, this inference contrasts with the EPMA results of pyroxenes (Tables 1 and 2). The Mg-rich augite in the trolite-rich replacement textures has higher Ca/Mg values than the relict pigeonite; whereas the Mg-rich ferrosilite in the replacement textures has lower Ca/Mg values than relict pigeonite (Table 1). The Mg-rich hedenbergite in the replacement textures from the tectonic clast has variable Ca/Mg values, generally comparable to those of the subcalcic augite rim (Table 2). Although the presence of Mg-rich ferrosilite can balance the high Ca/Mg values of augite, the Mg-rich ferrosilite was only observed as a very minor phase in two of nine pigeonite fragments. It is difficult to interpret the high Ca/Mg values of all augite only by the presence of Mg-rich ferrosilite. It seems more likely that some Mg was lost during sulfurization of pigeonite compared to Ca if there was no addition of Ca.

Different from the sulfurization of pyroxene in NWA 2339, X-ray mapping results indicate that plagioclase, after sulfurization, is not stable and Ca, Al, and Na were released (Fig. 8). It seems that sulfurization destroyed the crystal structure of plagioclase. Consequently, Ca, Al, and Na migrated out to various extents from the altered regions of plagioclase. All the above discussions indicate that some lithophile elements (such as Mn, Mg, Ca, Al, and Na) are mobile during sulfurization of pyroxene and plagioclase. The transport agent could be the S-rich vapor that reacted with pyroxene and plagioclase. This is consistent with the conclusion inferred from experimental results by Dohmen et al. (1998).

5.4. Composition and origin of S-rich vapors

Previous investigations of eucrites suggested that aqueous fluids could exist on the surface of 4 Vesta (Hasegawa et al., 2003; Treiman et al., 2004; Barrat et al., 2011; Mittlefehldt et al., 2011). So, it is necessary to evaluate whether the S-rich vapors reacting with pyroxene and plagioclase also contained H and other volatile elements (such as C and P). In this study, we observed that a few merrillite grains are closely associated with the replacement textures from NWA 2339 (e.g., Fig. 8). Although we cannot totally preclude that merrillite is not a late-stage crystallization phase, these merrillite grains are probably the reaction products between Ca released from plagioclase or pyroxene and P in the S-rich vapors. However, no phyllosilicate or C-rich minerals were detected in the replacement textures. This indicates that concentrations of C and H in the S-rich vapors must have been very low. Moreover, if H had been abundant in the S-rich vapors, probably there would have been no sulfurization of pyroxene and plagioclase because H and S combine readily to form very stable H₂S (cf. Petaev et al., 2011). Thus, the S-rich vapors that caused sulfurization of pyroxene and plagioclase could have been rich in S–O–P and H-poor. Such S-rich vapors could have been formed either by indigenous processes (e.g., emplacement of intrusions) or by exogenous processes (e.g., impact process).

In this study, the unaltered plagioclase grains closely associated with both the sulfurized pigeonite fragments and in the sulfurized lithic clast contain higher albite components than other plagioclase grains in NWA 2339, and the Fe-rich pigeonite fragments have distinctly lower Fe/Mn values than eucritic pyroxene. On one hand, these features imply that the sulfurized pigeonite and lithic clast might have been derived from different parent bodies from the parent body of eucrites. On the other hand, the various Fe/Mn values and internal textures (exsolution lamellae) indicate that they might also have different source regions from each other. Keeping these differences in mind, sulfurization on materials from different regions indicates that sulfurization of pyroxene and plagioclase should be a relatively large-scale and/or common process. Meanwhile, petrographic observations reveal that troilite-rich replacement textures were restricted to individual pyroxene fragments and lithic clasts. This feature implies that sulfurization of pyroxene and plagioclase took place prior to the final formation of the breccia. In addition, importantly, the change of Fe/Mn values from the Fe-rich pigeonite to the fine-grained augite and Mg-rich ferrosilite implies that the pigeonite was not in situ sulfurized. They must have been sulfurized after having migrated to a region where the physicochemical conditions were similar to those for most eucrite samples, but prior to the final formation of the breccia. This conclusion strongly argues against the interpretation that the sulfurization of pigeonite in NWA 2339 was due to an indigenous process, such as emplacement of intrusions that was proposed for the sulfurization of olivine in lunar samples (Norman et al., 1995; Shearer et al., 2012).

Instead, impact could be the more likely process that resulted in formation of the S-rich vapors and sulfurization of pyroxene and plagioclase. A large-scale impact event might be energetic enough to form S–O–P vapors. The S–O–P vapors might be derived from the preexisting ejecta blankets on the surface of Vesta, or from the impactors, or from both. The S–O–P vapors would react with Fe-rich pyroxene and plagioclase in ejecta blankets. This is consistent with the occurrence of sulfurized pyroxene and plagioclase always as breccias; especially, one sulfurized pigeonite fragment occurs in a breccia clast (Fig. 4f). When the temperature in ejecta blankets was kept at or above 800 °C, two weeks might be sufficient for the reaction between the S–O–P vapors and pyroxene or plagioclase to
establish phase equilibria (Kullerud and Yoder, 1964). Although the actual duration of sulfurization could be longer, such a process on the asteroid surface should not last very long, consistent with the lack of exsolution lamellae in the relict pigeonite fragments. After sulfurization of pyroxene and plagioclase, later impact events might further transport these sulfurized materials to other regions where the NWA 2339 breccia were finally formed and ejected from the surface of Vesta.

6. CONCLUSIONS

In this study, we studied sulfurization of pyroxene and plagioclase in the NWA 2339 brecciated eucrite. A few Fe-rich pigeonite fragments have unusual Fe/Mn values (17–20) and are partly replaced by fine-grained troilite, augite, silica, and minor ilmenite and Mg-rich ferrosilite. The fine-grained augite and ferrosilite have Fe/Mn values (~30) similar to other eucrite pyroxenes. A lithic clast consisting mainly of Fe-rich, subcalcic augite and plagioclase was also sulfurized. The subcalcic augite is replaced by fine-grained troilite, Mg-rich hedenbergite, silica, and minor ilmenite; whereas, Mg-rich pigeonite (core) remains intact. The subcalcic augite and Mg-rich hedenbergite have similar Fe/Mn values, consistent with other eucrite pyroxenes. Some plagioclase grains in this clast are porous and contain many tiny troilite grains. The porous regions are enriched in Si and depleted in Al, Na, and Ca.

The replacement textures observed in pyroxene were explained by reaction between FeSiO₃ component in pyroxenes and S-rich vapors. The replacement of plagioclase was explained by reaction between Fe²⁺ in plagioclase and S-rich vapor.

Based on petrographic observations, we suggest that the S-rich vapors should be dry S–O–P vapors. They should be formed by volatilization of pre-existing S,P-bearing materials due to impact processes on the surface of Vesta rather than due to emplacement of intrusions. The sulfurization might take place in ejecta blankets and was accompanied by some lithophile elements, such as Mn, Ca, Mg, Na, and Al.

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