Geochemistry of 4 Vesta based on HED meteorites: Prospective study for interpretation of gamma ray and neutron spectra for the Dawn mission

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Abstract–Asteroid 4 Vesta, believed to be the parent body of the howardite, eucrite, and diogenite (HED) meteorites, will be investigated by the Dawn orbiting spacecraft. Dawn carries a gamma ray and neutron detector (GRaND) that will measure and map some major- and trace-element abundances. Drawing on HED geochemistry, we propose a mixing model that uses element ratios appropriate for the interpretation of GRaND data.

Because the spatial resolution of GRaND is relatively coarse, the analyzed chemical compositions on the surface of Vesta will likely reflect mixing of three endmember components: diogenite, cumulate eucrite, and basaltic eucrite. Reliability of the mixing model is statistically investigated based on published whole-rock data for HED meteorites. We demonstrate that the mixing model can accurately estimate the abundances of all the GRaND-analyzed major elements, as well as of minor elements (Na, Cr, and Mn) not analyzed by this instrument. We also show how a similar mixing model can determine the modal abundance of olivine, and we compare estimated and normative olivine data for olivine-bearing diogenites. By linking the compositions of well-analyzed HED meteorites with elemental mapping data from GRaND, this study may help constrain the geological context for HED meteorites and provide new insight into the magmatic evolution of Vesta.

INTRODUCTION

Dawn, the ninth NASA Discovery mission, will orbit and explore two of the largest Main Belt asteroids, 4 Vesta and 1 Ceres, which are complementary protoplanets that have remained intact since their formation (Rayman et al. 2006; Russell et al. 2004). Vesta is highly differentiated and is thought to be the parent body for the voluminous howardite, eucrite, and diogenite (HED) suites (Binzel and Xu 1993; Keil 2002; McCord et al. 1970). Ceres apparently incorporated water ice during accretion and may contain liquid water (McCord and Sotin 2005); its materials might be akin to carbonaceous chondrites.

The Dawn spacecraft is equipped with a gamma ray and neutron detector (GRaND) (Prettyman et al. 2003). GRaND can directly measure the abundances and map the surface distributions of some major (O, Si, Fe, Ti, Mg, Al, and Ca) and trace (U, Th, H, and K) elements (Prettyman et al. 2006, 2004). A similar analytical technique has been used successfully on lunar and Mars orbiters (e.g., Evans et al. 2004; Lawrence et al. 2000, 2002). The ability of GRaND to determine elemental abundances on Vesta is influenced by the mission scenario; for example, its spatial resolution varies roughly in proportion to orbiting altitude. GRaND analyses will be carried out at three different altitudes (survey, high-altitude mapping orbit [HAMO], and low-altitude mapping orbit [LAMO]) (Fig. 1). Even at LAMO, GRaND's spatial resolution (~300 km) (Prettyman et al. 2004) is larger than that of compositional heterogeneity of Vesta's surface (<50 km) as observed by the Hubble Space Telescope (Fig. 1) (Binzel et al. 1997).

Based on its spectral similarities to HED meteorites, Vesta is interpreted to have a basaltic surface (e.g., Binzel and Xu 1993). Most eucrites and diogenites are brecciated and many are polymict rocks; the scale of compositional variability of HED meteorites (approximately centimeter-size) (Mittlefehldt et al. 1998) is much smaller than the spatial resolution of GRaND. Ground-based telescope and Hubble observations (Binzel et al. 1997; Gaffey 1997) suggest that the average surface of Vesta is analogous to polymict eucrite and/or howardite (regolith breccias mainly composed of eucrite and diogenite fragments) assemblages, although the diogenite spectral signature is also sporadically observed. GRaND will therefore likely yield data that mimics the mixing of HED meteorites.

In this study, we compile 55 published whole-rock
elemental compositions of 44 HED meteorites and propose a mixing model for interpreting GRaND data for the Dawn mission. In this model, we focus on element ratios that are sensitive to difference in mineral mode for HED meteorites. Furthermore, we demonstrate that the HED mixing model can be used to estimate the abundances of some elements not analyzed by GRaND (if there is an adequate HED database), as well as the modal abundances of olivine that occurs in some diogenites and is expected to comprise much of Vesta’s interior.

A TWO-DIMENSIONAL DIAGRAM FOR A MIXING MODEL WITH THREE ENDMEMBER COMPONENTS

A mixing model is proposed by postulating that GRaND analyses of the surface of Vesta are analogous to HED meteorites. The HED suite contains three main igneous lithologies: basalt, cumulate gabbro, and orthopyroxenite, which correspond to basaltic eucrite, cumulate eucrite, and diogenite, respectively (Mittlefehldt 2003). Since polymict HED rocks are mixtures of diogenite and basaltic or cumulate eucrites (Mittlefehldt 2003), GRaND analyses are expected to reflect the mixture of these three rock types. Mixing relations of three endmember components can be displayed on appropriate two-dimensional diagrams.

Many two-dimensional diagrams can be drawn by selecting any two element ratios from 11 elements that will be measured by GRaND analysis. However, most of them (e.g., Mg/Si versus Mg/Fe) are not diagnostic for displaying mixing relations in the HED suite (Fig. 2). Selecting appropriate element ratio pairs that are sensitive to differences in mineral modes for each meteorite suite is critical to proper interpretation. In this paper, a pair of molar element ratios, (Mg + Fe)/Si and Al/Si (hereafter abbreviated as [M/Si]_mol and [Al/Si]_mol, respectively), are employed (Fig. 3). HED meteorites mainly consist of low- and high-Ca pyroxenes and plagioclase. Both pyroxenes have compositions with variable Mg/Fe ratios and little Al_2O_3 contents (<1 wt%). By employing [M/Si]_mol, we are able to cancel out such variability in Fe/Mg ratios; [M/Si]_mol has a value of 1.0 for enstatite-ferrosilite solid solutions and 0.5 for diopside-hedenbergite solid solutions. Thus all pyroxenes in HED meteorites have [M/Si]_mol values from 0.5 to 1 with a constant

Fig. 1. a) An image of Vesta (computer reconstructed, after Zellner and Thomas 1997). b) A false-color (RGB) interpretive geological map of the near-equatorial region of Vesta from Hubble observations obtained during Vesta’s rotation (Binzel et al. 1997). The eastern hemispher region shown in green may represent eucrite-rich rock, whereas the western hemisphere, shown as relatively “warm” colors, may represent diogenite-rich rock. Red circles show the size of spatial resolution of GRaND at LAMO, which is given by the full-width-at-half-maximum (FWHM) of the spatial response function (~300 km in diameter) of GRaND for 200 km altitude (Prettyman et al. 2004). Altitude for each orbit mode is given by Rayman et al. (2006). The scales of (a) and (b) are comparable.
[Al/Si]mol value of ~0. Conversely, plagioclase contains very little MgO and FeO total (<1 wt%) but has abundant Al₂O₃ (>30 wt%), resulting in high [Al/Si]mol with [M/Si]mol value of ~0. Therefore, a [M/Si]mol versus [Al/Si]mol molar ratio plot is expected to discriminate among the three endmember lithologies diogenite, basaltic eucrite, and cumulate eucrite.

The quality of GRaND data depends critically on the orbital altitude at which the measurements are made and the duration of the measurements. The performance of GRaND during the Dawn mission was investigated based on results from the Lunar Prospector Gamma Ray Spectrometer (LPGRS), because LPGRS has a gamma ray sensor with approximately the same volume, detection efficiency, and pulse height resolution (Prettyman et al. 2004). On this basis, Prettyman et al. (2004) concluded that the spectrum obtained at LAMO is enough above background to map abundances of major rock forming elements, radioactive elements, and light elements such as H, C, and N at Vesta and Ceres. Therefore, GRaND data sets should allow construction of the mixing diagram employing [M/Si]mol and [Al/Si]mol.

Figure 3 shows whole-rock compositions of howardites, eucrites, and diogenites plotted on the [M/Si]mol versus [Al/Si]mol diagram (meteorite names, classification, and source of chemical analyses are given in Table 1). Diogenites have distinctly lower [Al/Si]mol and higher [M/Si]mol values than those of basaltic and cumulate eucrites. Basaltic eucrites have higher [Al/Si]mol and lower [M/Si]mol values than those of cumulate eucrites. Diogenites and basaltic eucrites have relatively uniform compositions compared to the polymict rocks. The polymict rocks (howardite and polymict eucrite) plot between basaltic eucrite, cumulate eucrite, and diogenite, which is consistent with previous geochemical and petrographical studies (e.g., Mittlefehldt 2003; Mittlefehldt et al. 1998). Such characteristics were also observed in all other element ratio plots (Usui and McSween 2006).

To evaluate the contribution of the three rock types to GRaND spectra, we propose two endmember sets, each consisting of three meteorites. One set consists of Shalka, Serra de Magé, and Nuevo Laredo as endmembers representing diogenite, cumulate eucrite, and basaltic eucrite, respectively (hereafter referred to as endmember set I [EM-I]). The other substitutes Stannern instead of Nuevo Laredo as a basaltic eucrite endmember (hereafter referred to as endmember set II [EM-II]). The elemental compositions of these four endmembers are given in Table 2. Shalka is a typical diogenite consisting of >90 vol% coarse-grained cumulus orthopyroxene (Mittlefehldt 1994). The cumulative
## Table 1. List of analyzed samples.

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Sample</th>
<th>Reference</th>
<th>Rock type</th>
<th>Sample</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diogenite</td>
<td>Jonstown A&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8</td>
<td>Basaltic eucrite</td>
<td>Béréba A&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2</td>
</tr>
<tr>
<td>Diogenite</td>
<td>Jonstown B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13</td>
<td>Basaltic eucrite</td>
<td>Béréba B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3</td>
</tr>
<tr>
<td>Diogenite</td>
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<td>8</td>
<td>Basaltic eucrite</td>
<td>Pasamonte</td>
<td>2</td>
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<tr>
<td>Diogenite</td>
<td>Shalka B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13</td>
<td>Basaltic eucrite</td>
<td>Juvinas A&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Diogenite</td>
<td>Y-75032</td>
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<td>Basaltic eucrite</td>
<td>Cachari A&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2</td>
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<td>Diogenite</td>
<td>Y-75032,79</td>
<td>4</td>
<td>Basaltic eucrite</td>
<td>Cachari B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3</td>
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<tr>
<td>Diogenite</td>
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<td>Diogenite</td>
<td>Ibbenbühren</td>
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<td>Basaltic eucrite</td>
<td>Sioux County A&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2, 9</td>
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<tr>
<td>Diogenite</td>
<td>Tatahouine</td>
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<td>Basaltic eucrite</td>
<td>Sioux County B&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Diogenite</td>
<td>Manegaon</td>
<td>14</td>
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<td>Basaltic eucrite</td>
<td>Lakangaon A&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Cumulate eucrite</td>
<td>Moama</td>
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<td>Basaltic eucrite</td>
<td>Nuevo Laredo B&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Cumulate eucrite</td>
<td>Serra de Mangé B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3</td>
<td>Basaltic eucrite</td>
<td>ALHA81001, 16 A&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>Cumulate eucrite</td>
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<td>Basaltic eucrite</td>
<td>ALHA81001, 16 B&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Cumulate eucrite</td>
<td>Binda A&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2, 9</td>
<td>Howardite</td>
<td>Bholghati</td>
<td>8</td>
</tr>
<tr>
<td>Cumulate eucrite</td>
<td>Binda B&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3</td>
<td>Howardite</td>
<td>Kapoeta</td>
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<td>Polymict eucrite</td>
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<td>Howardite</td>
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<td>Polymict eucrite</td>
<td>Macibini</td>
<td>2, 9</td>
<td>Howardite</td>
<td>Le Teilleul</td>
<td>3</td>
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<td>Howardite</td>
<td>Le Teilleul</td>
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<td>Howardite</td>
<td>Le Teilleul</td>
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<td>Polymict eucrite</td>
<td>EETA79004.53</td>
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<td>Howardite</td>
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<td>Polymict eucrite</td>
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<td>Olivine diogenite</td>
<td>NWA 1459</td>
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<td>2</td>
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<td></td>
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</table>

<sup>a</sup>1 = Lovering (1975); 2 = McCarthy et al. (1973); 3 = Palme et al. (1978); 4 = Mittlefehlt and Lindstrom (1993); 5 = Palme et al. (1983); 6 = Wänke et al. (1972); 7 = Warren and Jerde (1987); 8 = Mittlefehlt et al. (1998); 9 = Mittlefehlt (2003); 10 = Irving et al. (2003); 11 = Takeda (1979); 12 = Sack et al. (1991); 13 = Fredriksson et al. (1976); 14 = MacCarthy et al. (1974).

<sup>b</sup>A and B are used to differentiate different data sources for the same meteorite.

## Table 2. Whole-rock compositions of the endmember components for the mixing model.

<table>
<thead>
<tr>
<th>Shalka A&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Serra de Mangé B&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Stannern&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Nuevo Laredo A&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>51.6</td>
<td>48.5</td>
<td>49.7</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.062</td>
<td>0.13</td>
<td>0.98</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.60</td>
<td>14.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.4</td>
<td>0.63</td>
<td>0.34</td>
</tr>
<tr>
<td>FeO&lt;sup&gt;total&lt;/sup&gt;</td>
<td>16.3</td>
<td>14.4</td>
<td>17.8</td>
</tr>
<tr>
<td>MnO</td>
<td>0.55</td>
<td>0.48</td>
<td>0.53</td>
</tr>
<tr>
<td>MgO</td>
<td>25.8</td>
<td>10.7</td>
<td>7.0</td>
</tr>
<tr>
<td>CaO</td>
<td>0.73</td>
<td>9.8</td>
<td>10.7</td>
</tr>
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<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.040</td>
<td>0.25</td>
<td>0.62</td>
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<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>0.012</td>
<td>0.066</td>
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<tr>
<td>Total</td>
<td>98.1</td>
<td>99.8</td>
<td>100.1</td>
</tr>
<tr>
<td>[M/Si]&lt;sub&gt;mol-b&lt;/sub&gt;</td>
<td>1.0</td>
<td>0.58</td>
<td>0.51</td>
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<tr>
<td>[Al/Si]&lt;sub&gt;mol-b&lt;/sub&gt;</td>
<td>0.014</td>
<td>0.36</td>
<td>0.29</td>
</tr>
<tr>
<td>[Ca/Si]&lt;sub&gt;mol-b&lt;/sub&gt;</td>
<td>0.015</td>
<td>0.22</td>
<td>0.23</td>
</tr>
</tbody>
</table>

<sup>a</sup>Data sources are in Table 1.

<sup>b</sup>Definitions are described in the text.
Geochemistry of Vesta based on HED meteorites

Eucrite Serra de Magé is rich in coarse-grained plagioclase with equant cumulate texture, resulting in high whole-rock Al content (Mittlefehldt et al. 1998). The basaltic eucrites Nuevo Laredo and Stannern have similar values of \( [\text{M}/\text{Si}]_{\text{mol}} \) and \( [\text{Al}/\text{Si}]_{\text{mol}} \) (Table 2; Fig. 3b inset) but are otherwise geochemically distinct. Previous studies showed that most basaltic eucrites were chemically classified into three types (the main group eucrites and eucrites of the Nuevo Laredo and Stannern trends), based on a plot of whole-rock data for Mg/(Mg + Fe) versus an incompatible element such as Ti (BVSP 1981; Stolper 1977). The Nuevo Laredo and Stannern trends are defined as extending from the main group composition toward Nuevo Laredo and Stannern, respectively, in this plot. While the Nuevo Laredo trend is characterized by increasing incompatible element abundances with decreasing Mg/(Mg + Fe), the Stannern trend has increasing incompatible element abundances with constant Mg/(Mg + Fe). Although the nature of the process governing these two trends remains controversial, both Nuevo Laredo and Stannern may represent the most differentiated rocks in the HED suite. Because Nuevo Laredo and Stannern have distinct chemical features, we propose two chemical endmember sets for the mixing model and examine which one can better explain the surface compositions of Vesta (discussed later). Using the three endmember components, we can delineate mixing lines in the \([\text{M}/\text{Si}]_{\text{mol}} \) versus \([\text{Al}/\text{Si}]_{\text{mol}} \) plot (Fig. 3) and thus obtain a unique value of a mixing ratio for GRaND data (see Appendix for the mathematical formulation). Because these four meteorites, used as endmember components, plot near the ends of the ranges of individual meteorite groups in Fig. 3 (and also in any other compositional diagram), most chemical compositions on the surface of Vesta could likely be explained by the mixing of the components Shalka, Serra de Magé, and either Nuevo Laredo or Stannern.

### ACCURACY AND PRECISION OF THE MIXING MODEL

Once a mixing ratio of three endmember components is determined by applying the mixing model to GRaND analysis, we can reconstruct the entire chemical composition of the analyzed area by multiplying chemical compositions of the three endmember components (Table 2) and the mixing ratio. However, the mixing model is based only on \([\text{M}/\text{Si}]_{\text{mol}} \) and \([\text{Al}/\text{Si}]_{\text{mol}} \) ratios, not on other elements. Moreover, the surface of Vesta may not consist only of materials having the same compositions as the three endmember components; for example, it may include basaltic eucrite with a composition similar to that of main group eucrites. Therefore, the reliability of the mixing model proposed in this study must be examined in terms of its accuracy and precision.

### Table 3. Accuracy and precision of the mixing calculations.

<table>
<thead>
<tr>
<th>Diff. wt%</th>
<th>Diogenite (( n = 9 )) Ave.</th>
<th>St. dev. (1σ)</th>
<th>Howardite (( n = 6 )) Ave.</th>
<th>St. dev. (1σ)</th>
<th>Eucrite (( n = 34 )) Ave.</th>
<th>St. dev. (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \text{SiO}_2 )</td>
<td>2.3</td>
<td>0.7</td>
<td>-0.39</td>
<td>0.71</td>
<td>0.07</td>
<td>0.44</td>
</tr>
<tr>
<td>( \Delta \text{TiO}_2 )</td>
<td>0.008</td>
<td>0.043</td>
<td>-0.11</td>
<td>0.04</td>
<td>-0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>( \Delta \text{Al}_2\text{O}_3 )</td>
<td>0.45</td>
<td>0.28</td>
<td>0.01</td>
<td>0.22</td>
<td>-0.04</td>
<td>0.18</td>
</tr>
<tr>
<td>( \Delta \text{Cr}_2\text{O}_3 )</td>
<td>1.4</td>
<td>0.3</td>
<td>0.61</td>
<td>0.20</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>( \Delta \text{FeO}^{\text{total}} )</td>
<td>-0.40</td>
<td>0.89</td>
<td>-1.4</td>
<td>0.6</td>
<td>0.18</td>
<td>0.85</td>
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<tr>
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<td>0.47</td>
<td>0.42</td>
<td>0.49</td>
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<td>-0.14</td>
<td>0.54</td>
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</tr>
<tr>
<td>( \Delta \text{Na}_2\text{O} )</td>
<td>0.061</td>
<td>0.014</td>
<td>-0.050</td>
<td>0.029</td>
<td>0.003</td>
<td>0.11</td>
</tr>
<tr>
<td>( \Delta \text{K}_2\text{O} )</td>
<td>0.002</td>
<td>0.007</td>
<td>-0.011</td>
<td>0.009</td>
<td>-0.006</td>
<td>0.013</td>
</tr>
<tr>
<td>( \Delta \text{Cr}_2\text{O}_3^{(\text{corr})} )</td>
<td>0.09</td>
<td>0.17</td>
<td>-0.16</td>
<td>0.14</td>
<td>0.004</td>
<td>0.063</td>
</tr>
</tbody>
</table>

**ACCURACY AND PRECISION OF THE MIXING MODEL**

Once a mixing ratio of three endmember components is determined by applying the mixing model to GRaND analysis, we can reconstruct the entire chemical composition of the analyzed area by multiplying chemical compositions of the three endmember components (Table 2) and the mixing ratio. However, the mixing model is based only on \([\text{M}/\text{Si}]_{\text{mol}} \) and \([\text{Al}/\text{Si}]_{\text{mol}} \) ratios, not on other elements. Moreover, the surface of Vesta may not consist only of materials having the same compositions as the three endmember components; for example, it may include basaltic eucrite with a composition similar to that of main group eucrites. Therefore, the reliability of the mixing model proposed in this study must be examined in terms of its accuracy and precision.
Fig. 4. Absolute differences between estimated and reference whole-rock elemental abundances (expressed as oxide wt%), based on the mixing model employing EM-I. Black diamonds show data for individual meteorites and open diamonds with error bars (standard deviation = 1σ) show the mean values of diogenites (n = 9), howardites (n = 6), and eucrites (n = 34). If the mixing calculation correctly estimates a whole-rock elemental abundance, the value must be zero within an error. The results are summarized in Table 3.
Fig. 4. Continued. Absolute differences between estimated and reference whole-rock elemental abundances (expressed as oxide wt%), based on the mixing model employing EM-I. Black diamonds show data for individual meteorites and open diamonds with error bars (standard deviation = 1σ) show the mean values of diogenites (n = 9), howardites (n = 6), and eucrites (n = 34). If the mixing calculation correctly estimates a whole-rock elemental abundance, the value must be zero within an error. The results are summarized in Table 3.
Fig. 5. Absolute differences between estimated and reference whole-rock elemental abundances (expressed as oxide wt%), based on the mixing model employing EM-II. Symbols are as in Fig. 4. The results are summarized in Table 3. The scale of ordinate axis and sample order are the same as in Fig. 4 for ease of comparison.
Fig. 5. Continued. Absolute differences between estimated and reference whole-rock elemental abundances (expressed as oxide wt%), based on the mixing model employing EM-II. Symbols are as in Fig. 4. The results are summarized in Table 3. The scale of ordinate axis and sample order are the same as in Fig. 4 for ease of comparison.
We will assess the accuracy and precision of the mixing model by assuming that HED meteorites not used as endmember components represent some portion of Vesta’s surface analyzed by GRaND. First, a mixing ratio for each HED meteorite is calculated by employing its [M/\text{Si}]_{\text{mod}} and [\text{Al}/\text{Si}]_{\text{mod}} ratios. Note that the mixing ratio should vary from 0 to 1 (see Appendix). However, some meteorites that plot outside of the mixing triangle (Fig. 3) have negative values. By considering that a goal of the Dawn mission is to measure elemental abundances with a precision \leq 20\% (Rayman et al. 2006), a negative mixing ratio is compensated as follows. If a meteorite sample yields a mixing ratio smaller than \(-0.2\), this sample is omitted and not employed for calculating the mean value. If a sample has a mixing ratio ranging from \(-0.2\) to 0, the ratio is converted to 0 and the other two ratios are normalized so that their summation should be 1. Second, a whole-rock composition of each meteorite (as wt\% oxides) is calculated for the major elements (SiO\(_2\), Al\(_2\)O\(_3\), FeO\(_{\text{total}}\), MgO, and CaO) and minor elements (TiO\(_2\) and K\(_2\)O) analyzed by GRaND. We also include several oxides not analyzed by GRaND (Cr\(_2\)O\(_3\), MnO, and Na\(_2\)O) in this step, and will consider the reliabilities of their estimates in a later section. A comparison of the modeled whole-rock composition with its reference value in the literature yields an uncertainty involved in the mixing model. When these procedures are performed on all HED meteorites, we obtain a mean value and variability for each meteorite class, diogenite, diogenite, and howardite (Table 3). Accuracy is expressed as the difference between the mean value and the reference value, and precision is expressed as the variability of investigated samples for each meteorite suite.

Figure 4 shows absolute differences between calculated and reference whole-rock compositions by employing EM-I. This mixing model adequately estimates most surface elemental compositions for all three meteorite classes: diogenite, howardite, and eucrite. For example, the mean difference value in CaO contents (wt\%, hereafter referred as \(\Delta\text{CaO}\)) for eucrites is \(-0.28 \pm 0.36\) wt\% (Table 3). This indicates that for an actual whole-rock CaO content of 10.00 wt\% (appropriate for a eucrite), the mixing model yields a CaO content of 9.72 \pm 0.36 wt\%, which is identical within error to the actual value of 10.00 wt\%. Some elements estimated by the mixing model do show some scatter (e.g., SiO\(_2\) and MgO in diogenites). However, Si and Mg are abundant elements in diogenites (\(>50\) wt\% for SiO\(_2\) and \(>20\) wt\% for MgO), so the observed discrepancies in modeled oxide abundances (Fig. 4) would not be crucial. One element for which the mixing model produces large errors is Cr (Figs. 4d and 5d). Cr\(_2\)O\(_3\) contents are systematically overestimated in some eucrites, all howardites, and especially in diogenites. This may be explained as an effect of variations in the abundance of chromite (the principal host for Cr), which is apparently not adequately addressed by the endmembers in the mixing model. Because Cr occurs as a minor element in HED meteorites, the discrepancy between the calculated and reference values (e.g., 1.4 \pm 0.3 wt\% for diogenite) constitutes a fatal error for the estimation of Cr content. For example, if the actual whole-rock Cr\(_2\)O\(_3\) content of a diogenite is 1.0 wt\%, the mixing model yields a Cr\(_2\)O\(_3\) content of 2.4 \pm 0.3 wt\%, which is more than twice the actual amount. An empirical correction for Cr is discussed below.

Reliability of the mixing model employing EM-II is assessed in Fig. 5. The data points in Fig. 5 are more scattered than those in Fig. 4; standard deviations of EM-I and EM-II values for diogenite are 0.043 and 0.068 for \(\Delta\text{TiO}_2\), respectively; 0.28 and 0.37 for \(\Delta\text{Al}_2\text{O}_3\); 0.89 and 1.1 for \(\Delta\text{FeO}_{\text{total}}\); 0.054 and 0.061 for \(\Delta\text{MnO}\); 0.28 and 0.31 for \(\Delta\text{CaO}\); and 0.014 and 0.033 for \(\Delta\text{Na}_2\text{O}\) (Table 3). Furthermore, EM-II is more likely than EM-I to underestimate FeO\(_{\text{total}}\) content for howardites and eucrites. These observations indicate that EM-II is less reliable than EM-I.

It should be noted that the samples employed as the endmember components do not necessarily represent their meteorite suites; Nuevo Laredo, for example, is exceptionally rich in incompatible elements compared to the main group eucrites that dominate the basaltic eucrite suite. The endmember set is chosen only mathematically so that the mixing model predicts the surface elemental compositions as accurately and precisely as possible, and so that it covers as broad a compositional range as possible. Moreover, because the mixing model is proposed by a conclusively unproven hypothesis that the surface of Vesta is analogous to HED meteorites, the reliability of the mixing model must be further assessed based on comprehensive data sets from other onboard instruments such as framing camera (FC) and visible and infrared mapping spectrometer (VIR).

ESTIMATION OF ELEMENTS NOT ANALYZED BY GRaND

The elements that can be analyzed by GRaND are limited (Prettyman et al. 2003). The mixing model can theoretically estimate not only major elements but also minor and trace elements such as Ni, Cr, Mn, P, rare earth elements, and others, if they are given by the three endmember components and a sufficient HED database exists. Here we demonstrate the reliability of estimating the abundances of the minor elements Na, Mn, and Cr in HED meteorites, which will not be analyzed by the Dawn mission. Estimation of these elements is carried out by employing EM-I. As is seen in Fig. 4f and Table 3, \(\Delta\text{MnO}\) values for three meteorite types are equal to zero within errors, and these errors (0.054 for diogenite, 0.020 for howardite, and 0.033 for eucrite) are more than ten times smaller than typical MnO content in these meteorites (\(\sim 0.5\) wt\%). This suggests that the mixing model can estimate MnO contents of Vesta’s surface materials with relative error of <10\%. \(\Delta\text{Na}_2\text{O}\) values (Fig. 4i; Table 3) are
also considered to be zero within errors, although that of 
Na$_2$O content can be adequately estimated. However, 
contributions of these errors to the estimation of Na are larger 
than those for Mn, considering the low Na$_2$O contents of HED 
meteorites (<0.1 wt% for diogenite, ~0.2 wt% for howardite, 
~0.4 wt% for eucrite) (Mittlefehldt et al. 1998).

$\Delta$Cr$_2$O$_3$ obviously has positive values (Table 3), 
suggesting that the mixing model must be modified to 
correct its discrepancy. $\Delta$Cr$_2$O$_3$ values are evidently 
correlated with meteorite types, from high $\Delta$Cr$_2$O$_3$ in 
diogenite to moderate in howardite and low in eucrite 
(Fig. 4d). This relationship is best explained by a Cr versus 
[M/Si]$_{\text{mol}}$ plot (Fig. 6). This figure shows a strong positive 
correlation between Cr and [M/Si]$_{\text{mol}}$, from which we obtain 
the regression equation:

$$\Delta Cr = 0.035 \times [M/\text{Si}]_{\text{mol}} - 0.018$$  \hspace{1cm} (1)$$

where $\Delta$Cr is difference in molar abundance of Cr between the 
reference and calculated values. The Cr$_2$O$_3$ content can be 
corrected as follows:

$$\text{Cr}_2\text{O}_3(\text{corr}) = \text{Cr}_2\text{O}_3(\text{cal}) - \frac{\Delta \text{Cr} \times M}{2}$$  \hspace{1cm} (2)$$

where $\text{Cr}_2\text{O}_3(\text{cal})$ and $\text{Cr}_2\text{O}_3(\text{corr})$ are the initially calculated 
$\text{Cr}_2\text{O}_3$ concentration (wt%) by the mixing model and its 
corrected value, respectively, and M is molecular weight of 
$\text{Cr}_2\text{O}_3$. Using this correction, $\Delta$Cr$_2$O$_3$ values are significantly 
suppressed from 1.4 ± 0.3 to 0.09 ± 0.17 for diogenite, 0.61 ± 
0.20 to −0.16 ± 0.14 for howardite, and 0.18 ± 0.20 to 0.004 ± 
0.063 for eucrite (Table 3; Fig. 7). These values are 
sufficiently accurate for estimating the Cr concentration of 
Vesta’s surface materials.

**ESTIMATION OF MODAL OLIVINE ABUNDANCE**

Vesta has experienced significant impact events, one of 
which excavated a huge crater (460 km in diameter and 
13 km in depth) near its south pole (Thomas et al. 1997). 
Spectral variations within this large crater demonstrate 
compositional stratigraphy, probably reflecting a high-Ca 
pyroxene-rich plutonic assemblage deep within the crust 
and/or the exposure of olivine present within the upper 
mantle (Thomas et al. 1997). Models of a differentiated 
asteroid support the idea of an olivine-rich mantle (e.g., 
Jones 1984). However, these studies appear to be 
inconsistent with the fact that few olivine-bearing meteorites 
occur in the HED suite (e.g., Mittlefehldt et al. 1998). Most 
telescopic observations have been limited to the equatorial 
regions of Vesta (e.g., Binzel et al. 1997; Gaffey 1997), so 
the possibility that other olivine-bearing units are exposed in 
smaller craters or as volcanic flows on the asteroid’s surface 
cannot be ruled out.

In this section, we demonstrate that it is possible to 
estimate the abundance of olivine from elemental data 
obtained by GRaND. Similar to the previously 
described mixing model, a molar element ratio plot is used. 
An [M/Si]$_{\text{mol}}$ versus [Ca/Si]$_{\text{mol}}$ plot (Fig. 8) yields an 
approximately linear trend for HED meteorites, unlike the 
[M/Si]$_{\text{mol}}$ versus [Al/Si]$_{\text{mol}}$ plot (cf. Fig. 3). This linearity may 
be due to the presence of high-Ca pyroxene. Since 
high-Ca pyroxene does not affect [Al/Si]$_{\text{mol}}$ but does affect 
[Ca/Si]$_{\text{mol}}$, it obscures differences in the modal abundance of 
plagioclase in the HED classes. Because the [M/Si]$_{\text{mol}}$ versus 
[Ca/Si]$_{\text{mol}}$ plot discriminates two rather than three 
endmember components, it can be used to estimate a third, 
olivine, which plots off the linear HED trend. From the [M/
Si$_{\text{mol}}$/[Ca/Si]$_{\text{mol}}$ plot (Fig. 8), the following regression equation is obtained:

$$\text{[M/Si]$_{\text{mol}}$} = -2.4 \times \text{[Ca/Si]$_{\text{mol}}$} + 1.1 \quad (3)$$

If olivine is present in units exposed on the surface of Vesta, the GRaND [M/Si]$_{\text{mol}}$ and [Ca/Si]$_{\text{mol}}$ values for these units should plot above this regression line in Fig. 8. To evaluate the contribution of olivine to HED meteorites, we propose two endmember components from EM-I: Shalka as the diogenite and Nuevo Laredo as eucrite. The [Ca/Si]$_{\text{mol}}$ values of the diogenite and eucrite endmember components are given in Table 2, and their [M/Si]$_{\text{mol}}$ values are derived by substitution of their [Ca/Si]$_{\text{mol}}$ values into Equation 3 so that these endmember components plot exactly on the regression line. The olivine component in Fig. 8 is represented by the composition of the forsterite-fayalite solid solution (Mg,Fe)$_2$SiO$_4$, resulting in [M/Si]$_{\text{mol}} = 2$ and [Ca/Si]$_{\text{mol}} = 0$. To estimate the proportions of these three endmembers, linear mixing lines are delineated (Fig. 8). Although olivine is generally absent from HED meteorites, some recently recovered northern African olivine diogenites contain >40 vol% olivine (Irving et al. 2005, 2003). To evaluate the olivine mixing model, the whole-rock compositions of NWA 1459, ALHA77256, and EETA79002 (Irving et al. 2003; Sack et al. 1991; Takeda 1979) are plotted in Fig. 8. We also calculated the CIPW norms for these compositions and recalculated the normative proportion of olivine as mol% for comparison. NWA 1459, ALHA77256, and EETA79002 have 42 mol%, 17 mol%, and 18 mol% of normative olivine, respectively. These values are consistent with the estimation of the mixing model.

In addition to GRaND, the Dawn spacecraft is equipped with a VIR, which can identify some minerals on Vesta with higher spatial resolution than that of GRaND (Russell et al. 2004). In particular, diagnostic absorption bands for olivine and pyroxenes occur in the visible and near-infrared regions. Experiments by Cloutis et al. (1986) showed that the ratio of the area of an absorption band near 2 $\mu$m (band II) relative to the area of an absorption band near 1 $\mu$m (band I) has a strong linear correlation with the abundance ratio of olivine to orthopyroxene. The abundance of olivine also shows a correlation with [M/Si]$_{\text{mol}}$ measured by GRaND. Thus, data from GRaND and VIR complement each other, and combining these comprehensive data sets can strengthen mineralogical interpretations and yield new insights into mapped surface lithologies on Vesta.

CONCLUSIONS

We propose a quantitative mixing model for geochemical data of asteroid 4 Vesta to be obtained by the GRaND
spectrometer on the Dawn asteroid orbiter, based on the chemical compositions of HED meteorites. As inferred from telescopic spectra, the surface of Vesta mainly consists of polymict rocks that are mixtures of diogenites and basaltic and cumulate eucrites. The spatial resolution of GRaND analyses dictates that they will almost certainly reflect mixtures of these three rock types. We have employed a two-dimensional element ratio plot (molar ratio of (Mg + Fe)/Si versus Al/Si) to resolve and model the three endmember components. Because these element ratios amplify the difference in modal abundances of plagioclase and low- and high-Ca pyroxene (the major phases in HED meteorites), this plot discriminates the three prospective endmember lithologies, diogenite, basaltic, and cumulate eucrites.

To evaluate the contribution of the three rock types to GRaND spectra, we proposed two endmember sets (EM-I and EM-II). EM-I consists of Shalka, Serra de Magé, and Nuevo Laredo as endmembers representing diogenite, cumulate eucrite, and basaltic eucrite, respectively. EM-II substitutes Stannern for Nuevo Laredo as the basaltic eucrite endmember component. Because these endmember meteorites plot near the ends of the ranges of HED classes in the [M/Si]_mol versus [Al/Si]_mol plot, most chemical compositions of the surface of Vesta could likely be explained by the simple mixing of these three components.

Once a mixing ratio of three end-components is determined for an HED meteorite, its whole-rock composition can be estimated from the compositions of the endmembers. By comparing the estimated whole-rock data for all the HED meteorites with their published chemical analyses, the reliability of the mixing model was investigated. The mixing model employing EM-I more accurately and precisely estimates HED compositions than that employing EM-II. Furthermore, assuming the HED meteorites used in this study are fully representative of Vesta’s surface, we demonstrated that the mixing model can be used to estimate elements that will not be analyzed by GRaND, such as Na, Mn, and Cr, although estimation of Cr requires an empirical correction because variations in chromite abundance are apparently not adequately addressed by the endmembers in the mixing model.

Telescopic observations and theoretical models of Vesta suggest an olivine-rich mantle or lower crust, but olivine is absent or occurs only as a minor constituent mineral in most HED meteorites. We also propose another mixing model employing GRaND data, by which we can estimate the modal abundance of olivine in HED meteorites and thus surface units on Vesta. GRaND-derived mineral abundances will complement data from other Dawn spectrometers.

This study provides a way to leverage the large geochemical and mineralogical database on HED meteorites as a tool for interpreting chemical analyses by GRaND of mapped units on the surface of Vesta. We expect that the new data sets to be provided by Dawn will constrain the geologic context for HED meteorites and provide significant new insights into the structure and igneous evolution of one of the few surviving protoplanets in the solar system.

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REFERENCES


APPENDIX

Here we present a general method for calculating a mixing ratio based on a three-component mixing model that uses a two-dimensional ratio-ratio plot (Fig. A1). We assume that component $C_m$ is obtained by mixing three endmember components, $C_1$, $C_2$, and $C_3$ with a mixing ratio of $c_1$, $c_2$, and $c_3$, which satisfy the equation:

$$c_1 + c_2 + c_3 = 1$$

(A1)

Symbols used are: $x$, $y$ = general variables along the abscissa and ordinate, respectively; $x_i$, $y_i$ = coordinates of data point $C_i$ (note that subscript $i$ is for all three endmember components, $C_1$, $C_2$, and $C_3$); $n_{xi}$, $n_{yi}$ = numerator of $x_i$ and $y_i$; $d_{xi}$, $d_{yi}$ = denominator of $x_i$ and $y_i$; $y_{xm}$, $y_{yn}$ = coordinates of data point $C_m$, $x_m$ and $y_m$ are given by measurements (e.g., HED analyses or a GRaND analysis). Simple mass balance calculation gives the following equations:

$$x_m = \sum_{i=1}^{3} c_i n_{xi} / \sum_{i=1}^{3} c_i d_{xi}$$

$$y_m = \sum_{i=1}^{3} c_i n_{yi} / \sum_{i=1}^{3} c_i d_{yi}$$
From Equations A1 and A2, we obtain the matrix product:

\[
\begin{bmatrix}
X_1 & X_2 & X_3 \\
Y_1 & Y_2 & Y_3 \\
1 & 1 & 1
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
c_3
\end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}
\]

(A3)

where \(X_i = x_m d_{xi} - n_{xi}\) and \(Y_i = y_m d_{yi} - n_{yi}\).

Solving Equation A3, we obtain the mixing ratios \(c_1, c_2,\) and \(c_3\) as follows:

\[
c_1 = \frac{\alpha}{\alpha + \beta + \gamma}
\]

\[
c_2 = \frac{\beta}{\alpha + \beta + \gamma}
\]

\[
c_3 = \frac{\gamma}{\alpha + \beta + \gamma}
\]

(A4)

where

\[
\alpha = Y_2 X_3 - X_2 Y_3
\]

\[
\beta = Y_3 X_1 - X_3 Y_1
\]

\[
\gamma = X_2 Y_1 - Y_2 X_1
\]

(A5)

This formulation explains how to calculate the plot of any two element ratios. For example, to construct Fig. 3, \(x\) and \(y\) correspond to the molar abundance ratios of \((\text{Mg} + \text{Fe})/\text{Si}\) and \(\text{Al}/\text{Si}\), respectively. \(n_{xi}\) and \(n_{yi}\) are the molar abundances of \(\text{Al}\) and \((\text{Mg} + \text{Fe})\), and both \(d_{xi}\) and \(d_{yi}\) represent the molar abundances of \(\text{Si}\).