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Geochemistry and Sm–Nd chronology of a Stannern-group eucrite, Northwest Africa 7188

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Abstract

We report the results of a detailed study of the basaltic eucrite Northwest Africa (NWA) 7188, including its mineralogical and bulk geochemical characteristics, oxygen isotopic composition, and $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ mineral isochron ages. The texture and chemical composition of pyroxene and plagioclase demonstrate that NWA 7188 is a monomict eucrite with a metamorphic grade of type 4. The oxygen isotopic composition and the Fe/Mn ratios of pyroxene confirmed that NWA 7188 belongs to the howardite-eucrite-diogenite meteorite suite, generally considered to originate from asteroid 4 Vesta. Whole-rock TiO_2 , La, and Hf concentrations and a CI chondrite-normalized rare earth element pattern are in good agreement with those of representative Stannern-group eucrites. The $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ isochrons for NWA 7188 yielded ages of 4582 ± 190 and 4554^{+17}_{-19} Ma, respectively. The closure temperature of the Sm–Nd system for different fractions of NWA 7188 was estimated to be >865 °C, suggesting that the Sm–Nd decay system has either been resistant to reheating at ~ 800 °C during the global metamorphism or only partially reset. Therefore, the ^{146}Sm – ^{142}Nd age of NWA 7188 corresponds to the period of initial crystallization of basaltic magmas and/or global metamorphism on the parent body, and is unlikely to reflect Sm–Nd disturbance by late reheating and impact events. In either case, NWA 7188 is a rare Stannern-group eucrite that preserves the chronological information regarding the initial crustal evolution of Vesta.

1 INTRODUCTION

2 Eucrites are differentiated achondrites and belong to the howardite–eucrite–
 3 diogenite (HED) suite of meteorites that most likely originated from the crust of asteroid
 4 4 Vesta (McCord et al. 1970; Consolmagno and Drake 1977; Binzel and Xu 1993; Drake
 5 2001; McSween et al. 2011, 2013; Mittlefehldt 2015). The linkage between the HED
 6 meteorites and Vesta was originally proposed in the 1970s (e.g., McCord et al. 1970)
 7 based on similarities between laboratory and astronomically observed visible and near-
 8 infrared spectra. The linkage between the HEDs and Vesta obtained additional support as
 9 a result of lithological mapping of Vesta’s surface using the visible and infrared mapping
 10 spectrometer on board NASA’s Dawn spacecraft (De Sanctis et al. 2012). From an orbital
 11 dynamics perspective, it is difficult for the fragments ejected from Vesta in the main belt
 12 to come to Earth through Jovian or secular resonances directly. However, Vestoids—
 13 which are small asteroids (< 10 km) believed to have originated from Vesta based on
 14 Vesta-like spectra—could solve this problem by expanding the area from which
 15 fragments of Vesta can be ejected to Earth (McSween et al. 2011).

16 Vesta is generally thought to have experienced large-scale melting that led to core–
 17 mantle segregation and silicate differentiation (Schiller et al. 2011). This probably
 18 occurred a few million years (Myr) after Solar System formation, based on the evidence
 19 from chronometers using short-lived radionuclides, such as ^{26}Al ($t_{1/2} = 0.7$ Myr), ^{53}Mn
 20 ($t_{1/2} = 3.7$ Myr), and ^{182}Hf ($t_{1/2} = 9$ Myr). The ^{182}Hf – ^{182}W ages of eucrites and diogenites
 21 suggest that metal segregation on Vesta occurred ~ 1 – 4 Myr after the formation of calcium
 22 and aluminum-rich inclusions (CAIs) (Kleine et al. 2004, 2009; Quitté and Brick 2004;
 23 Touboul et al. 2015). In contrast, the ^{53}Mn – ^{53}Cr and ^{26}Al – ^{26}Mg whole-rock isochron ages
 24 of eucrites and diogenites suggest that global silicate mantle differentiation continued for
 25 approximately 2–10 Myr after CAI formation (Lugmair and Shukolyukov 1998; Bizzarro
 26 et al. 2005; Trinquier et al. 2008). Although analytical uncertainties are large, the ^{147}Sm –
 27 ^{143}Nd and ^{176}Lu – ^{176}Hf whole-rock isochron ages of eucrites (4587 ± 150 and 4532 ± 170
 28 Ma, respectively), both of which most likely indicate the timing of crust formation, are
 29 consistent with each other (Bouvier et al. 2015). The sequential processes of partial (15–
 30 20%) or total melting and differentiation homogenized the oxygen isotope compositions
 31 among HED meteorites (Greenwood et al. 2005, 2017). In addition, the Fe/Mn ratios in
 32 pyroxene are relatively uniform among basaltic eucrites ($\text{Fe/Mn} = 30 \pm 2$), because Fe
 33 and Mn do not fractionate during the magmatic process (Mittlefehldt et al. 1998; Papike
 34 1998; Papike et al. 2003).

35 Eucrites mainly consist of pyroxene and plagioclase and are petrographically
 36 classified into basaltic and cumulate eucrites. Basaltic eucrites are composed of pigeonite

37 and plagioclase with a subophitic texture, indicating that they crystallized near the surface.
 38 In contrast, cumulate eucrites—which are composed of orthopyroxene and plagioclase—
 39 have a gabbroic texture and are therefore considered to have crystallized more slowly,
 40 from a residual melt, almost certainly at a deeper level in Vesta than the basaltic eucrites
 41 (McSween et al. 2011). Based on the whole-rock Mg/(Mg + Fe) molar ratio and the
 42 incompatible element concentrations, basaltic eucrites are further classified into four
 43 distinct chemical groups: main group, Nuevo Laredo-group, Stannern-group, and residual
 44 eucrites (BVSP 1981; Warren and Jerde 1987; Yamaguchi et al. 2009). The Nuevo
 45 Laredo-group eucrites are characterized by lower Mg/(Mg + Fe) ratios than those of the
 46 main-group and Stannern-group eucrites (Mittlefehldt 2015). On the other hand, the
 47 Stannern-group eucrites are characterized by having higher Ti and incompatible element
 48 concentrations than those of the combined main-group–Nuevo Laredo-group eucrites. In
 49 CI chondrite-normalized rare earth element (REE) diagrams, the Stannern-group eucrites
 50 show variable yet nearly parallel REE patterns with distinctive negative Eu anomalies
 51 (Eu/Eu^* ; $\text{Eu}^* = \frac{\text{Sm}_{\text{CI chondrite-normalized}} + \text{Gd}_{\text{CI chondrite-normalized}}}{2}$), where the abundance
 52 of La ranges from 17 to $28 \times \text{CI}$ (Shimizu and Masuda 1986; Barrat et al. 2007). The
 53 residual eucrites (e.g., Dar al Gani 945), which most likely represent a complement to the
 54 Stannern-group eucrites, are characterized by depletions in light-REEs (LREEs; La–Sm)
 55 relative to heavy-REEs (HREEs; Gd–Lu) coupled with positive Eu anomalies in the CI
 56 chondrite-normalized REE patterns (Yamaguchi et al. 2009). This compositional
 57 diversity amongst eucrites provides an important clue to understanding the igneous
 58 differentiation processes on Vesta. In addition to the above-mentioned geochemical
 59 classification, nearly all of the basaltic eucrites are classified into one of seven
 60 metamorphic grades (types 1–7) on the basis of pyroxene petrographic and compositional
 61 criteria (Takeda and Graham 1991; Yamaguchi et al. 1996). The Stannern-group eucrites
 62 commonly have metamorphic grades of types 1–4, indicative of very low to moderate
 63 metamorphism, whereas most of the main-group eucrites are classified as types 5–7
 64 because they are highly metamorphosed with peak temperatures of $\sim 1000^\circ\text{C}$ (Takeda and
 65 Graham 1991).

66 Most recently, the desert meteorite Northwest Africa (NWA) 7188, which had been
 67 simply categorized as a basaltic eucrite (Ruzicka et al. 2015), was found to be a new
 68 member of monomict Stannern-group eucrites (Kagami et al. 2017, 2018). In addition,
 69 petrological observations revealed that NWA 7188 had a very low shock stage and a low
 70 degree of terrestrial weathering, making it a suitable specimen to investigate in detail the
 71 origin of the Stannern-group eucrites. In this study, we have conducted detailed

72 geochemical analyses of NWA 7188, including major and trace element abundances,
73 oxygen isotope measurements of the bulk rock, mineralogical analysis, as well as
74 determining $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ isochron ages for mineral separates. Sm–Nd systematics
75 have a number of advantages for eucrite dating: 1) Sm and Nd are REEs that are not
76 significantly fractionated from each other during secondary alteration, and 2) the Sm–Nd
77 systematics are not easily reset by thermal metamorphism compared to the U–Pb, ^{87}Rb –
78 ^{87}Sr , and ^{39}Ar – ^{40}Ar systems (Bogard and Garrison 2003). The goal of this study was to
79 understand the petrogenesis of NWA 7188 in order to provide crucial constraints on the
80 thermal evolution of the Stannern-group eucrites on Vesta.

81 **SAMPLES**

82 NWA 7188 is a hot desert meteorite found in 2011, with a total mass of ~455 g. It
83 was originally classified as a basaltic eucrite based on petrological observations and
84 mineralogical data. NWA 7188 consists of exsolved pigeonite, calcic plagioclase, silica
85 polymorphs, ilmenite, and troilite (Ruzicka et al. 2015). The pyroxenes have
86 clinopyroxene lamellae with an FeO/MnO ratio of 32 within a low-Ca pyroxene host with
87 an FeO/MnO ratio of 33–35.

88 In this study, we investigated three commercially sourced specimens of NWA 7188,
89 which were named specimens A (6.9 g), B (24.8 g), and C (79.8 g). The fusion crust
90 covering the surface of specimens B and C was carefully removed using a micro-drill
91 equipped with a ceramic grinding stone. In addition, the brown altered part near the rim
92 of these specimens was discarded. Because the three specimens had a similar texture,
93 specimen A was used for textural and mineralogical observations and O isotope analyses,
94 while specimens B and C were used for chemical and Nd isotope analyses.

ANALYTICAL METHODS

Figure S1 shows a flowchart for the experimental work conducted as part of this study. Although NWA 7188 has two distinct textures, we used sample batches that included both lithologies for the analyses of bulk chemical composition, isotopic systematics and Sm–Nd isochron studies. It is reasonable to include both textural types because we have been able to confirm that they are co-genetic (see the Petrology and Mineral Chemistry in Results section). The procedures used for individual experiments are described in detail below.

Textual and Mineralogical Observations

Specimen A was mounted in an epoxy resin disk and polished with 3, 1, and 1/4 μm diamond paste to make a thick section (Fig. S1). The polished thick section was examined using a scanning electron microprobe (SEM; S-3400N, Hitachi High-Technologies, Japan) instrument equipped with an energy dispersive spectrometer (EDS) at the Tokyo Institute of Technology (Tokyo Tech). Elemental mapping of Al, Ca, Fe, Mg, P, Si, Ti, and Zr was undertaken using the SEM-EDS to identify major minerals such as plagioclase and pyroxene. In addition, a field-emission-type electron microprobe analyzer (FE-EPMA; JXA-8530F, JEOL, Japan) installed at Tokyo Tech was used to obtain the elemental maps for Zr, Ca, Ti, and Fe with an accelerating voltage of 15 kV and a beam current of 30 nA in order to find zircon and ilmenite minerals. The chemical compositions of pyroxene and plagioclase were also measured by employing FE-EPMA analyses with an accelerating voltage of 15 kV, a beam current of 10 nA, and an analytical beam spot of 2–3 μm . The following samples supplied from JEOL were used as standards of FE-EPMA analyses: SiO_2 for Si, TiO_2 for Ti, Al_2O_3 for Al, Fe_2O_3 for Fe, MnO, for Mn, MgO for Mg, CaSiO_3 for Ca, $\text{NaAlSi}_3\text{O}_8$ for Na, and KAlSi_3O_8 for K. The modal abundance of major mineral phases in NWA 7188 was determined using image analysis software (JMicroVision, Switzerland; Roduit 2008). Elemental maps for Fe, Si, Al, and Mg were combined and divided into quarters. We counted ca. 330 points per image, with a size of 5120 pixels \times 2577 pixels (1.1 cm \times 5.6 cm).

Sm–Nd Dating

For the application of Sm–Nd radiometric dating, specimens B and C-1 were crushed and sieved into four fractions: G1) 250–500 μm , G2) 106–250 μm , G3) 45–106 μm , and G4) <45 μm (Fig. S1). The fractions G2–G4 were separated into magnetic and non-magnetic mineral fractions with a neodymium magnet. Then, grains of pyroxene and plagioclase were handpicked from the magnetic and non-magnetic fractions of G2,

131 respectively. All of these samples were cleaned with distilled acetone and Milli-Q water
132 and then powdered using an agate mortar and pestle.

133 The chemical procedures for Sm–Nd dating are described in detail elsewhere
134 (Yokoyama et al. 1999; Kagami and Yokoyama 2016; Fukai et al. 2017), here we give an
135 outline summary of the methodology followed in this study. The powdered sample of G1
136 was weighed in a polytetrafluoroethylene (PTFE) insert (50 mL volume) of a high-
137 pressure digestion system, DAB-2 (Berghof, Germany), together with 30 M HF (AAS
138 grade with distillation, Kanto Chemical, Japan) and 16 M HNO₃ (EL grade, Mitsubishi
139 Chemical, Japan). The sample was dissolved in the digestion system at 225 °C for 48 h
140 to ensure complete dissolution of refractory minerals such as zircons. After the sample
141 dissolution, 12 M HClO₄ (AA–100 grade, TAMA Chemicals, Japan) was added to the
142 sample solution. In contrast, the powdered samples of the G2–G4 fractions were weighed
143 into PTFE vessels (7 mL) together with 30 M HF, 16 M HNO₃, and 12 M HClO₄. The
144 sample solutions of the G1–G4 fractions containing HF, HNO₃, and HClO₄ were
145 subsequently heated in a stepwise fashion at 120 °C for 12 h, 165 °C for 16 h, and 195 °C
146 until dryness. Next, the sample was re-dissolved in 12 M HClO₄ and treated in the same
147 manner as described above to suppress the formation of insoluble fluorides. The dried
148 sample was dissolved with 6 M HCl (EL grade, Mitsubishi Chemical, Japan), which was
149 then dried at 120 °C. The sample was finally dissolved in 1 M HCl.

150 For the determination of Sm/Nd ratios of individual fractions, a ~10% aliquot of the
151 sample solution was accurately weighed in a clean Teflon vessel and mixed with the
152 ¹⁴⁵Nd- and ¹⁴⁹Sm-enriched spike solutions. After the removal of potential interfering
153 elements by passing the sample solution through an extraction chromatographic resin
154 TRU (50–100 μm; Eichrom, USA), the Nd and Sm concentrations were determined by
155 the isotope dilution (ID) method using a quadrupole type ICP-MS instrument (X-Series
156 2, Thermo Fisher Scientific, USA) installed at Tokyo Tech (Kagami and Yokoyama 2016).

157 The remaining ~90% of the sample solution was used for high-precision Nd isotope
158 measurements by thermal ionization mass spectrometry at Tokyo Tech (TIMS; Triton *plus*,
159 Thermo Fisher Scientific, USA). Prior isotopic analysis, a three-step column chemistry
160 procedure utilizing a cation exchange resin and an extraction chromatographic resin (Ln
161 Resin, Eichrom, USA) was undertaken to purify Nd (Kagami and Yokoyama 2016).
162 Subsequently, the ¹⁴²Nd/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd ratios were determined using a dynamic
163 multi-collection method with a two-jump cup configuration in a single measurement
164 (Fukai et al. 2017). The instrumental mass fractionation was corrected by the exponential
165 law and normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and ¹⁴⁶Nd/¹⁴⁵Nd = 2.072016 (Boyet and
166 Carlson, 2005) for ¹⁴²Nd/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd, respectively. The reproducibility of the

167 $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for the standard, JNdi-1 (500 ng), were 6.5 ppm and
168 5.2 ppm (2SD), respectively. The $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured on JNdi-
169 1 during sample measurements in this study are equal to 1.141837 ± 7 and 0.512102 ± 3 ,
170 respectively. The total procedural blank for Nd (~ 36 pg) was negligible compared with
171 the amount of Nd used in a single isotopic measurement (> 100 ng). Sm–Nd ages were
172 calculated using Isoplot 3.6 (Ludwig 2009).

173

174 **Determination of Major and Trace Element Abundances**

175 The bulk chemical compositions of five major elements (Mg, Ca, Fe, Ti, and Mn)
176 and twenty-six trace elements (Rb, Sr, Zr, Nb, Y, Cs, Ba, lanthanoids, Hf, Ta, Pb, Th, and
177 U) for NWA 7188 were determined by using powdered samples from specimens C-2-1
178 and C-2-2 (Fig. S1). These specimens were cleaned with distilled acetone and Milli-Q
179 water and then powdered using an agate mortar and pestle. Subsequently, C-2-2 was
180 cleaned with distilled acetone and Milli-Q water once again. In addition to NWA 7188,
181 we prepared a reference rock material BHVO-2 (Basalt, USGS, USA) for evaluating the
182 accuracy of the analyses.

183 Approximately 50 mg of the powdered sample was weighed in a PTFE insert of
184 DAB-2 together with two types of mixed-spike solutions (^{113}In – ^{203}Tl and ^{91}Zr – ^{179}Hf) and
185 a ^{49}Ti spike solution. Subsequently, 0.2 mL Al solution (~ 10000 $\mu\text{g/g}$, Agilent
186 Technologies, USA) was added to achieve full recoveries of HFSEs (Tanaka et al. 2003).
187 The sample was dissolved with 30 M HF in the pressure digestion system at 225 °C for
188 48 h. After the dissolution, the sample solution was dried and dissolved with 5 mL 0.5 M
189 HF. The sample solution, containing insoluble fluorides, was thoroughly shaken and
190 homogenized using an ultrasonic bath until it became a milky suspended solution without
191 visible precipitates. Immediately after the homogenization, an $\sim 5\%$ aliquot of the
192 suspended solution was transferred to a polypropylene tube and centrifuged. The
193 supernatant liquid was diluted with 0.5 M HF and used for the measurement of high field
194 strength elements (HFSEs; Ti, Zr, Nb, Hf, and Ta) using ICP-MS by the ID method for
195 Ti, Zr, and Hf and by the calibration curve method for Nb and Ta. We used a custom-
196 made mix standard solution (Cat. No. XSTC-3493-100, SPEX CertiPrep, USA)
197 containing HFSEs in 1.7% HF (Ti: 4964 ± 30 $\mu\text{g/g}$, Zr: 98.8 ± 0.5 $\mu\text{g/g}$, Nb: 9.86 ± 0.05
198 $\mu\text{g/g}$, Hf: 2.96 ± 0.06 $\mu\text{g/g}$, Ta: 1.00 ± 0.02 $\mu\text{g/g}$) for the standard material. Typical
199 analytical reproducibility for HFSEs was less than 2% (2SD).

200 For the determination of major and trace elements, excluding HFSEs, the remainder
201 of the suspended sample solution was transferred to a Teflon vessel with the addition of
202 12 M HClO_4 and 16 M HNO_3 , which was heated in a stepwise fashion (120 °C for 12 h,

203 165 °C for 16 h, and 195 °C until dryness). This procedure was repeated twice to suppress
 204 the formation of insoluble fluorides. After the treatment with 6 M HCl, the sample was
 205 diluted with 0.5 M HNO₃ to measure major and trace elements, excluding HFSEs, by
 206 ICP-MS. The concentrations of major and trace elements, excluding HFSEs, were
 207 determined by the calibration curve method coupled with the internal standardization
 208 using ¹¹³In and ¹¹³In–²⁰³Tl, respectively (Yokoyama et al. 2017). We used a rock reference
 209 material, JB-3 (basalt, Geological Survey, Japan), as the standard in the determination of
 210 major and trace elements, excluding HFSEs. The concentrations for JB-3 reported by Kon
 211 and Hirata (2015) were used here. Analytical reproducibility was typically less than 2%
 212 for REE, 4% for Mg, Ca, Fe, Mn, and trace elements, excluding REEs and Pb, and 14%
 213 for Pb (2SD).

214

215 **Oxygen Isotope Analyses**

216 Oxygen isotope analysis was carried out using an infrared laser-assisted fluorination
 217 system at the Open University (Miller et al. 1999; Greenwood et al. 2017). An
 218 approximately 200 mg piece of specimen A was crushed and homogenized and two
 219 aliquots of this powder, each ~2 mg, were loaded for oxygen isotope analysis. Oxygen
 220 gas was released by heating in the presence of BrF₅ and then purified by passing it through
 221 two cryogenic nitrogen traps and over a bed of heated KBr. The purified oxygen gas was
 222 analyzed using a MAT 253 dual inlet mass spectrometer (Thermo Scientific, USA).
 223 Overall system precision, as defined by replicate analyses of our internal obsidian
 224 standard (n = 38), is ±0.053‰ for δ¹⁷O (2σ); ±0.095‰ for δ¹⁸O (2σ); ±0.018‰ for Δ¹⁷O
 225 (2σ) (Starkey et al. 2016).

226 Oxygen isotopic analyses are reported in standard δ notation, where δ¹⁸O has been
 227 calculated as: δ¹⁸O = [(¹⁸O / ¹⁶O)_{sample} / (¹⁸O / ¹⁶O)_{VSMOW} - 1] × 1000 (‰) and similarly for
 228 δ¹⁷O using the ¹⁷O / ¹⁶O ratio. Δ¹⁷O, which represents the deviation from the terrestrial
 229 fractionation line, has been calculated using the linearized format of Miller (2002):

$$230 \quad \Delta^{17}\text{O} = 1000 \ln(1 + \delta^{17}\text{O}/1000) - \lambda 1000 \ln(1 + \delta^{18}\text{O}/1000)$$

231 where λ = 0.5247, which was determined using 47 terrestrial whole-rock and mineral
 232 separate samples (Miller et al. 1999; Miller 2002).

233 RESULTS

234 Petrology and Mineral Chemistry

235 In each specimen of NWA 7188, at least two distinct textures with different grain
 236 sizes can be recognized: fine-grained (FG) and coarse-grained (CG) crystalline areas.
 237 These textures are separated by a boundary that can be observed under a stereoscopic
 238 microscope (Fig. S2a). The FG area has a subophitic texture composed of lath shaped
 239 plagioclase and anhedral pyroxene (Fig. 1a). In addition, the FG area partly contains
 240 regions that are composed of fine-grained micro-minerals with sizes of several tens of
 241 μm . The CG area is composed of lath shaped plagioclase crystal of up to 0.5×2.6 mm
 242 and pyroxene of up to 1.0×2.3 mm.

243 The SEM observations and elemental maps obtained from FE-EPMA revealed that
 244 the FG area contains mesostasis-rich regions including a silica mineral (possibly
 245 tridymite), troilite, Ca-phosphate mineral, and ilmenite (Fig. 1b). In addition, tiny zircons
 246 (5–20 μm) exist in contact with ilmenite, plagioclase, and pyroxene (Fig. 1c). The
 247 elemental maps obtained from SEM and EPMA analyses indicated that NWA 7188
 248 consists of pyroxene (49 vol%), plagioclase (44 vol%), silica minerals (5 vol%), and the
 249 other accessory minerals (ilmenite, spinel, Ca-phosphate mineral, troilite, and zircon) (Fig.
 250 S2b).

251 The chemical composition of pyroxene and plagioclase in the FG and CG areas are
 252 listed in Table 1. In the Ca–Mg–Fe ternary phase diagram (Fig. 2a), the composition of
 253 pyroxene in the CG area ranges from $\text{Wo}_{3.94}\text{En}_{33.9}\text{Fs}_{62.2}$ to $\text{Wo}_{26.1}\text{En}_{29.6}\text{Fs}_{44.3}$ ($n = 13$),
 254 while those in the FG area show a larger variation with an overlap with the CG area
 255 ($\text{Wo}_{4.22}\text{En}_{34.1}\text{Fs}_{61.7}$ – $\text{Wo}_{40.4}\text{En}_{29.0}\text{Fs}_{30.6}$; $n = 16$). Overall, the compositional variation of
 256 pyroxene trends from pigeonite to augite, implying that NWA 7188 should be classified
 257 as an ordinary or equilibrated eucrite (Reid and Barnard 1979; Pun and Papike 1996). The
 258 Ca-Fe pyroxene compositional trends in the FG and CG areas are closely similar,
 259 suggesting that NWA 7188 is a monomict eucrite.

260 We estimate the equilibration temperature by using the QUILF (quartz-ulvöspinel-
 261 ilmenite-fayalite) two-pyroxene geothermometer (Andersen et al. 1993). The
 262 geothermometer can be applied to augite lamella in pigeonite, which exists in NWA 7188
 263 as explained below. The calculation of the equilibration temperature requires the Wo and
 264 En values in the FG and CG areas, which are summarized in Table 1. The equilibration
 265 temperatures determined by QUILF calculation for pyroxene are 896 ± 60 °C and $907 \pm$
 266 44 °C in the FG and CG areas respectively and so are essentially indistinguishable from
 267 each other. This suggests that the two lithologies originated from the same protolith (i.e.,
 268 monomict). This petrographic variety in monomict basaltic eucrites, for example

269 Stannern, NWA 4523, and Millbillillie, has already been reported (Barrat et al. 2007;
270 Yamaguchi et al. 1994).

271 Most pigeonite grains in NWA 7188 have sub- μm augite lamellae, with the width
272 near the rim being thicker than that of lamellae near the core (Fig. 1d). NWA 7188 can be
273 classified as type 4 due to the characteristics mentioned above and the presence of
274 remnant Ca-zoning, similar to that reported by Yamaguchi et al. (1996) in Stannern
275 pyroxenes (type 4). Figure 3 shows that the Fe/Mn ratios of pyroxene in NWA 7188 range
276 from 29.0 to 35.3 with a mean value of 32.3 ($n = 29$), which is consistent with those of
277 the other basaltic eucrites.

278 The composition of plagioclase in the FG area range from $\text{Or}_{1.69}\text{An}_{78.0}\text{Ab}_{20.4}$ to
279 $\text{Or}_{0.47}\text{An}_{90.7}\text{Ab}_{8.81}$ ($n = 14$), and those in the CG area range from $\text{Or}_{1.93}\text{An}_{77.0}\text{Ab}_{21.1}$ to
280 $\text{Or}_{0.35}\text{An}_{86.2}\text{Ab}_{13.4}$ ($n = 22$) (Fig. 2b). The chemical composition of plagioclase in FG and
281 CG areas are similar to each other, which have a large variation of An content (14 mol%;
282 An_{77-91}) compared with most other basaltic eucrites with the variation of An content
283 (about 5–10 mol%) (Mayne et al. 2009). This result suggests that plagioclase (Si and Al
284 in albite-anorthite substitution) were not equilibrated.

285

286 **Bulk Chemical Compositions**

287 Major, minor, and trace element compositions of a bulk sample of NWA 7188 are
288 shown in Table 2, while those of the reference rock BHVO-2 are listed in Table S1 with
289 the values reported previously. The concentrations of major and trace elements in BHVO-
290 2 obtained in this study are in good agreement with those reported in Kon and Hirata
291 (2015), confirming the accuracy of our measurements. The results of Ti and trace
292 elements for C-2-1 and C-2-2 are consistent with each other. This result confirms that the
293 washing procedure for C-2-1 effectively removed the terrestrial materials that were
294 physically adsorbed onto the rock surface, although inter-mineral redistribution of
295 elements due to terrestrial weathering must be separately evaluated (see the discussion).
296 In the following, the mean values of C-2-1 and C-2-2 for individual elements are used as
297 concentrations representing the bulk chemical composition of NWA 7188.

298 The concentrations of FeO^{T} and MgO in NWA 7188 are 17.2 wt.% and 5.99 wt.%,
299 respectively, which gives $\text{FeO}/\text{MgO} = 2.88$ (Table 2). The concentrations of TiO_2 (0.97
300 wt.%), La (5.20 $\mu\text{g}/\text{g}$), and Hf (2.49 $\mu\text{g}/\text{g}$) in NWA 7188 are higher than those in most
301 basaltic eucrites, whereas the FeO/MgO ratio is within the range of the other eucrites
302 (2.3–3.7; Fig. 4). Figure 5 shows the CI chondrite-normalized REE pattern of NWA 7188.
303 The bulk composition shows a LREE-enriched and HREE-depleted pattern with
304 pronounced negative Eu anomaly, whose La, Eu, and Lu concentrations are $22 \times \text{CI}$, 13

305 \times CI, and $16 \times$ CI, respectively. As well as Hf, the concentrations of Zr (89.48 $\mu\text{g/g}$), Nb
 306 (6.40 $\mu\text{g/g}$), and Ta (0.33 $\mu\text{g/g}$) are higher than those of the main-group–Nuevo Laredo-
 307 group eucrites, but are consistent with those of the Stannern-group eucrites. The Zr/Hf
 308 and Nb/Ta ratios of basaltic eucrites range from 33.9 to 40.9 and from 17.0 to 20.9,
 309 respectively (Barrat et al. 2000, 2007; Jochum et al. 2000; Weyer et al. 2002; Münker et
 310 al. 2003; Roszjar et al. 2011), which are similar to the chondritic ratios (Zr/Hf = $34.3 \pm$
 311 0.3 , Nb/Ta = 19.9 ± 0.6 ; Münker et al. 2003). The Zr/Hf (= 36.0) and Nb/Ta (= 19.6) ratios
 312 of NWA 7188 are within the range of those for basaltic eucrites.

313

314 **Oxygen Isotope Compositions**

315 Figure 6 shows the oxygen isotope composition of NWA 7188 obtained in this study
 316 along with the data for other HED meteorites compiled by Greenwood et al. (2017). The
 317 $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values of NWA 7188 are $1.968 \pm 0.008\text{‰}$ (2σ), $4.224 \pm 0.016\text{‰}$
 318 (2σ), and $-0.245 \pm 0.016\text{‰}$ (2σ), respectively. The $\Delta^{17}\text{O}$ value for NWA 7188 is within
 319 error of the mean eucrite value of $-0.240 \pm 0.018\text{‰}$ (2σ) (Greenwood et al. 2017).

320

321 **^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd Isochron Ages**

322 Sm and Nd concentrations and Nd isotope ratios are presented in Table 3. The data
 323 for the G1 fraction was reported in Kagami and Yokoyama (2016). All the data from each
 324 fraction plot on a single line within the analytical uncertainties in both of ^{147}Sm – ^{143}Nd
 325 and ^{146}Sm – ^{142}Nd isochron diagrams (Figs. 7a and 7b). The ^{147}Sm – ^{143}Nd isochron yields
 326 an age of 4582 ± 190 Ma (2σ , MSWD = 1.1) with an initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50662
 327 ± 0.00025 . In contrast, the slope of ^{146}Sm – ^{142}Nd isochron provides the $^{146}\text{Sm}/^{144}\text{Sm}$ ratio
 328 (R_{Sm}) of 0.00757 ± 0.00093 (2σ , MSWD = 1.9) at the formation of NWA 7188. To derive
 329 the ^{146}Sm – ^{142}Nd isochron age of NWA 7188 from the observed R_{Sm} , the half-life of ^{146}Sm
 330 ($= t_{1/2}^{146}$) and the initial Solar System $^{146}\text{Sm}/^{144}\text{Sm}$ ratio ($= R_{\text{Sm}}^0$) are required. In this study,
 331 we adopted $t_{1/2}^{146} = 103$ Myr and $R_{\text{Sm}}^0 = 0.00828 \pm 0.00044$ (Marks et al. 2014) for
 332 calculation of ^{146}Sm – ^{142}Nd age of NWA 7188. Consequently, the obtained R_{Sm} of NWA
 333 7188 corresponds to an age of 4554^{+17}_{-19} Ma, with an initial Nd isotope ratio of
 334 $^{142}\text{Nd}/^{144}\text{Nd} = 1.141511 \pm 0.000035$. The ^{146}Sm – ^{142}Nd age of NWA 7188 is the oldest age
 335 measured for the subset of basaltic eucrites for which ^{146}Sm – ^{142}Nd ages have been
 336 obtained.

337 **DISCUSSION**

338 **Effect of Terrestrial Weathering**

339 It has been reported that some Saharan meteorites occasionally show elevated Sr and
340 Ba concentrations as a result of terrestrial weathering that caused the formation of
341 secondary carbonates and sulfates within the meteorites (Crozas et al. 2003). For this
342 reason, Sr and Ba concentrations can be useful as a means of evaluating the extent of
343 terrestrial weathering in desert meteorites. In addition, Th/U and Hf/Sm ratios in
344 meteorites have been used to investigate the extent of terrestrial aqueous alteration in a
345 particular sample (Barrat et al. 2003, 2007). This is because U and Sm are fluid mobile
346 elements compared to Th and Hf, respectively, while these ratios are not changed
347 significantly by magmatic processes due to the similar incompatibilities of each pair of
348 elements. In fact, the Th/U ratio in eucrites including weathered meteorites ranges from
349 1.9 to 7.2 (Mittlefehldt and Lindstrom 1991; Yamaguchi et al. 2009), with this variation
350 being twice as large as that for fall eucrites (2.7–5.1; Barrat et al. 2003). Additionally, the
351 Hf/Sm ratio of Antarctic eucrites (0.5–3.2; Mittlefehldt and Lindstrom 1991) are variable
352 compared with that of unweathered eucrites (0.6–1.0; Barrat et al. 2003).

353 The measured Sr (132 $\mu\text{g/g}$) and Ba (69 $\mu\text{g/g}$) concentrations in NWA 7188 are
354 substantially higher than those determined for either fall or Antarctic basaltic eucrites (Sr:
355 ~ 70 to ~ 100 $\mu\text{g/g}$, Ba: ~ 15 to ~ 60 $\mu\text{g/g}$; Barrat et al. 2003). This indicates that the
356 influence of terrestrial weathering on this meteorite persists despite the use of the
357 acetone–H₂O washing procedure. On the other hand, the ratios of Th/U (= 3.1) and Hf/Sm
358 (= 0.8) in NWA 7188 are within the range of unweathered eucrites. These results indicate
359 that terrestrial weathering of NWA 7188 in a hot desert environment has increased the
360 concentration of Sr and Ba without modifying the Th/U and Hf/Sm ratios. Therefore, we
361 consider that the concentrations of U, Sm, and possibly the rest of REEs have not been
362 redistributed among minerals in NWA 7188 via terrestrial alteration, in which case the
363 concentrations of these elements in the bulk rock and individual minerals of NWA 7188
364 represent the original values that were acquired on the meteorite parent body.

365

366 **Classification of NWA 7188**

367 The Fe/Mn ratio of pyroxene and the oxygen isotopic composition of basaltic
368 eucrites have been widely used as a means of evaluating potential genetic links between
369 basaltic eucrites. Previous studies argued that pyroxene in Ibitira exhibits higher Fe/Mn
370 ratios (33–39; 36.4 on average) than has been measured in the other basaltic eucrites (30
371 ± 2) (Papike et al. 2003; Mittlefehldt 2005). In addition, Ibitira has a distinct oxygen
372 isotopic composition compared to other eucrites (Wiechert et al. 2004). These

373 observations have led researchers to conclude that Ibitira originated from a parent body
374 other than Vesta (Mittlefehldt 2005). Although basaltic achondrites, Pasamonte and
375 Caldera, have pyroxene Fe/Mn ratios indistinguishable from other basaltic eucrites, their
376 oxygen isotope compositions are different from those of the other eucrites (Wiechert et
377 al. 2004). The consistency of the Fe/Mn ratios of pyroxene and oxygen isotope
378 composition in NWA 7188 with those of the other basaltic eucrites indicates that NWA
379 7188 is a normal member of HED meteorites and as a consequence most likely originated
380 from Vesta.

381 On a diagram of TiO₂ concentration vs. FeO/MgO ratio, the main-group, Nuevo
382 Laredo-group, and Stannern-group eucrites plot in different fields, with the TiO₂
383 concentrations of the Stannern-group eucrites being higher than those of the main-group–
384 Nuevo Laredo-group eucrites (e.g., Stolper 1977; Warren and Jerde 1987). Therefore, this
385 diagram has been used to distinguish the chemical groups of basaltic eucrites (e.g., Barrat
386 et al. 2000; Mittlefehldt 2015). As shown in Fig. 4a, NWA 7188 has a higher Ti
387 concentration than those of the main-group–Nuevo Laredo-group eucrites and plots
388 within the field of Stannern-group eucrites. As well as TiO₂ concentration, diagrams of
389 La and Hf concentration vs. FeO/MgO ratio can also be used to discriminate between the
390 various chemical groups of basaltic eucrites (e.g., Barrat et al. 2000; Mittlefehldt 2015).
391 The La vs. FeO/MgO and Hf vs. FeO/MgO diagrams indicate that NWA 7188 has much
392 higher La and Hf concentrations than those of the main-group–Nuevo Laredo-group
393 eucrites at a given FeO/MgO (Figs. 4b and 4c). Based on the diagrams of Ti, La, and Hf
394 concentrations vs. FeO/MgO ratios, NWA 7188 can be unambiguously classified as a
395 member of the Stannern group of eucrites.

396 The various chemical groups of basaltic eucrites are also distinguishable by their
397 REE patterns. Figure 5 shows the REE pattern for NWA 7188 in relation to various
398 representative eucrites from each of the main chemical group. The main-group eucrites
399 have a flat REE pattern with no Eu anomaly, and their REE concentrations are $\sim 11 \times \text{CI}$.
400 In contrast, the REE patterns of Nuevo Laredo-group and Stannern-group eucrites are
401 characterized by LREE-enriched and HREE-depleted patterns with pronounced negative
402 Eu anomalies. In detail, these two groups can be distinguished by the differences in the
403 degree of Eu anomaly and the slope from Gd to Lu (Gd_N/Lu_N) in the REE pattern. The
404 Stannern-group eucrites have lower Eu/Eu^* (0.57–0.67) and higher Gd_N/Lu_N ratios (1.26–
405 1.31) compared to the Nuevo Laredo-eucrites ($\text{Eu}/\text{Eu}^* = 0.76\text{--}0.78$ and $\text{Gd}_N/\text{Lu}_N = 1.05\text{--}$
406 1.16) (Barrat et al. 2011; Roszjar et al. 2011). The observation that the Eu/Eu^* and Gd_N
407 $/\text{Lu}_N$ ratios of NWA 7188 (0.64 and 1.26, respectively; Table 2) are within the range of
408 the Stannern-group eucrites reinforces the likelihood that NWA 7188 is a new member of

409 the Stannern-group.

410 The oxygen isotope ratios of five Stannern-group eucrites measured to date indicate
 411 that there is no significant difference between members of the Stannern-group and the
 412 main-group–Nuevo Laredo-group eucrites (Fig. 6) (Clayton and Mayeda 1996; Wiechert
 413 et al. 2004; Greenwood et al. 2005; Barrat et al. 2007; Roszjar et al. 2011). In support of
 414 this observation, the oxygen isotope composition of NWA 7188 measured in this study
 415 falls within the $\Delta^{17}\text{O}$ range measured for the main-group–Nuevo Laredo-group eucrites
 416 (Fig. 6). NWA 7188 has a slightly elevated $\delta^{18}\text{O}$ composition compared with the majority
 417 of eucrites plotted in Fig. 6, which may reflect the influence of terrestrial weathering.
 418 However, in terms of its $\delta^{18}\text{O}$ value NWA 7188 plots within the range of values measured
 419 in other eucrites (Greenwood et al. 2017) and so the extent of terrestrial weathering is
 420 relatively limited.

421

422 **Geochemical Characteristics of NWA 7188 as a Stannern-Group Eucrite**

423 Approximately ten Stannern-group eucrites have been identified to date based on the
 424 diagrams of Ti, La, and Hf concentrations vs. FeO/MgO ratios, and/or the Mg# (= molar
 425 $100 \times \frac{\text{MgO}}{\text{FeO}+\text{MgO}}$) and REE compositions (Mittlefehldt 2015). NWA 7188 and some
 426 representative Stannern-group eucrites, such as Stannern, Bouvante, NWA 4523, NWA
 427 5073, and Yamoto (Y)-75011 have variable REE concentrations that are characterized by
 428 enhanced LREE/HREE ratios with negative Eu anomalies (Fig. 5). In particular, NWA
 429 7188 has similar modal REE abundances and pattern (Eu/Eu*: 0.64, Gd_N/Lu_N: 1.26, and
 430 La_N/Sm_N: 1.00) to those of Stannern (0.65, 1.26, and 1.00, respectively) when compared
 431 to those of the other Stannern-group eucrites (0.58–0.68, 1.30–1.35, and 1.02–1.08,
 432 respectively).

433 Among the representative Stannern-group eucrites shown in Fig. 5, Stannern,
 434 Bouvante, and NWA 4523 are monomict basaltic eucrites. In contrast, NWA 5073 is an
 435 unbrecciated basaltic eucrite that contains large pyroxene phenocrysts with different
 436 modal abundances of pyroxene (64.7 vol.%) and plagioclase (26.4 vol.%) (Roszjar et al.
 437 2011) compared with those of the other basaltic eucrites (51.2 and 43.3 vol.%,
 438 respectively; Delaney et al. 1984). Additionally, Roszjar et al. (2016) reported that the
 439 ^{182}Hf – ^{182}W dates of some zircons in NWA 5073 yielded younger ages down to ~4530 Ma,
 440 which led the authors to suggest that NWA 5073 may have experienced a reheating event.
 441 Therefore, the relatively low REE concentration of NWA 5073 may not be representative
 442 of the original chemical composition of Stannern-group eucrites. On the other hand, Y-
 443 75011 is a polymict breccia and contains a variety of pyroxene fragments, including

444 Binda-type (cumulate eucrite) and Juvinas-type pyroxenes (Takeda et al. 1979). The
445 lower REE concentration of Y-75011 compared to the monomict Stannern group suggests
446 the incorporation of various clasts with non-Stannern group chemical compositions. In
447 addition to Y-75011, a polymict Stannern-group eucrite Y-74450 shows lower REE
448 concentrations than the other monomict Stannern group (Shimizu and Masuda 1986). In
449 summary, the evidence seems to point to Stannern, Bouvante, and NWA 4523 as being
450 relatively pristine examples of monomict Stannern-group eucrites and appear to preserve
451 the original chemical composition of the Stannern group. Given that NWA 7188 is a
452 monomict Stannern-group eucrite, with a similar modal abundance and REE pattern to
453 Stannern, it is also clearly a member of this relatively pristine group. This evidence
454 indicates that NWA 7188 also preserves the initial composition of the Stannern-group
455 eucrites.

456 In addition to the similarity of the major and trace element compositions, the
457 metamorphic grades of NWA 7188, Stannern, and Bouvante all belong to type 4 (Takeda
458 et al. 1983; Michel-Lévy et al. 1987). Taking the geochemical and petrological evidence
459 into account, these three Stannern-group eucrites are believed to have been formed by a
460 similar process and probably experienced similar thermal metamorphism. However, the
461 ^{81}Kr exposure ages of Stannern and Bouvante are 35.1 ± 0.7 Ma and 6.7 ± 0.4 Ma
462 respectively, which are clearly different from each other (Shukolyukov and Begemann
463 1996; Miura et al. 1998). This result might indicate that they were ejected from Vesta by
464 different impact events and consequently different regions of Vesta. It is currently not
465 known whether NWA 7188 is related to either the Stannern or Bouvante ejection event or
466 to a third distinct event. Further study and in particular determining the exposure ages for
467 NWA 7188 and other Stannern-group eucrites will provide new insights into the
468 distribution of the Stannern-group eucrites on Vesta.

469

470 **Chronology of Eucrites**

471 *Review of Chronological Studies on Eucrites*

472 Some short-lived chronometers have shown that the accretion, core–mantle
473 differentiation, silicate differentiation (crustal formation), and initial crystallization of
474 basaltic magmas on Vesta started within a few million years after CAI formation. Here,
475 we focus on monomict eucrites and exclude from the chronological discussion ages
476 determined for polymict eucrites. This is because polymict eucrites are mixtures of more
477 than two different rock types (e.g., sub-groups of basaltic eucrites) and so the
478 chronological evidence they furnish may not be related to actual events in the history of
479 their parent body. The timing of core–mantle segregation for Vesta has been estimated to

480 be within ~1 Myr after CAI formation on the basis of the ^{182}Hf – ^{182}W systematics
 481 (Touboul et al. 2015). The silicate differentiation followed the core–mantle segregation
 482 and occurred at 4564.8 ± 0.9 Ma according to ^{53}Mn – ^{53}Cr whole-rock isochron data
 483 (Lugmair and Shukolyukov 1998). This timing was also recorded by the ^{26}Al – ^{26}Mg
 484 whole-rock isochron age of eucrites, which was $2.88^{+0.14}_{-0.12}$ Myr after CAI formation
 485 (Hublet et al. 2017). The ^{53}Mn – ^{53}Cr ages obtained from inter-mineral isochrons of Juvinas,
 486 Chervony Kut, and Asuka (A)-881394 yielded 4562.5 ± 1.0 Ma, 4563.6 ± 0.9 Ma, and
 487 4564 ± 2 Ma, respectively (Lugmair and Shukolyukov 1998; Nyquist et al. 2003). The
 488 ^{26}Al – ^{26}Mg inter-mineral isochrons of eucrites was determined to be 2–3 Myr after CAI
 489 formation (Schiller et al. 2010; Hublet et al. 2017). These ages suggest that the igneous
 490 crystallization of basaltic magmas began simultaneously with crust formation on Vesta.

491 The period of initial crystallization of basaltic crust has been discussed based on the
 492 ^{207}Pb – ^{206}Pb zircon dates for basaltic eucrites. Because the ^{207}Pb – ^{206}Pb dates of eucritic
 493 zircons have clustered around 4550 Ma, the volcanism on Vesta is considered to have
 494 lasted until around 4550 Ma (e.g., Misawa et al. 2005; Zhou et al. 2013) (Fig. 8a). In
 495 contrast, some zircons found in highly metamorphosed basaltic eucrites are recognized to
 496 have formed during subsolidus reheating caused by global metamorphism (Haba et al.
 497 2014; Roszjar et al. 2014). Iizuka et al. (2015) argued that the ^{207}Pb – ^{206}Pb date of zircons
 498 in a highly metamorphosed basaltic eucrites Agoult (4554.5 ± 2.0 Ma) corresponds to the
 499 timing of global metamorphism on Vesta. Thus, the global metamorphism on Vesta may
 500 have occurred contemporaneously with the initial crystallization of eucrite magmas
 501 during the very early stages of Vesta’s evolution, most likely due to the internal heat of
 502 deeply buried lavas (Yamaguchi et al. 1996, 1997).

503 ^{207}Pb – ^{206}Pb or ^{182}Hf – ^{182}W zircon dates for only two monomict Stannern-group
 504 eucrites, Stannern and NWA 4523, have been reported. The ^{207}Pb – ^{206}Pb zircon date for
 505 Stannern was 4550 ± 10 Ma (Ireland and Bukovanská 1992). This age would correspond
 506 to the timing of volcanism or the global metamorphism because we cannot identify the
 507 characteristics of zircons reported by Ireland and Bukovanská (1992), whereas Stannern
 508 contains zircons formed during the global metamorphism (Haba et al. 2014). In addition,
 509 the ^{182}Hf – ^{182}W dates for zircons from the Stannern-group eucrite NWA 4523 ranged from
 510 4558 to 4565 Ma (Roszjar et al. 2016). This age corresponds to the timing of initial
 511 crystallization of basaltic crust because the ^{182}Hf – ^{182}W system in zircon is not reset by
 512 later metamorphism due to its high closure temperature (~1400 °C). The observed
 513 overlapping of zircon dates from the Stannern-group (4550–4565 Ma) and the main-
 514 group eucrites, of which the weighted mean ^{207}Pb – ^{206}Pb age yielded 4553.4 ± 2.6 Ma,
 515 suggests that the initial crystallization and global metamorphism of the Stannern-group

516 eucrites took place during the same period as the main-group eucrites.

517 The Sm–Nd ages of a few basaltic eucrites have given dates older than 4.53 Ga
 518 (Lugmair 1974; Lugmair and Galer 1992; Wadhwa and Lugmair 1996; Kumar et al. 1999),
 519 whereas some basaltic eucrites record much younger ^{146}Sm – ^{142}Nd and ^{147}Sm – ^{143}Nd ages
 520 of 4.40–4.53 Ga (Lugmair and Scheinin 1975; Nyquist et al. 1986, 1997; Wadhwa and
 521 Lugmair 1995; Tera et al. 1997; Yamaguchi et al. 2001) (Fig. 8b). The earlier date appears
 522 to represent the timing of igneous activity and global metamorphism on Vesta and was
 523 apparently not disturbed by later short-term reheating events, as indicated by the
 524 consistent range of the ^{207}Pb – ^{206}Pb dates for eucritic zircons. Numerical simulations of
 525 the thermo-chemical evolution of Vesta (Neumann et al. 2014), suggest that the
 526 temperature of Vesta’s eucritic upper crust (~20 km thick) (Mandler and Elkins-Tanton
 527 2013), was $< \sim 600$ °C at ~30 Ma after CAI formation. The internal heat source of the
 528 igneous activity and global metamorphism, from the decay of short-lived ^{26}Al , was absent
 529 in the upper crust of Vesta at that time. Thus, the observed young ages indicate that the
 530 $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ decay system of some basaltic eucrites was likely disturbed during
 531 secondary events such as impact on Vesta.

532 The ^{244}Pu –Xe ages reported by previous studies (Michel and Eugster 1994;
 533 Shukolyukov and Begemann 1996; Miura et al. 1998; Park and Nagao 2005) suggest that
 534 the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ and ^{244}Pu –Xe ages are generally in reasonable agreement with each
 535 other (Fig. 8c). The $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ and ^{244}Pu –Xe systems were affected to the same
 536 degree by resetting during impact reheating (Figs. 8b and 8c). In general, mineral closure
 537 temperatures of pyroxene and plagioclase for the U–Pb system (~800 °C; Iizuka et al.
 538 2014) are lower than those for the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ system, suggesting that the ^{207}Pb –
 539 ^{206}Pb ages are less resistant to resetting by local reheating and/or impact events than
 540 $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ ages. Actually, all of the ^{207}Pb – ^{206}Pb ages for basaltic eucrites derived
 541 from the whole rock and mineral samples are younger than 4.53 Ga (Fig. 8d). Overall,
 542 the younger $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$, ^{244}Pu –Xe and U–Pb ages suggest that the reheating events
 543 postdated the initial crystallization and global metamorphism, and although the
 544 temperatures attained were subsolidus, they were also high enough to reset the $^{147,146}\text{Sm}$ –
 545 $^{143,142}\text{Nd}$, ^{244}Pu –Xe, and U–Pb systems for bulk rocks and minerals, with the exception of
 546 zircons.

547

548 *The ^{146}Sm – ^{142}Nd Chronology of NWA 7188*

549 Sm–Nd systematics provide two chronometers that utilize long-lived ^{147}Sm ($t_{1/2}$ =
 550 106 Gyr) with a daughter nuclide ^{143}Nd and short-lived ^{146}Sm ($t_{1/2}$ = 103 Myr) with a
 551 daughter nuclide ^{142}Nd . In some situations, the ^{147}Sm – ^{143}Nd ages of eucrites can be

552 significantly affected by secondary events, whereas the ^{146}Sm – ^{142}Nd systematics is
 553 undisturbed (Prinzhofer et al. 1992; Wadhwa et al. 2006). Prinzhofer et al. (1992)
 554 suggested that the ^{147}Sm – ^{143}Nd systematics can be disturbed by partial re-equilibration of
 555 plagioclase and phosphates that episodically occur within a short period of time, whereas
 556 the ^{146}Sm – ^{142}Nd age are not affected by such a re-equilibration event. Hereafter, we
 557 discuss the Sm–Nd chronology of NWA 7188 by using the ^{146}Sm – ^{142}Nd age ($4554^{+17/-}$
 558 $_{19}$ Ma).

559 As noted above (see the Review of Chronological Studies on Eucrites in this section),
 560 the thermal evolution of Vesta was discussed based on chronological data reported in
 561 previous works. Because the ^{146}Sm – ^{142}Nd age of NWA 7188 is in good agreement with
 562 the timing of the initial crystallization or global metamorphism at ~ 4.55 Ga, the Sm–Nd
 563 decay system was not disturbed by this later reheating such as by intermittent impact
 564 events. Therefore, NWA 7188 is also a rare and important basaltic eucrite with respect to
 565 the chronological information it can furnish about Vesta's early evolution.

566

567 ***Closure Temperature of the Sm–Nd System in NWA 7188***

568 The Sm–Nd closure temperatures for pyroxene and plagioclase have not been
 569 quantitatively discussed in the literature to date, while those in other minerals such as
 570 garnet have been examined in detail in previous studies (e.g., Tirone et al. 2005; Scherer
 571 et al. 2010). To evaluate the degree of isotopic resetting in the ^{147}Sm – ^{143}Nd chronometer,
 572 Nyquist et al. (1991a, b) compared three ^{147}Sm – ^{143}Nd internal isochrons consisting of
 573 plagioclase (density < 2.85 g/cm³) and pyroxene (density = 3.45 – 3.55 g/cm³ and 3.55 – 3.7
 574 g/cm³) minerals and whole rock that were prepared from unheated, moderately (790 °C)
 575 heated and heavily (990 °C) heated samples of a lunar basalt 15555. The results showed
 576 that the ^{147}Sm – ^{143}Nd isochron of the heavily heated samples had been disturbed, while
 577 that of the moderately heated samples appeared to be only slightly perturbed compared to
 578 the unheated samples. Thus, Sm–Nd systematics would be reset by heating at the
 579 subsolidus temperatures of basaltic eucrites (< 1060 °C; Stolper 1977).

580 In order to better constrain the thermal event that corresponds to the ^{146}Sm – ^{142}Nd
 581 age obtained for NWA 7188, we have estimated the Sm–Nd closure temperature of the
 582 constituent minerals of basaltic eucrites in two different ways, as discussed below. First,
 583 we compare the Sm–Nd ages with the ^{207}Pb – ^{206}Pb ages of whole rock and minerals
 584 (pyroxene and plagioclase) and the ^{207}Pb – ^{206}Pb dates of zircons among basaltic eucrites.
 585 Some basaltic eucrites have Sm–Nd ages that appear to correspond to the initial
 586 magmatism or metamorphism at around 4550 Ma. In contrast, all of the ^{207}Pb – ^{206}Pb whole
 587 rock and mineral ages are younger than 4530 Ma (Figs. 8b and 8d). On the other hand,

588 the Sm–Nd ages of some basaltic eucrites are also much younger than 4530 Ma, while
 589 most of the ^{207}Pb – ^{206}Pb dates of eucritic zircons are older than 4530 Ma (Figs. 8a and 8b).
 590 These comparisons reveal that the closure temperature of the Sm–Nd decay system is
 591 higher than that of the U–Pb system for whole rocks and minerals, but lower than that of
 592 eucritic zircons. Then, the Pb closure temperatures in plagioclase, pyroxene, and zircon
 593 of basaltic eucrites are estimated to constrain the Sm–Nd closure temperature by adapting
 594 the cooling rate and grain size of basaltic eucrites. We note the data required to calculate
 595 the closure temperature as follows. The diffusion coefficients of Pb (D_{Pb}) in plagioclase,
 596 pyroxene (augite), and zircon used in the calculation are given as follows (Cherniak 1995;
 597 2001; Cherniak and Watson 2003);

$$598 \quad D_{\text{Pb in plagioclase}} = 3.75 \times 10^{-6} \times e^{-327 \text{ kJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}$$

$$599 \quad D_{\text{Pb in pyroxene}} = 3.8 \times 10^{-5} \times e^{-372 \text{ kJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}$$

$$600 \quad D_{\text{Pb in zircon}} = 1.1 \times 10^{-1} \times e^{-550 \text{ kJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}$$

601 where R and T are the gas constant and temperature, respectively. Although there are two
 602 different Pb diffusion coefficients for zircon (Lee et al. 1997; Cherniak and Watson 2003),
 603 we use that from Cherniak and Watson (2003) to obtain the maximum closure temperature
 604 of U–Pb decay system in zircon. The closure temperature is given by employing the
 605 formalism developed by Dodson (1973);

$$606 \quad T_c = \frac{E/R}{\ln\left(\frac{ART_c^2 D_0/a^2}{E \, dT/dt}\right)}$$

607 where E and D_0 are the activation energy and pre-exponential factors for diffusion of the
 608 relevant species, A is a geometric factor ($A = 55$ for spherical geometry), dT/dt is the
 609 cooling rate, and a is the effective diffusion radius. It should be noted that the cooling rate
 610 for the U–Pb decay system for whole rocks and minerals depends on the thermal event
 611 that caused the resetting of the system. According to Haba et al. (2019), the Pb–Pb ages
 612 of whole rocks and minerals probably correspond to a large-scale collision on Vesta
 613 4525.4 Ma. Although the cooling rate during the collision has not been estimated, it
 614 should have been slower than that of a local impact due to heat insulation by the
 615 collisional debris. In the calculation, we utilize the cooling rate during the extensive
 616 metamorphism (0.01 °C/year) obtained from a basaltic eucrite, Sioux County
 617 (metamorphic grade: type 5) (Miyamoto et al. 1996). This estimate should provide the
 618 minimum closure temperature of U–Pb decay system of whole rock and minerals. The
 619 effective diffusion radius is assumed to be 125 μm for plagioclase and pyroxene and 8
 620 μm for zircon, because most basaltic eucrites have fine- to medium-grained pyroxene and

621 plagioclase (McSween et al. 2011) and zircon grain sizes are a few–30 μm (Haba et al.
 622 2014). The closure temperature of Pb is estimated to be ~ 855 $^{\circ}\text{C}$ for plagioclase and
 623 ~ 930 $^{\circ}\text{C}$ for pyroxene, whereas that for zircon is ~ 1040 $^{\circ}\text{C}$. Therefore, the Sm–Nd closure
 624 temperature of basaltic eucrites is most likely to be between ~ 855 $^{\circ}\text{C}$ and ~ 1040 $^{\circ}\text{C}$.

625 Second, we estimate the Sm–Nd closure temperature of NWA 7188 by the
 626 diffusion calculation as well as those for Pb closure temperature above. Ganguly et al.
 627 (1998) reported that the diffusion coefficient of Sm (D_{Sm}) in garnet is 5–10% larger than
 628 that of Nd (D_{Nd}) because of the smaller ionic radius of Sm (1.09 \AA) compared to Nd (1.12
 629 \AA). Although the D_{Sm} values for pyroxene and plagioclase at ~ 1000 $^{\circ}\text{C}$ are not available
 630 at present, it is conceivable that the D_{Sm} values for these minerals are also $\sim 10\%$ higher
 631 than the D_{Nd} values. Therefore, we estimate the closure temperature of the Sm–Nd system
 632 for plagioclase and pyroxene using the D_{Nd} values of the minerals that were used for
 633 deriving the Sm–Nd isochron age. The D_{Nd} in plagioclase used in the calculation is given
 634 as follows (Cherniak 2003);

$$635 \quad D_{\text{Nd in plagioclase}} = 5.9 \times 10^{-6} \times e^{-398 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}.$$

636 Sano et al. (2011) argued that the D_{Nd} in pyroxene (enstatite) are given as follows;

$$637 \quad D_{\text{Nd in pyroxene}} = 9.2 \times 10^{-13} \times e^{-222 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}.$$

638 The diffusion equation and parameters excluding effective diffusion radius are the same
 639 as those used in the calculation of Pb closure temperature above. The effective diffusion
 640 radius of 22.5 μm was employed for both plagioclase and pyroxene, because the minimum
 641 grain size of mineral fraction used for the Sm–Nd isochron of NWA 7188 is 45 μm (G3
 642 fraction). Although the G4 fraction includes grains smaller than 45 μm in diameter, these
 643 small grains are probably fragments of original minerals. Indeed, almost all of the
 644 pyroxene and plagioclase observed in NWA 7188 are much larger than 45 μm (Fig. 1a).
 645 Therefore, the closure temperature that we discuss here is the minimum value and the
 646 most rigorous estimate available. As shown in Fig. S3, the closure temperatures of Nd are
 647 estimated to be ~ 965 $^{\circ}\text{C}$ for plagioclase and ~ 865 $^{\circ}\text{C}$ for pyroxene. Even if the D_{Sm} for
 648 plagioclase and pyroxene are 10% larger than D_{Nd} of these minerals. The resulting closure
 649 temperatures for Sm are not significantly different from those of Nd. The Sm–Nd closure
 650 temperatures obtained for NWA 7188 are consistent with those predicted from the heating
 651 experiment using lunar basalt (Nyquist et al. 1991b) and the chronological comparison
 652 among the Sm–Nd and U–Pb ages of whole rock and minerals and U–Pb dates of zircons.

653 According to the estimated closure temperatures of Sm–Nd system for plagioclase
 654 and pyroxene by the two different procedures as discussed above, it appears that the

655 global metamorphism could not completely reset the Sm–Nd system in NWA 7188
656 because it has been reported that eucrites with the metamorphic grade of type 4
657 experienced metamorphism at ~800 °C (Barrat et al. 2007). Therefore, it is likely that the
658 ^{146}Sm – ^{142}Nd age obtained in this study corresponds to the timing of initial crystallization
659 of basaltic magmas, although partial resetting of the ^{146}Sm – ^{142}Nd age due to global
660 metamorphism cannot be rejected completely.

661 Concluding remarks

662 In this study, we performed textual observations, geochemical and chronological
663 studies on a basaltic eucrite NWA 7188. The textual observations and chemical
664 composition of pyroxene and plagioclase revealed that NWA 7188 is a monomict basaltic
665 eucrite. The augite lamella in pigeonite showed Ca-zoning, which indicates that the
666 metamorphic grade of NWA 7188 is defined as type 4. The oxygen isotope composition
667 confirmed that NWA 7188 was derived from the same parent body as that of the HED
668 clan. The CI chondrite-normalized REE pattern demonstrated a LREE-enriched and
669 HREE-depleted pattern with a distinct negative Eu anomaly. Because this REE pattern is
670 consistent with those of the Stannern-group eucrites, NWA 7188 is considered to be a new
671 Stannern-group eucrite. This result is also supported by the higher Hf and Ti
672 concentrations than those of the main-group basaltic eucrites. The ^{147}Sm – ^{143}Nd and
673 ^{146}Sm – ^{142}Nd mineral isochrons for NWA 7188 yielded ages of 4582 ± 190 and $4554^{+17}/_{-}$
674 $_{19}$ Ma, respectively. The closure temperature of $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ systems calculated in
675 this study suggests that the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ decay system for NWA 7188 has not been
676 totally reset during global metamorphism on Vesta. Therefore, we conclude that the
677 ^{146}Sm – ^{142}Nd age of NWA 7188 corresponds to the timing of initial crystallization of the
678 basaltic magmas that formed the Stannern-group eucrites or shows the partially reset age
679 during the global metamorphism.

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1026 **Figure Caption**

1027 Fig. 1. Back-scattered electron images of NWA 7188. (a) Pyroxene and plagioclase grains
 1028 in the FG area. (b) Mesostasis area in the NWA 7188. (c) The largest zircon and
 1029 surrounding minerals. (d) Thick and dense augite lamellae in the rim (dark gray)
 1030 and thin lamellae in the core. White is opaque minerals and black is cracks and/or
 1031 holes. Mineral abbreviations are as follows: pyx = pyroxene, plag = plagioclase,
 1032 and ilm = ilmenite.

1033

1034 Fig. 2. Compositions of major minerals in NWA 7188 plotted in the part of triangle
 1035 diagram. Minerals in the FG and CG areas are shown as red squares and blue
 1036 circles, respectively. (a) Pyroxene compositions. (b) Plagioclase compositions.

1037

1038 Fig. 3. Diagram of Mn vs. Fe (atoms per six-oxygen formula unit: afu) for pyroxene in
 1039 NWA 7188. Minerals in the FG and CG areas are shown as red squares and blue
 1040 circles, respectively. Slope (= 0.031) of the correlation corresponds to the Fe/Mn
 1041 ratio of 32.3.

1042

1043 Fig. 4. (a) TiO₂ (b) La and (c) Hf vs. FeO/MgO plots for NWA 7188 and various basaltic
 1044 eucrites. In these plots, basaltic eucrites are distinguished into three different
 1045 groups (main group, Nuevo Laredo group, and Stannern group). The FeO
 1046 concentration is calculated as the total of Fe content. The data excluding NWA
 1047 7188 are taken from the compiled data of Mittlefehldt (2015).

1048

1049 Fig. 5. CI chondrite-normalized REE patterns of NWA 7188 (red square) and the other
 1050 basaltic eucrites. Open diamond (Y-75011), gray diamond (NWA 5073), open
 1051 square (Bouvante), gray triangle (NWA 4523), and inverted triangle (Stannern)
 1052 are Stannern-group eucrites. Nuevo Laredo and Juvinas (main-group eucrite) are
 1053 shown as open circles and open triangles, respectively. The REE compositions
 1054 other than NWA 7188 are obtained from Barrat et al. (2003), Barrat et al. (2007),
 1055 and Roszjar et al. (2011). The reference of CI chondrite compositions is obtained
 1056 from McDonough and Sun (1995).

1057

1058 Fig. 6. Oxygen three isotope plot showing the data for NWA 7188 (this study) and the
 1059 other basaltic eucrites (Greenwood et al. 2017). Symbols are the same as Fig. 4.
 1060 Gray field is 2σ of the data for eucrites and diogenite, falls only, and the eucrite
 1061 fractionation line (EFL) is shown as dashed line of $\Delta^{17}\text{O} = -0.240 \pm 0.014$ (2σ)

1062 (Greenwood et al. 2017).

1063

1064 Fig. 7. (a) ^{147}Sm – ^{143}Nd and (b) ^{146}Sm – ^{142}Nd isochron diagrams of NWA 7188. Isochron
1065 and error envelope are shown as solid line and dashed curves, respectively. Error
1066 bars are 2SE. Some error bars are smaller than the size of symbols. MSWDs of
1067 the ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd isochrons are 1.1 and 1.9, respectively.

1068

1069 Fig. 8. Comparison of eucrite ages dated by various chronometers. Histogram (gray field)
1070 and probability density curve (black curve) of (a) ^{207}Pb – ^{206}Pb dates for zircons
1071 from monomict basaltic eucrites, (b) $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ mineral isochron ages for
1072 monomict basaltic eucrites, (c) ^{244}Pu – Xe mineral isochron ages for monomict
1073 basaltic eucrites, and (d) ^{207}Pb – ^{206}Pb ages for monomict basaltic eucrites.
1074 Probability density curve is not shown for Sm–Nd age because of the shortage of
1075 data. Red dashed line indicates the ^{146}Sm – ^{142}Nd age of NWA 7188. The ^{146}Sm –
1076 ^{142}Nd isochron ages are recalculated using the ^{146}Sm half-life and the Solar System
1077 initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio of Marks et al. (2014). The ages used for (a), (b), (c), and
1078 (d) are summarized in Table S2.