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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}Sm–^{143,142}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}Sm–^{143,142}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 ℃ 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.

INTRODUCTION

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

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

Eucrites mainly consist of pyroxene and plagioclase and are petrographically 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*; $Eu^* = \frac{Sm_{CI\ chondrite-normalized} + Gd_{CI\ chondrite-normalized}}{2}$), where the abundance

52   of La ranges from 17 to 28 × 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 ~1000 ℃ (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}Sm–^{143,142}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.

SAMPLES

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

In this study, we investigated three commercially sourced specimens of NWA 7188, which were named specimens A (6.9 g), B (24.8 g), and C (79.8 g). The fusion crust covering the surface of specimens B and C was carefully removed using a micro-drill equipped with a ceramic grinding stone. In addition, the brown altered part near the rim of these specimens was discarded. Because the three specimens had a similar texture, specimen A was used for textual and mineralogical observations and O isotope analyses, 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, $NaAlSi_3O_8$ 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 HNO_3 (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 $HClO_4$ (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 HNO_3, and 12 M $HClO_4$. The
144 sample solutions of the G1–G4 fractions containing HF, HNO_3, and $HClO_4$ 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 $HClO_4$ 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 ^{145}Nd- and ^{149}Sm-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 ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd 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 ^{146}Nd/^{144}Nd = 0.7219 and ^{146}Nd/^{145}Nd = 2.072016 (Boyet and
166 Carlson, 2005) for ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd, respectively. The reproducibility of the

167    $^{142}Nd/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios for the standard, JNdi-1 (500 ng), were 6.5 ppm and

168   5.2 ppm (2SD), respectively. The $^{142}Nd/^{144}Nd$ and $^{143}Nd/^{144}Nd$ 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 µg/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 ~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 µg/g, Zr: 98.8 ± 0.5 µg/g, Nb: 9.86 ± 0.05

198   µg/g, Hf: 2.96 ± 0.06 µg/g, Ta: 1.00 ± 0.02 µg/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 HNO_3 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 ^{113}In and ^{113}In–^{203}Tl, 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 BrF_5 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 δ^{17}O (2σ); ±0.095‰ for δ^{18}O (2σ); ±0.018‰ for Δ^{17}O

225   (2σ) (Starkey et al. 2016).

226   Oxygen isotopic analyses are reported in standard δ notation, where δ^{18}O has been

227   calculated as: $\delta^{18}O = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{VSMOW} -1] \times 1000$ (‰) and similarly for

228   δ^{17}O using the $^{17}O/^{16}O$ ratio. Δ^{17}O, which represents the deviation from the terrestrial

229   fractionation line, has been calculated using the linearized format of Miller (2002):

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

231   where $\lambda = 0.5247$, which was determined using 47 terrestrial whole-rock and mineral

232   separate samples (Miller et al. 1999; Miller 2002).

RESULTS

Petrology and Mineral Chemistry

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

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

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

We estimate the equilibration temperature by using the QUILF (quartz-ulvöspinel-ilmenite-fayalite) two-pyroxene geothermometer (Andersen et al. 1993). The geothermometer can be applied to augite lamella in pigeonite, which exists in NWA 7188 as explained below. The calculation of the equilibration temperature requires the Wo and En values in the FG and CG areas, which are summarized in Table 1. The equilibration temperatures determined by QUILF calculation for pyroxene are 896 ± 60 °C and 907 ± 44 °C in the FG and CG areas respectively and so are essentially indistinguishable from each other. This suggests that the two lithologies originated from the same protolith (i.e., 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 $Or_{1.69}An_{78.0}Ab_{20.4}$ to

279    $Or_{0.47}An_{90.7}Ab_{8.81}$ (n = 14), and those in the CG area range from $Or_{1.93}An_{77.0}Ab_{21.1}$ to

280    $Or_{0.35}An_{86.2}Ab_{13.4}$ (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 FeO/MgO = 2.88 (Table 2). The concentrations of TiO_2 (0.97

300   wt.%), La (5.20 μg/g), and Hf (2.49 μg/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 × CI, 13

305 × CI, and 16 × CI, respectively. As well as Hf, the concentrations of Zr (89.48 µg/g), Nb
306 (6.40 µg/g), and Ta (0.33 µg/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 ±
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 δ^{17}O, δ^{18}O, and Δ^{17}O values of NWA 7188 are 1.968 ± 0.008‰ (2σ), 4.224 ± 0.016‰
318 (2σ), and –0.245 ± 0.016‰ (2σ), respectively. The Δ^{17}O value for NWA 7188 is within
319 error of the mean eucrite value of –0.240 ± 0.018‰ (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}Nd/^{144}Nd ratio of 0.50662
327 ± 0.00025. In contrast, the slope of ^{146}Sm–^{142}Nd isochron provides the ^{146}Sm/^{144}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}Sm/^{144}Sm ratio (= R_{Sm}^{0}) are required. In this study,
331 we adopted $t_{1/2}^{146}$ = 103 Myr and R_{Sm}^{0} = 0.00828 ± 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}Nd/^{144}Nd = 1.141511 ± 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.

DISCUSSION

Effect of Terrestrial Weathering

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

The measured Sr (132 µg/g) and Ba (69 µg/g) concentrations in NWA 7188 are substantially higher than those determined for either fall or Antarctic basaltic eucrites (Sr: ~70 to ~100 µg/g, Ba: ~15 to ~60 µg/g; Barrat et al. 2003). This indicates that the influence of terrestrial weathering on this meteorite persists despite the use of the acetone–H_2O washing procedure. On the other hand, the ratios of Th/U (= 3.1) and Hf/Sm (= 0.8) in NWA 7188 are within the range of unweathered eucrites. These results indicate that terrestrial weathering of NWA 7188 in a hot desert environment has increased the concentration of Sr and Ba without modifying the Th/U and Hf/Sm ratios. Therefore, we consider that the concentrations of U, Sm, and possibly the rest of REEs have not been redistributed among minerals in NWA 7188 via terrestrial alteration, in which case the concentrations of these elements in the bulk rock and individual minerals of NWA 7188 represent the original values that were acquired on the meteorite parent body.

Classification of NWA 7188

The Fe/Mn ratio of pyroxene and the oxygen isotopic composition of basaltic eucrites have been widely used as a means of evaluating potential genetic links between basaltic eucrites. Previous studies argued that pyroxene in Ibitira exhibits higher Fe/Mn ratios (33–39; 36.4 on average) than has been measured in the other basaltic eucrites (30 ± 2) (Papike et al. 2003; Mittlefehldt 2005). In addition, Ibitira has a distinct oxygen 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 TiO_2 concertation vs. FeO/MgO ratio, the main-group, Nuevo
382   Laredo-group, and Stannern-group eucrites plot in different fields, with the TiO_2
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 TiO_2 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 ~11 × 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 (Eu/Eu* = 0.76–0.78 and Gd_N/Lu_N =1.05–
406   1.16) (Barrat et al. 2011; Roszjar et al. 2011). The observation that the Eu/Eu* and Gd_N
407   /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

13

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 $\Delta^{17}O$ range measured for the main-group–Nuevo Laredo-group eucrites
416 (Fig. 6). NWA 7188 has a slightly elevated $\delta^{18}O$ 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 $\delta^{18}O$ 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 $100 \times \dfrac{MgO}{FeO+MgO}$) 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

15

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 <~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}Sm–^{143,142}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}Sm–^{143,142}Nd and ^{244}Pu–Xe ages are generally in reasonable agreement with each

535 other (Fig. 8c). The ^{147,146}Sm–^{143,142}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}Sm–^{143,142}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}Sm–^{143,142}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}Sm–^{143,142}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}Sm–

545 ^{143,142}Nd, ^{244}Pu–Xe, and U–Pb systems for bulk rocks and minerals, with the exception of

546 zircons.

547

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

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/cm^3) and pyroxene (density = 3.45–3.55 g/cm^3 and 3.55–3.7
574   g/cm^3) 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    $$D_{Pb\ in\ plagioclase} = 3.75 \times 10^{-6} \times e^{-327\ KJ\ mol^{-1}/RT}\ m^2\ s^{-1}$$

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

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

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

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 °C for plagioclase and

623   ~930 °C for pyroxene, whereas that for zircon is ~1040 °C. Therefore, the Sm–Nd closure

624   temperature of basaltic eucrites is most likely to be between ~855 °C and ~1040 °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 Å) compared to Nd (1.12

629   Å). Although the D_{Sm} values for pyroxene and plagioclase at ~1000 ℃ are not available

630   at present, it is conceivable that the D_{Sm} values for these minerals are also ~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
$$D_{\text{Nd in plagioclase}} = 5.9 \times 10^{-6} \times e^{-398\,\text{KJ mol}^{-1}/RT}\ \text{m}^2\ \text{s}^{-1}.$$

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

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

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 °C for plagioclase and ~865 °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 ℃ (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 $4554 \, ^{+17}/_{-19}$
674 Ma, respectively. The closure temperature of ^{147,146}Sm–^{143,142}Nd systems calculated in
675 this study suggests that the ^{147,146}Sm–^{143,142}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.

680 **Acknowledgments**

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688   **References**

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Figure Caption

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

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

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

Fig. 4. (a) TiO_2 (b) La and (c) Hf vs. FeO/MgO plots for NWA 7188 and various basaltic eucrites. In these plots, basaltic eucrites are distinguished into three different groups (main group, Nuevo Laredo group, and Stannern group). The FeO concentration is calculated as the total of Fe content. The data excluding NWA 7188 are taken from the compiled data of Mittlefehldt (2015).

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

Fig. 6. Oxygen three isotope plot showing the data for NWA 7188 (this study) and the other basaltic eucrites (Greenwood et al. 2017). Symbols are the same as Fig. 4. Gray field is 2σ of the data for eucrites and diogenite, falls only, and the eucrite fractionation line (EFL) is shown as dashed line of $\Delta^{17}O = -0.240 \pm 0.014$ (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]Sm–[143,142]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]Sm/[144]Sm ratio of Marks et al. (2014). The ages used for (a), (b), (c), and

1078   (d) are summarized in Table S2.