Geochemistry and petrography of martian meteorite Northwest Africa 11115: A rare earth element-enriched olivine-phyric shergottite closely linked to Northwest Africa 1068

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Abstract

The shergottite family of meteorites shows a remarkable petrographic and geochemical variety, revealing information about mantle processes and basalt formation on Mars. Northwest Africa (NWA) 11115, found in Morocco in 2016, is one of the newest meteorites in this family. We report bulk-rock major and trace element abundances of NWA 11115, bulk oxygen isotope systematics, and the petrography and mineralogy of a thick section, and compare the geochemistry of this recent find to other martian rocks. NWA 11115 is an olivine-phyric shergottite with an enriched rare earth element pattern, and shares similarities with NWA 1068, another enriched olivine-phyric shergottite. The large (< 2.5 mm) olivine phenocrysts are likely to be cumulates, similar to NWA 1068. However, the abundant maskelynite (~30 vol. %) in NWA 11115 places the bulk chemistry somewhat closer to the basaltic shergottites. We suggest that NWA 11115 is genetically linked to NWA 1068, perhaps crystallizing slightly above in the same cumulate pile. NWA 11115 contains one of the lowest K/Th ratios among the martian meteorites (K/Th = 2987 ± 810), and far lower than the surface of Mars (K/Th = 5300). Finally, while NWA 11115 contains abundant (~0.4 vol. %) fracture-filling calcite (presumably from hot desert alteration during its terrestrial residence), diagnostic bulk element mass ratios were not indicative of the presence of terrestrial alteration (Th/U [?] 4.09, Sr/Nd [?] 12.26, K/La [?] 526.94, Ce/Ce* [?] 1.01).

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21 Abstract

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37 1. INTRODUCTION

Northwest Africa (NWA) 11115 is a martian shergottite meteorite found at an undisclosed location in Morocco in 2016. A 34.2 g aliquot of the main mass (246.76 g) was donated to the Field Museum of Natural History (FMNH) in Chicago by T. Boudreaux, and its official name was approved in February 2017 (The Meteoritical Society 2017). Here, we describe the geochemistry, mineralogy and petrography of NWA 11115 in relation to other martian meteorites and the surface of Mars, we use oxygen isotope systematics to confirm its provenance, and we show that it belongs to the uncommon group of rare earth element (REE) enriched olivine-phyric shergottites.

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In the following work, we provide a general introduction to the shergottite meteorites to provide context for the study of NWA 11115. We then explain the analytical methods used to study chemical composition, oxygen isotopes, mineralogy and petrography of NWA 11115 in §2, and then report the detailed results of the analyses in §3. In §4, we discuss and interpret the results, focusing on the provenance of NWA 11115 and its relationship to other shergottites, and the evidence for terrestrial weathering. Finally, we provide our conclusions and suggestions for further study of NWA 11115 in §5.

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53 **1.1. Shergottites: a primer**

54 Martian meteorites probe the chemistry of the interior of Mars, and complement the analyses and 55 discoveries carried out by landed and orbiting spacecraft. The petrologic and geochemical properties of martian 56 materials are characteristic of specific geologic processes that occurred on Mars and can, for example, inform 57 about the degree of magmatic differentiation, volcanism, aqueous alteration and the effects of impact. 58 Therefore, every martian meteorite recovered is scientifically significant in that it can help unravel a portion 59 of Mars' geologic history. Until samples are returned from Mars, the only martian rocks physically available 60 for study in terrestrial laboratories are meteorites. Of the 152 currently named martian meteorites, the 61 shergottites are the most numerous group, comprising 132 rocks as of May 2021, not counting paired rocks, 62 i.e. fragments belonging to the same meteor (Irving 2021). The shergottites' geochemical, mineralogic and 63 petrographic characteristics have informed about the composition of the martian mantle, crust and atmosphere, 64 and about igneous processes and the formation of basalts on Mars.

65 Petrographically and mineralogically, the shergottites are broadly divided into the olivine-phyric, poikilitic 66 (formerly lherzolitic), and pyroxene-phyric/basaltic groups (e.g., Goodrich 2002; Papike et al. 2009). The 67 olivine-phyric shergottites (e.g. NWA 2990, Tissint and Yamato 980459) are related by their olivine-porphyritic 68 textures within finer-grained groundmass, with low augite contents, and with chromite in addition to Fe-Ti 69 oxides. The olivine-phyric shergottites represent rocks that crystallized from melt (e.g. Y-980459) or that 70 contain olivine crystal cumulates (Filiberto and Dasgupta 2011; e.g., Usui et al. 2008). The poikilitic 71 shergottites (e.g. Allan Hills 77005 and NWA 2646) are coarse-grained and the most olivine-rich (~30 - 60 72 vol. % olivine) of the shergottites. They additionally contain pyroxene, chromite and maskelynite, and are 73 likely cumulates (e.g., Goodrich 2002; Papike et al. 2009). On the other hand, the pyroxene-phyric/basaltic 74 meteorites (e.g. Zagami, Shergotty, NWA 7032, NWA 7635 and NWA 8159) are a diverse group containing 75 almost no olivine and chromite, but instead are almost entirely formed of augite, pigeonite and maskelynite, 76 and vary widely in their grain size, probably as a result of different cooling rates within lavas (e.g. Goodrich, 77 2002; Papike et al., 2009). Finally, polymict breccia NWA 7034 and its pairs contain numerous matrix-78 supported clasts of varying petrologic types and compositions that match the shergottite lithologies (e.g. Agee 79 et al., 2013; Humayun et al., 2013; Wittmann et al., 2015; Santos et al., 2015).

80 Separate from their petrologic grouping, shergottites are also divided geochemically into the light rare-earth 81 element (LREE) enriched, intermediate, and depleted groups (e.g. McSween, 1994; Filiberto, 2017), relative 82 to the abundance of their heavy REE (HREE), and CI chondrite REE concentrations. Enriched shergottites 83 (e.g. Shergotty and NWA 4468) have moderately flat REE abundance profiles with no significant enrichments 84 or depletions in any specific REE (La/Yb > 0.7). However, their REE abundances are all $\sim 10 \times$ enriched 85 relative to CI chondrites, most likely as a result of subsolidus equilibration, melt fractionation and assimilation 86 from crustal sources (e.g. Treiman, 1996; Borg and Draper, 2003; Papike et al., 2009). Depleted shergottites 87 (e.g. NWA 7032 and Tissint) have significantly different LREE concentrations relative to their HREE 88 abundances (La/Yb < 0.3), and the LREE tend to be depleted compared to CI chondrites (LREE < $1 \times CI$ 89 chondrite LREE). Finally, the intermediate shergottites are somewhat more enriched in HREE relative to LREE 90 $(0.3 \le \text{La/Yb} \le 0.7)$, and their overall REE abundances are somewhat elevated compared to CI chondrites $(1 - 1)^{-1}$ 91 $10 \times \text{CI}$ chondrite REE) (e.g. Papike et al., 2009; Taylor, 2013).

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93 2. ANALYTICAL METHODS

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2.1. X-ray computed tomography

Before cutting, the complete specimen of NWA 11115 was scanned using X-ray computer tomography (CT) with a GE v|tome|x s 240 scanner at the University of Chicago's PaleoCT lab. X-ray CT enabled us to quantify the porosity of the meteorite and the interconnectivity of the pores. We used a voltage of 190 kV and a current of 150 μ A at a voxel size of 30.3 μ m; a 0.5 mm Sn filter was used. The total scan time was 6 hours 43 minutes. The scan was performed in several segments that were stitched together in the reconstruction. We used the *Fiji* distribution of the *ImageJ* software (Schindelin et al. 2012) to analyze the tomographic dataset. The tomographic reconstruction is available in the electronic appendix.

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103 **2.2.** Mineralogy and petrography using electron microscopy

A chip of NWA 1115 was cut using water-free high-purity (Optima[™]) isopropanol with a low-speed Buehler IsoMet wafering saw outfitted with a thin diamond blade. The chip was embedded in a 1-inch diameter epoxy round (Buehler EpoxiCure® 2; pre-2016 formulation), polished with diamond film and water-free Optima[™] isopropanol, and coated with carbon for characterization by electron microscopy. The sample was analyzed at the FMNH with a Zeiss EVO 60 Scanning Electron Microscope (SEM) equipped with an Oxford Instruments X-Max 50 silicon drift detector, and at the University of Chicago with a TESCAN LYRA3 FIB- 110 SEM equipped with two Oxford Instruments X-Max-80 silicon drift detectors. Quantitative analyses of the 111 mineral compositions, backscattered electron (BSE) and elemental mapping were carried out with Oxford 112 Instruments energy dispersive spectroscopy (EDS) systems attached to both SEMs, with a 15 kV acceleration 113 voltage and a beam current of \sim 2-4 nA. We used a set of mineral reference standards to calibrate the EDS, and 114 calibrated and monitored stability of the e-beam current by using bracketed analyses of a Cu standard in 115 between 10 - 20 sample spots. We report only compositions that give total weights of 100 ± 2 wt. %. Oxford 116 Instruments' AZtec software was used to produce the raw BSE and element map images; Fiji and the GNU 117 Image Manipulation Program (GIMP) were used to produce image composites, for mineral phase mapping 118 and for modal mineralogy.

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2.2.1.Bulk composition using LA-ICP-MS

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122 Around 0.462 g of NWA 11115 were milled with an agate mortar to measure major and trace elements by 123 LA-ICP-MS on "Pressed Powder Pellets" following the protocol of Peters and Pettke (2017) at the University 124 of Bern. The USGS glass standard GSD-1G was used for instrument calibration. To check the accuracy of the 125 analyses the basaltic reference glass KL2-G was measured three times before and after the analyses of the 126 unknowns. Due to limited sample availability, we were not able to produce a powder with a grain size of below 127 5 μ m, and certain elements like Cr and P₂O₅ might thus be subjected to nugget effects (due to chromite and 128 apatite, respectively). Therefore, to obtain a representative average of the major and trace element 129 concentration of NWA 11115 we performed 27 consecutive analyses. Except for Cr, the mean and median 130 values of the 27 individual analyses agree to around \pm 5 % with each other, indicating that our data is 131 representative of the bulk rock. In addition, Se concentrations measured in the KL2-G standard differed from 132 the values reported in literature, so we consider the Se concentrations measured in NWA 11115 to be uncertain 133 and report them only in the Supplementary Spreadsheet File S1. We note that we reported preliminary bulk 134 geochemical analyses of this meteorite (Melwani Daswani et al. 2017), but that those results were likely 135 contaminated or affected by the sample preparation procedure. The results we report below are the authoritative 136 version. We include the sidelined analyses in the Supplementary Information for comparison and completion. 137

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2.2.2. Oxygen isotope systematics using laser fluorination

The oxygen isotopic composition of NWA 11115 was determined by infrared laser-assisted fluorination at the Open University on two aliquots of homogenized powder each weighing $\sim 2 \text{ mg}$ (Greenwood et al. 2017; Miller et al. 1999) at the Open University. These were loaded into a Ni sample block along with obsidian internal standards. The sample block was then positioned into a two-part chamber, made vacuum tight using a compression seal fitted with a copper gasket and clamped by a quick-release KFX clamp (Greenwood et al. 2017; Miller et al. 1999). Following loading, the cell was heated under vacuum for a minimum of 24 hours to a temperature in excess of 70 °C so as to remove any adsorbed atmospheric moisture. Prior to fluorination, the

- 146 system blank was systematically reduced by flushing the chamber with aliquots of BrF₅, with the final blank
- 147 being less than 60 nmol O₂. Sample heating in the presence of BrF₅ was carried out using an integrated 50 W
- 148 infrared CO_2 laser (10.6 μ m) and video system mounted on an X-Y-Z gantry supplied by Photon Machines Inc.
- 149 (Greenwood et al., 2017). After fluorination, the released O₂ was purified by passing it through two cryogenic
- 150 (liquid nitrogen) traps and over a bed of heated KBr. The isotopic composition of the purified oxygen was
- 151 analyzed using a Thermo Fisher MAT 253 dual inlet mass spectrometer (mass resolving power 200).
- 152 Interference at m/z = 33 by NF⁺ was monitored by performing scans for NF₂⁺ on the sample gas before
- 153 analyzing each sample; this was below interference levels during the analyses reported here. Our current
- 154 system precision based on repeat analyses (N = 39) of our obsidian internal standard is: ± 0.052 ‰ for δ^{17} O;
- 155 ± 0.094 ‰ for δ^{18} O; ± 0.017 ‰ for Δ^{17} O (2 σ) (Starkey et al. 2016).
- 156 Oxygen isotopic analyses are reported in standard δ notation, where $\delta^{18}O$ has been calculated as: $\delta^{18}O = 157 [({}^{18}O/{}^{16}O_{sample}/{}^{18}O/{}^{16}O_{ref}) 1] \times 1000 (\%)$ and, similarly, for $\delta^{17}O$ using the ${}^{17}O/{}^{16}O$ ratio. In order to compare our results with other published laser fluorination analyses of martian samples we have calculated $\Delta^{17}O$, which represents the deviation from the terrestrial fractionation line, as $\Delta^{17}O = \delta^{17}O 0.52 \times \delta^{18}O$.
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161 **3. RESULTS**

162 **3.1. Petrography and mineralogy**

163 The 1-inch round polished thick section of NWA 11115 consists of about 4 % pore space. We report the 164 porosity-removed modal mineralogy: olivine forms approximately 14 %, pyroxene (mainly pigeonite) forms 165 \sim 50 %, and plagioclase (as maskelynite) around \sim 30 %. The remainder consists of \sim 0.3 % sulfides, \sim 0.3 % 166 orthopyroxene, ~ 2 % Fe-Ti-Cr-oxides, ~ 2 % phosphates, and trace K-feldspar and silica (Figure 1). Abundant 167 $(\sim 0.4\%)$ secondary Mg-rich calcite (almost certainly produced by terrestrial fluids) infills pores, especially 168 within the numerous cracks in and around olivine grains. Most mineral phases are medium grained and 169 subhedral, except for sulfides and Fe-oxides, which are fine-grained. Olivine crystals up to 2.5 mm across are 170 visible, along with elongated grains of pyroxene of about the same length. Maskelynite infills the interstices 171 between grains, and mineral grains follow no preferential orientation. Also visible within the section are 172 numerous shock melt pockets of mixed pyroxene and feldspathic glass. Overall, the large grain size of the 173 olivine and pyroxene in the sample is consistent with martian gabbros (e.g. NWA 6963; Filiberto et al., 2014) 174 rather than typical olivine-phyric shergottites, whose olivine grains are significantly larger than the remaining 175 mineral phases (mostly pyroxene and plagioclase), and which form a fine-grained groundmass or matrix (e.g. 176 NWA 6234/2990; Gross et al., 2013). However, the modal mineralogy of NWA 11115 lies between pyroxene-177 phyric/basaltic and olivine-phyric shergottites, i.e. it contains significant amounts of plagioclase, but also 178 contains olivine. The tomographic reconstruction shows the same lithology throughout the complete sample 179 of NWA 11115 (electronic appendix), thus, we infer that the polished section is a representative sample of the 180 entire rock. Average compositions of the main mineral phases are shown in Table 1. 181



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Figure 1. BSE image mosaic of a representative section of NWA 11115. Refractory phases are colored in the image in order to distinguish them: chromite grains are red, ilmenite grains are blue, and sulfides are yellow. Black areas are secondary pores and fractures.

| | ^a Oliv | vine | ^b Pigeor | nite | Enstat | ite | Aug | ite | Maskelyn | ite |
|-------------------------------|-------------------|---------------|---------------------|---------------|------------------|------|-------|---------------|----------|------|
| | N = | 57 | N = 2 | .4 | N = | 8 | N = | 2 | N = 74 | |
| | Wt. % | $\pm 1\sigma$ | Wt. % | $\pm 1\sigma$ | Wt. % | ±1σ | Wt. % | $\pm 1\sigma$ | Wt. % | ±1σ |
| SiO_2 | 34.68 | 1.91 | 51.60 | 1.07 | 53.95 | 0.42 | 21.22 | 0.54 | 55.81 | 1.22 |
| TiO_2 | nd ^c | - | 0.22 | 0.17 | bdl ^d | - | 0.37 | 0.04 | bdl | 0.03 |
| Al_2O_3 | nd | - | 1.54 | 0.33 | 0.45 | 0.20 | 1.54 | 0.33 | 27.10 | 0.81 |
| Cr_2O_3 | nd | - | 0.40 | 0.19 | 0.41 | 0.06 | 0.63 | 0.02 | nd | - |
| FeO _T ^e | 41.00 | 9.35 | 20.94 | 3.28 | 16.49 | 0.27 | 17.14 | 2.32 | 0.76 | 0.17 |
| MnO | 0.78 | 0.18 | 0.69 | 0.14 | 0.58 | 0.06 | 0.60 | 0.01 | nd | - |
| MgO | 22.71 | 7.87 | 18.60 | 3.02 | 25.03 | 0.31 | 16.09 | 1.01 | 0.02 | 0.05 |
| CaO | 0.26 | 0.11 | 5.26 | 1.35 | 2.21 | 0.12 | 11.32 | 2.40 | 9.90 | 0.93 |
| NiO | nd | - | nd | - | nd | - | nd | - | nd | - |
| Na ₂ O | nd | - | bdl | - | bdl | - | bdl | - | 5.40 | 0.42 |
| K ₂ O | nd | - | nd | - | nd | - | nd | - | 0.34 | 0.09 |
| Р | 0.03 | 0.09 | bdl | - | bdl | - | bdl | - | nd | - |
| S | 0.05 | 0.27 | nd | - | nd | - | nd | - | nd | - |
| Total | 99.50 | 0.81 | 98.71 | 0.59 | 99.11 | 0.87 | 98.89 | 1.12 | 99.34 | 0.93 |
| Mg# | 48.88 | 14.29 | 61.03 | 7.46 | 73.02 | 0.41 | 62.66 | 1.70 | | |
| Fe/Mn | 53.01 | 6.43 | 30.44 | 2.79 | 28.84 | 2.80 | 28.53 | 3.19 | | |

Table 1. Average major oxide concentrations of the major phases in the thick section.

| Fo | 48.88 | 14.29 | | | | | | | | | |
|----|-------|-------|-------|------|-------|------|-------|------|-------|------|--|
| Wo | | | 11.11 | 2.94 | 4.43 | 0.24 | 24.08 | 5.51 | | | |
| Fs | | | 34.55 | 6.21 | 25.79 | 0.34 | 28.39 | 3.35 | | | |
| An | | | | | | | | | 49.30 | 4.42 | |
| Ab | | | | | | | | | 48.66 | 3.95 | |
| Or | | | | | | | | | 2.05 | 0.57 | |
| | | | | | | | | | | | |

^aThe compositions of zoned olivine are averaged for modeling bulk mineral abundance. See text for
 chemical zoning of olivine. ^bSee Fig. 3 for compositions of zoned pigeonite. ^cNot determined. ^dBelow detection
 limit. ^eIncludes Fe₂O₃.

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188 *3.1.1.Olivine*

189 Olivine crystals in NWA 11115 are 250 µm to 2.5 mm in size and are mostly subhedral. All olivine grains show

some degree of chemical zonation from core to rim, although the larger crystals more strongly so (\sim Fo₇₀ to Fo₄₅); smaller olivine grains are much more ferroan (\sim Fo₂₁ to Fo₃₅). Some larger olivine crystals appear to form

191 Fo₄₅); smaller olivine grains are much more ferroan (\sim Fo₂₁ to Fo₃₅). Some larger olivine crystals appear to form

192 clumps or glomerophyres consisting of annealed crystals, and each sub-crystal contains its own distinct

193 chemical zonation from core to rims (Figure 2). We address the origin of the olivine crystals in §4.1.



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Figure 2. False color composites of an olivine glomerophyre surrounded by maskelynite and pigeonite, and with numerous spinel grains. A) Red = iron, green = magnesium, blue = silicon. B) Cyan = calcium, yellow = sulfur, magenta = aluminum. Abundant calcite (arrows) infills fractures in the olivine phenocrysts, The scale bar is 2.5 mm across.

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196 *3.1.2.Pyroxene*

197 Most pyroxene crystals in the meteorite are subhedral to anhedral pigeonite, with grain sizes comparable 198 to the olivine grains, reaching up to ~ 2 mm in length. The pigeonite crystals are compositionally zoned from 199 core to rim (Figure 1 & Figure 2). Enstatite and augite are also present as accessory grains in the sample.

200 Analyzed pyroxene compositions are shown in Table 1 and Figure 3.





Figure 3. Compositional variability of the pyroxenes in NWA 11115. Darker points indicate lower Fe/Mn mass ratios and lighter points represent higher Fe/Mn mass ratios.

203 *3.1.3.Maskelynite*

Plagioclase feldspar in NWA 11115 is found in the form of maskelynite. Most of the plagioclase is K-poor (< 0.5 wt%) and does not exhibit substantial compositional variation (Table 1), however, some accessory Kenriched plagioclase does occur (K \approx 5–10 wt. %; Figure 4). These K-enriched alkali feldspar zones are most often found adjacent to Ca-rich phosphate minerals and Cr-Fe-Ti-oxides (Figure 4).

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Figure 4. Complex mineral intergrowths of K-rich plagioclase, phosphate, and Cr-Fe-Ti spinel. A) BSE image. B) False color composite. Red = iron, green = phosphorus, blue = potassium, background = silicon. Mineral abbreviations are: Msk = maskelynite, Kplag = K-rich plagioclase, Phs = phosphate, Pgt = pigeonite, Ol = olivine, Ilm = ilmenite, Slf =sulfide.

211 *3.1.1.Iron oxides and sulfides*

Spinel minerals are abundant throughout NWA 11115, poikilitically growing in olivine and pyroxene grains, but also occurring separately adjacent to olivine and pyroxene grains. The spinel minerals are intergrown magnesian chromite – hercyinite – ulvöspinel solid solutions (Table 2 and Figure 5), that occasionally also intergrow with sulfides (Figure 4). Individually measured compositions are therefore variable, as for example in their TiO_2 concentration. Spinel grains with higher concentration of magnesium also tend to have higher concentration of aluminum and lower concentration of chromium (Figure 5). Spinels with higher concentration of Ti tend to occur in contact with phosphates and K-rich feldspar (Figure 4).

| | | Wt. % | | | | |
|------------------|-------|---------------|-------------------|---------------|--|--|
| | Mean | 25 % quartile | Median | 75 % quartile | | |
| SiO ₂ | 0.36 | 0.30 | 0.35 | 0.38 | | |
| TiO ₂ | 1.68 | 0.69 | 0.77 | 0.89 | | |
| Al_2O_3 | 6.63 | 6.34 | 6.64 | 6.83 | | |
| Cr_2O_3 | 53.51 | 55.65 | 56.26 | 56.69 | | |
| V_2O_3 | 0.52 | 0.40 | 0.44 | 0.59 | | |
| $Fe_2O_3^a$ | 3.52 | 2.29 | 2.52 | 2.97 | | |
| FeO | 29.38 | 26.69 | 29.38 | 30.03 | | |
| MnO | 0.60 | 0.52 | 0.61 | 0.67 | | |
| MgO | 3.12 | 2.27 | 2.68 | 4.31 | | |
| CaO | 0.01 | 0 | 0 | 0 | | |
| ZnO | 0.14 | 0.01 | 0.11 | 0.24 | | |
| Total | 99.46 | 99.18 | 99.52 | 99.82 | | |
| | | | | | | |
| | | | apfu ^c | | | |
| Si | 0.01 | 0.01 | 0.01 | 0.01 | | |
| Ti | 0.05 | 0.02 | 0.02 | 0.02 | | |
| Al | 0.28 | 0.27 | 0.28 | 0.28 | | |
| Cr | 1.50 | 1.54 | 1.57 | 1.59 | | |
| V | 0.01 | 0.01 | 0.01 | 0.02 | | |
| Fe ³⁺ | 0.09 | 0.06 | 0.07 | 0.08 | | |
| Fe ²⁺ | 0.87 | 0.79 | 0.88 | 0.89 | | |
| Mn | 0.02 | 0.02 | 0.02 | 0.02 | | |
| Mg | 0.16 | 0.12 | 0.14 | 0.23 | | |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 | | |
| Zn | 0.00 | 0.00 | 0.00 | 0.01 | | |

Table 2. Composition of spinel group minerals in NWA 11115 (n = 42).

| Total | 3.00 | 3.00 | 3.00 | 3.00 |
|-----------------------------------------------|---------------|----------------|-----------------|------|
| | Atomic | ratios | | |
| $Mg/(Mg+Fe^{2+})$ | 0.16 | 0.12 | 0.14 | 0.22 |
| Cr/(Cr+Al) | 0.84 | 0.83 | 0.85 | 0.85 |
| Fe ³⁺ /(Fe ³⁺ +Al+Cr) | 0.06 | 0.03 | 0.04 | 0.04 |
| Ti/(Ti+Al+Cr) | 0.03 | 0.01 | 0.01 | 0.01 |
| | | | | |
| | Endmember mol | ar composition | on ^d | |
| $MgAl_2O_4^e$ | 0.02 | 0.02 | 0.02 | 0.03 |
| $FeAl_2O_4^{\rm f}$ | 0.12 | 0.11 | 0.12 | 0.12 |
| $MgFe^{3+}{}_{2}O_{4}{}^{g}$ | 0.01 | 0.00 | 0.01 | 0.01 |
| $Fe^{2+}Fe^{3+}_{2}O_{4}^{h}$ | 0.04 | 0.02 | 0.03 | 0.03 |
| $MgCr_2O_4{}^i$ | 0.12 | 0.09 | 0.11 | 0.18 |
| FeCr ₂ O ₄ ^j | 0.63 | 0.59 | 0.64 | 0.69 |
| MnCr ₂ O ₄ ^k | 0.01 | 0.01 | 0.01 | 0.02 |
| $FeV_2O_4^{l}$ | 0.01 | 0.00 | 0.01 | 0.01 |
| Fe ₂ TiO ₄ ^m | 0.02 | 0.01 | 0.01 | 0.01 |

^aCalculated on the basis of stoichiometry, using the method of Droop (1987) implemented in Ferracutti et al. (2015). ^bBelow detection limit. ^cAtoms per formula unit. ^dCalculated with the End-Members Generator (Ferracutti et al. 2015), for spinel group minerals with the formula $X^{2+}Y^{3+}_{2}O_{4}$, for a total charge of 8, normalized here to 1 mol. ^eSpinel. ^fHercynite. ^gMagnesioferrite. ^hMagnetite. ⁱMagnesiochromite. ^jChromite. ^kManganochromite. ^hCoulsonite. ^mUlvöspinel.

225



Figure 5. Compositional diversity in spinel group minerals analyzed in NWA 11115 (n = 42). All spinel minerals analyzed are Cr-rich.

227

3.1.2.Phosphates

Phosphates in NWA 11115 consist primarily of subhedral, elongated (up to ~0.6 mm) and fractured
merrillite crystals, although minor amounts of chlorine-bearing apatite are also found in the sample (Table 3).
Phosphate crystals are typically found in contact with K-rich feldspar and Cr-Fe-Ti spinels (Figure 4).

232

Table 3. Phosphates in NWA 11115.

| | Apatite | Merril | lite |
|-------------------|-------------------|--------|---------------|
| | N = 1 | N = 2 | 25 |
| Elements | Wt. % | Wt. % | $\pm 1\sigma$ |
| 0 | 39.63 | 41.67 | 0.44 |
| Na | bdl ^a | 1.24 | 0.17 |
| Mg | bdl | 1.37 | 0.12 |
| Al | bdl | 0.01 | 0.03 |
| Si | 0.24 | 0.07 | 0.13 |
| Р | 18.62 | 20.42 | 0.31 |
| S | bdl | 0.02 | 0.11 |
| Cl | 1.34 | bdl | nd |
| Ca | 37.85 | 33.04 | 0.36 |
| Mn | bdl | 0.02 | 0.05 |
| Fe | 0.70 | 2.31 | 0.25 |
| Total | 98.37 | 100.10 | 0.99 |
| Calculated OH (= | 0.20 | | |
| 100 - total - Cl) | 0.29 | - | - |
| | | | |
| | apfu ^b | apfu | $\pm 1\sigma$ |
| O ^c | 12 | 28 | - |
| Na | 0 | 0.58 | 0.08 |
| Mg | 0 | 0.61 | 0.05 |
| Al | 0 | 0 | 0.01 |
| Si | 0.04 | 0.03 | 0.05 |
| Р | 2.91 | 7.09 | 0.06 |
| S | 0 | 0.01 | 0.04 |
| Cl | 0.18 | 0 | - |
| Ca | 4.58 | 8.86 | 0.11 |
| Mn | 0 | 0 | 0.01 |
| Fe | 0.06 | 0.44 | 0.05 |
| Total +1 cations | 0 | 0.58 | 0.08 |

 $\Sigma + 2$ and + 3 cations 4.64 9.92 0.09

^aBelow detection limit. ^bAtoms per formula unit. ^cCations are normalized to the ideal number of oxygen atoms
per formula unit, i.e. 12 oxygen atoms in apatite (Ca₅(PO₄)₃(F,Cl,OH)) and 28 oxygen atoms in merrillite
(Ca₉NaMg(PO₄)₇).

236

3.1.3.Melt pockets

238 The numerous melt pockets in NWA 11115 appear to be composed of a mixture of primary minerals. 239 Representative chemical analyses of three melt pockets are shown in Table 4. We used least-squares regression 240 to calculate the mixing ratio of each of the mineral components that form three representative melt pockets. 241 As mineral endmembers, we used the mean of the olivine, pyroxene (including enstatite, pigeonite and augite), 242 maskelynite, merrillite and spinel compositions of NWA 11115 that we report here (Table 1 to Table 3). 243 Additionally, we added stoichiometric pyrite as an endmember since we have not yet carried out detailed 244 analyses of the sulfide compositions in the meteorite. The results of the regression calculation are shown in 245 Table 4.

Table 4. Compositional analyses of three melt pockets in NWA 11115, and results of the linear least-squares regression calculation to determine the proportion of mineral phase endmembers that form the melt pockets.

| | Melt p | ocket 1 | Melt p | ocket 2 | Melt p | ocket 3 |
|--------------------------------------|------------------|---------------|--------|---------------|--------|----------|
| | Ν | = 2 | Ν | = 3 | Ν | = 1 |
| | Wt. % | $\pm 1\sigma$ | Wt. % | $\pm 1\sigma$ | W | t. % |
| SiO ₂ | 50.17 | 0.32 | 48.91 | 1.26 | | 50.40 |
| TiO ₂ | 0.55 | 0.10 | 0.60 | 0.02 | | 0.38 |
| Al_2O_3 | 0.73 | 0.07 | 0.60 | 0.02 | | 0.90 |
| Cr_2O_3 | bdl ^a | - | 0.32 | 0.09 | | 0.36 |
| $\text{FeO}_{\text{T}}{}^{\text{b}}$ | 27.46 | 0.54 | 21.75 | 1.11 | | 23.80 |
| MnO | 0.78 | 0.01 | 0.54 | 0.05 | | 0.74 |
| MgO | 14.16 | 0.98 | 12.48 | 0.35 | | 16.08 |
| CaO | 5.72 | 0.47 | 9.27 | 0.76 | | 5.58 |
| Na ₂ O | bdl | - | 0.71 | 0.70 | | bdl |
| K ₂ O | bdl | - | bdl | - | | bdl |
| Р | bdl | - | 1.22 | 0.02 | | bdl |
| S | bdl | - | 1.05 | 0.19 | | bdl |
| Total | 99.55 | 0.27 | 101.03 | 1.05 | | 98.24 |
| Mg# | 47.86 | 2.23 | 50.58 | 1.96 | | 54.64 |
| Linear | Mixing | Standard | Mixing | Standard | Mixing | Standard |
| regression | ratio | Error | ratio | Error | ratio | Error |

| Olivine | 0.26 | 0.17 | 0.01 | 0.16 | 0.14 | 0.10 |
|----------------------------|------|------|------|------|------|------|
| Pyroxene | 0.66 | 0.20 | 0.82 | 0.19 | 0.79 | 0.12 |
| Plagioclase | 0.10 | 0.09 | 0.09 | 0.09 | 0.07 | 0.05 |
| Spinel | 0.00 | 0.05 | 0.01 | 0.05 | 0.01 | 0.03 |
| Merrilite | 0.01 | 0.03 | 0.06 | 0.04 | 0.01 | 0.02 |
| Pyrite | 0.03 | 0.05 | 0.06 | 0.04 | 0.02 | 0.03 |
| Adjusted R ² | | 0.98 | | 0.98 | | 0.99 |

^aBelow detection limit. ^bTotal Fe, including FeO and Fe₂O₃.

248

249 **3.1. Bulk-rock geochemistry**

Bulk sample chemistry of *Sample-UniBern* obtained by LA-ICP-MS (Table 5) revealed that NWA 11115 is
generally similar to other martian shergottites. Supplementary Table 1 contains the disregarded LA-ICP-MS
analysis carried out of *Sample-FMNH*, and an EMPA major element analysis on the same sample.

Bivariate Harker diagrams (Figure 6) allow for effective comparison of major element abundances between NWA 11115 and other martian meteorites. The concentration of major oxides in NWA 11115 is consistent with basaltic shergottites, apart from the MgO content, which lies between the average concentration in basaltic shergottites and in olivine-phyric shergottites (Figure 6). The average magnesium number $(100 \times Mg/(Fe +$ Mg)) of NWA 11115 is Mg# = 57.35. NWA 11115 shows an enriched REE pattern, similar to other enriched shergottites, between NWA 856 and Los Angeles (Figure 7).

Table 5. Whole rock chemistry of NWA 11115 Sample-UniBern, obtained by LA-ICP-MS from 27 repeat analyses. Oxides are reported in wt. %, and individual elements in $\mu g/g$. See Supplementary Information and Supplementary Spreadsheet File S1 for sidelined FMNH analyses and calibration measurements.

| | Mean | $\pm 2\sigma$ |
|-------------------|-------|---------------|
| SiO ₂ | 47.90 | 1.09 |
| TiO ₂ | 0.74 | 0.28 |
| Al_2O_3 | 6.53 | 0.97 |
| FeO _T | 20.97 | 1.43 |
| MnO | 0.51 | 0.03 |
| MgO | 12.27 | 0.74 |
| CaO | 8.67 | 0.48 |
| Na ₂ O | 1.30 | 0.18 |
| K ₂ O | 0.18 | 0.04 |
| P_2O_5 | 0.73 | 0.21 |
| Li | 4.34 | 0.50 |

| Be | 0.37 | 0.15 |
|----|---------|---------|
| В | 3.66 | 0.98 |
| Sc | 44.69 | 4.23 |
| V | 232.17 | 41.30 |
| Cr | 2348.05 | 1560.64 |
| Co | 47.00 | 4.04 |
| Ni | 138.03 | 20.90 |
| Cu | 15.44 | 4.62 |
| Zn | 91.22 | 13.44 |
| Ga | 14.79 | 2.52 |
| Ge | 0.80 | 0.12 |
| As | 0.19 | 0.04 |
| Rb | 6.86 | 2.91 |
| Sr | 56.13 | 6.77 |
| Y | 17.55 | 5.46 |
| Zr | 57.27 | 22.97 |
| Nb | 3.84 | 1.80 |
| Mo | 0.13 | 0.04 |
| Ag | 0.01 | 0.01 |
| Cd | 0.04 | 0.02 |
| In | 0.03 | 0.01 |
| Sn | 0.30 | 0.08 |
| Sb | 0.01 | 0.01 |
| Cs | 0.46 | 0.22 |
| Ba | 62.47 | 7.77 |
| La | 2.92 | 1.00 |
| Ce | 6.82 | 2.45 |
| Pr | 0.94 | 0.35 |
| Nd | 4.68 | 1.70 |
| Sm | 1.76 | 0.63 |
| Eu | 0.67 | 0.20 |
| Gd | 2.72 | 0.97 |
| Tb | 0.48 | 0.15 |
| Dy | 3.32 | 1.04 |
| Но | 0.68 | 0.21 |
| Er | 2.01 | 0.58 |
| Tm | 0.26 | 0.07 |
| Yb | 1.76 | 0.42 |

| Lu | 0.25 | 0.06 |
|-------------------|-------|-------|
| Hf | 1.69 | 0.60 |
| Ta | 0.18 | 0.09 |
| W | 0.50 | 0.15 |
| T1 | 0.03 | 0.01 |
| ²⁰⁸ Pb | 0.70 | 0.33 |
| Bi | 0.004 | 0.003 |
| Th | 0.51 | 0.14 |
| U | 0.13 | 0.02 |
| Mg# | 57.35 | 1.68 |

^aAt or below the detection limit. Values represent maximum concentration measured.



Figure 6. Harker diagram of major oxides in the bulk compositions of martian meteorites. Data for other meteorites are from the compilation by Filiberto (2017).



Figure 7. Rare earth element concentrations in enriched martian meteorites normalized to concentrations in CI chondrites. Data for CI chondrites are from the reported CI chondrite mean composition in Dauphas and Pourmand (2015), data for Shergotty and Zagami are from Barrat et al. (2001), and data for NWA 856 and Los Angeles are from the ICP-MS results by Jambon et al. (2002).



266

Figure 8. Comparison of K vs. Th concentration in NWA 11115 (red point), other martian meteorites (blue points), CI chondrites (green crossed diamond), bulk silicate Mars (orange square), bulk silicate Earth (yellow triangle) and Mars Odyssey's Gamma Ray Spectrometer measurements of the martian surface (black trend line). The blue line is a linear regression between all martian meteorites on the plot, apart from NWA 11115, and the grey area marks the 95 % confidence interval. Data for the martian meteorites apart from NWA 11115 are from the compilation by Filiberto (2017), CI chondrite data and bulk silicate Earth data are from McDonough and Sun (1995), and bulk silicate Mars is from Taylor (2013).

268

3.2. Oxygen isotopes

Laser-assisted fluorination of two aliquots of NWA 11115 gave an average isotopic composition of: $\delta^{17}O = +2.823 \pm 0.017(2\sigma) \%$, $\delta^{18}O = +4.796 \pm 0.072(2\sigma) \%$, and $\Delta^{17}O = 0.329 \pm 0.021(2\sigma) \%$ (where $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$). The data for NWA 11115 are shown in relation to other martian meteorites analyzed by laser fluorination (Fig. 6). The average $\Delta^{17}O$ of these martian samples is 0.307 ‰, i.e., slightly lower than the value obtained for NWA 11115 (Figure 9). However, the mean martian $\Delta^{17}O$ value of Franchi et al. (1999) is 0.321, i.e., closer to the value for NWA 1115. Thus, the oxygen isotope composition of NWA 11115 is consistent with it being a martian sample.



Figure 9. Oxygen isotope composition of NWA 11115 (error bars 2σ) and other martian meteorites analyzed by laser fluorination. MFL* is the mean $\Delta^{17}O$ of all the samples plotted in Fig. 6 with the exception of NWA 11115 and has a value of 0.307. TFL is the terrestrial fractionation line. Data: Franchi et al. (1999) and Meteoritical Bulletin Database oxygen isotope analyses for Tissint, DaG 478, DaG 670, JaH 479, LAR 06319, NWA 1669, NWA 2737, NWA 4222, NWA 5718, NWA 5790, NWA 6162, NWA 7032, NWA 7042, SaU 094, Y-000027, Y-000047, Y-000097.

278

279 4. DISCUSSION

Concentrations of elements between martian meteorites can be compared to understand the provenance and the relationship between martian rocks. Bulk element mass ratios of NWA 11115 (Fe/Mn, Na/Al, etc.) are typical of other martian meteorites, and more specifically shergottites (Table 6) although the whole-rock K/Th ratio (~ 2987) is significantly lower than the average surface of Mars (Taylor et al. 2006) and is also on the lower end compared to other martian meteorites (Figure 8).

285

Table 6. Element mass ratios used for provenance tests. Martian meteorite average ratios from Taylor (2013) unless otherwise noted.

Sample-UniBernMartian meteorite meanRatio $\pm 2\sigma$ Ratio $\pm 2\sigma$ Ratio

Martian meteorite tests

| Fe/Mn | 41.4 | 1.7 | 40.3 | 2.3 |
|--------------------|---------|--------|-------------------|--------------|
| Ni ppm/Mg wt.% | 18.649 | 2.465 | 17.946 | Nd |
| K/Th | 2987 | 810 | 5300 ^a | 220ª |
| P/Yb | 1802.14 | 211.60 | 2065.27 | Nd |
| Ga ppm/Al wt.% | 4.284 | 0.625 | 4.067 | Nd |
| Na/Al | 0.278 | 0.015 | 0.247 | Nd |
| MgO wt. %/Cu ppm | 0.812 | 0.242 | 0.611 | Nd |
| Shergottite tests | | | | |
| Rb/La | 2.3822 | 1.0451 | 2.9066 | Nd |
| Rb/K | 0.0045 | 0.0012 | 0.0047 | Nd |
| Cs/La | 0.1613 | 0.0781 | 0.1805 | Nd |
| Weathering tests | | | | |
| Th/I⊺ | 4.00 | 0.77 | >0.2 (ur | weathered) |
| | 4.09 | 0.77 | <0.2 | (weathered) |
| Sr/Nd | 12.26 | 3.53 | | |
| C_{a}/C_{a}^{*b} | 1.01 | 0.04 | < | 1 (leached) |
| | 1.01 | 0.04 | > 1 (oxidized of | or enriched) |
| K/La | 526.94 | 154.59 | | |

^aGlobal surface average from the Gamma Ray Spectrometer on Mars Odyssey (Taylor et al. 2006).

^bCI chondrite Ce abundance from Dauphas and Pourmand (2015).

288

289 4.1. Provenance on Mars

290 The relationship between Ti and K concentrations in martian meteorites and surface rocks on Mars has 291 previously been used to discern between processes that affected the rocks on the path to crystallization, as well 292 as post-crystallizaton processes such as metasomatism (e.g. Treiman and Filiberto, 2015; Filiberto, 2017). 293 Similarly, the relationship of bulk MgO vs. bulk Al₂O₃ also tracks the degree of igneous crystallization and 294 accumulation processes, since earlier crystallizing phases (forsteritic olivine, Mg-pyroxene) tend to be richer 295 in magnesium and poorer in aluminum, whereas later crystallizing phases (plagioclase feldspar) follow the 296 opposite trend (e.g. Filiberto, 2017). NWA 11115 is somewhat closer to the olivine-phyric shergottites in its Ti vs. K relationship (Figure 10), but on the other hand, it is more in line with the basaltic shergottites, when 297 298 comparing the relationship between MgO and Al₂O₃ (Figure 11). From these relationships, we would assume 299 that NWA 11115 crystallized relatively early on and did not experience much igneous fractionation (increasing 300 Al₂O₃) or mantle metasomatism (increasing K; Schmidt et al. 2014). However, this is at odds with the 301 moderately high bulk SiO₂ content (Figure 6 and Table 5), the large modal abundance of plagioclase feldspar 302 within NWA 11115, as well as abundant phosphates, which typically form later in the crystallization sequence. 303 Additionally, the highly enriched REE nature of the sample also appears to preclude early crystallization, 304 unless the mantle source of NWA 11115 was especially REE-enriched.

- 305 Overall, the petrography and major element geochemistry closely resemble those of NWA 1068. NWA 1068 is 306 an olivine-phyric shergottite with a similar modal mineralogy, petrography and bulk geochemistry (Barrat et 307 al. 2002; Filiberto et al. 2010). The only significant differences between the meteorites appear to be the slightly higher SiO₂ and lower MgO content of NWA 11115 (SiO₂ = 45.78 wt. % and MgO \approx 16.64 wt. % for NWA 308 309 1068), which can be accounted for by the decreased olivine modal abundance in NWA 11115 relative to NWA 310 1068 (~14 % vs ~22%, Barrat et al. 2002). We note, however, that the bulk SiO₂ concentration was not reported 311 for NWA 1068 by Barrat et al. (2002), but estimated by Filiberto et al. (2010). Thus, the petrologic experiments 312 by Filiberto et al. (2010) for NWA 1068 apply to NWA 11115 also: all the olivine in the meteorite are likely to 313 be settled cumulate crystals, and NWA 11115 probably originated in the same magmatic event close to, or 314 slightly above the NWA 1068 in the cumulate pile, which would be consistent with the somewhat more REE-315 enriched chemistry and differences in modal mineralogy. 316 The analyzed melt pockets are intriguing in that their compositions consistently undersample the plagioclase 317 composition of NWA 11115: while the meteorite is composed of ~ 30 vol. % maskelynite, the melt pockets 318 appear to be composed of < 10 wt. % maskelynite (as is apparent from the low Al₂O₃; Table 4) and > 66 wt. % 319 pyroxene (Table 4), which, even accounting for the lower density of plagioclase relative to pyroxene, is a 320 significant mismatch. In addition, the melting temperature of plagioclase is lower than that of pyroxene, so the 321 plagioclase composition should form a larger mass fraction of the melt pockets, unless shock melting is favored
- 322 by frictional heating along the grain boundaries of the large phenocrysts, i.e. olivine and pyroxene. Frictional 323 heating as the main mechanism for melt production would be consistent with the feathered texture along olivine

and pyroxene grains where melt pockets are found.

324 325



Figure 10. Semilog graph of bulk Ti concentration (wt. %) vs. bulk K concentration (wt. ppm). Data adapted from Filiberto (2017), with new data for NWA 11115. A data point from a Fe-Ti-P-rich clast of NWA 7034 is not plotted, as it contains high Ti concentration and lies far from the center of the graph.



327

*Figure 11. Bulk MgO wt. % vs. bulk Al*₂O₃ *wt. % in NWA 11115 and other martian meteorites. Data for meteorites other than NWA 11115 are from the compilation by Filiberto (2017).*

329

4.2. Terrestrial weathering

331 Bulk Th/U, Sr/Nd, and K/La mass ratios are often used as proxies for the degree of weathering meteorites 332 experienced during their residence on Earth (e.g. Barrat et al. 2001; Taylor 2013; Taylor et al. 2002), measuring 333 the relative excess of aqueously mobile versus immobile elements. Preferential depletion or enrichment of 334 cerium is also a common result of terrestrial weathering in meteorites (Crozaz et al. 2003; e.g. Floss and Crozaz 1991, 1993), which either causes the removal of Ce^{3+} by dissolution of REE-rich phases (e.g. Ca-phosphates), 335 or oxidizes the relatively soluble Ce³⁺ to relatively insoluble Ce⁴⁺, thereby enriching Ce in the sample relative 336 337 to REEs with similar masses (La and Pr). We quantify Ce concentration anomalies, by calculating the "Ce/Ce*" 338 ratio as in Dauphas and Pourmand (2015):

$$\frac{Ce}{Ce^*} = \frac{Ce_N}{La_N^{0.48} \times Pr_N^{0.52}}$$
(1)

where Ce_N , La_N , and Pr_N are the concentrations of these REE elements in the sample normalized to the concentrations of these in CI chondrites. (We use the CI chondrite values reported in Dauphas and Pourmand (2015).)

By these measures, NWA 11115 is, if at all, only slightly affected by terrestrial weathering: the Th/U ratio is near-chondritic, the relatively high Sr is tracked by high Nd, and the Ce/Ce^{*} ratio is close to 1 (Table 6). In addition, the bulk oxygen isotopes place the meteorite far from the terrestrial fractionation line (Figure 9). However, the meteorite clearly contains an abundance of large fractures infilled with calcite (e.g. Figure 2) and

other secondary phases, so the discrepancy is puzzling. A possible explanation is that the alteration was largely 346 347 isochemical, requiring only atmospheric water to react with the mineral phases in the meteorite to form the 348 alteration phases, the positive and negative Ce anomalies balance out, and the absence of a terrestrial oxygen 349 signature could be attributed to the preparation procedure of the sample for laser-assisted fluorination. This is 350 an unsatisfying explanation, however, because the CO₂ required to form the carbonates was likely atmospheric, 351 and not indigenous to the meteorite. We note that abundant martian carbonates are found in the Allan Hills 352 84001 meteorite and some nakhlite meteorites (e.g. Lafayette, Nakhla, Governador Valadares, e.g. Bridges et 353 al., 2019). However, we argue that the alteration phases are likely terrestrial because the calcite-filled fractures 354 cross-cut the fusion crust (see CT scan in the electronic appendix). Future targeted analyses of the carbon 355 isotopes in the calcite could more conclusively determine their origin.

356

357 5. CONCLUSIONS

358 NWA 11115 is an enriched olivine-phyric shergottite with some unusual properties, but is otherwise 359 petrographically and geochemically similar to NWA 1068, albeit with a higher concentration of SiO₂ as a result 360 of higher maskelynite modal abundance at the expense of cumulate olivine crystals. The bulk K/Th ratio of 361 NWA 11115 is low (K/Th \approx 2987) compared to other martian meteorites (Figure 8), and the surface of Mars 362 (K/Th \approx 5300 (Taylor et al. 2006)). This could be related to fractional crystallization, as in some Zagami 363 lithologies (McCoy et al. 1999). However, the K abundance is not especially low compared to other martian 364 meteorites. Instead, NWA 11115 is Th enriched. Most likely, the large phosphate crystals are the hosts of the 365 Th (as well as U, also relatively enriched). We recommend further analyses of the phosphate minerals, which 366 we also suspect are the main hosts of the REE. Given the similarity of NWA 1068 with NWA 11115, we suggest 367 that these meteorites are genetically linked, with NWA 11115 somewhat higher up in the cumulate pile 368 suggested by its higher REE-enrichment, and the differences in modal mineralogy mentioned above. In 369 addition, the analyzed melt pockets in NWA 11115 are intriguing because their compositions undersample the 370 abundant maskelynite in the meteorite (Table 4). Finally, while NWA 11115 is likely altered, as evidenced by 371 the abundant fracture-filling calcite, trace element proxies for alteration (e.g. Sr/Nd) do not correlate with other 372 martian meteorites known to have experienced hot desert alteration (e.g. Dhofar 019 and Dar al Gani 476/489; 373 see Folco et al. 2000; Taylor et al. 2002). Further analyses of the alteration mineralogy are an area of interest 374 to understand its provenance and effects on the geochemistry of the meteorite.

375

Data Availability

All data are available in the Supplementary Information file, and at the following Zotero link: [DOI and linkto be made live after review].

379

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- 390
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- 1 Supporting Information for *Geochemistry and petrography of martian meteorite Northwest Africa 11115:*
- 2 A rare earth element-enriched olivine-phyric shergottite closely linked to Northwest Africa 1068
- 3 M. Melwani Daswani, N. D. Greber, Jinping Hu, R. C. Greenwood, and P. R. Heck
- 4
- 5 1 Comparison between previously reported bulk chemistry data and superseding new 6 analyses 7 A chip of NWA 11115 (Sample-FMNH) was homogenized by using an agate mortar and pestle, 8 yielding approximately 31 mg of powder. The powder was fluxed with LiBO₂ and fused and quenched 9 into five glass beads. The beads were mounted in an epoxy on one sample holder and polished. NIST 10 Standard Reference Materials (SRM) 610 and 612 were used for measurement calibration. NIST SRM 11 610 followed by two blanks was used for bracketing unknowns. We carried out a total of 24 repeat 12 analyses of the sample. Data were reduced using the SILLS software (Guillong et al. 2008).
- 13 The bulk composition of *Sample FMNH* was analyzed at the Field Museum of Natural History 14 (Chicago) using Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS). The LA-ICP-MS 15 setup at the Field Museum's Elemental Analysis Facility is a ThermoFisher Scientific iCAP Qc 16 Quadrupole ICP-MS Spectrometer coupled to a New Wave UP213 UV laser ablation system. For this

17 study a laser aperture resulting in a $100 \,\mu\text{m}$ spot size was used.

- The LA-ICP-MS analyses carried out at the FMNH resulted in some anomalous values, some of which (including previously unknown K/Th ratios for the martian meteorites and surface) were reported in Melwani Daswani et al. (2017). Because some dubious element abundances were obtained, we carried out electron probe microanalyses (EPMA) of the glass sample prepared for the FMNH to test its compositional homogeneity and whether the unusual analyses were caused by the instrument. EPMA analyses confirmed that the K concentration of the sample was low, but there were significant differences in the concentrations of other elements (Supplementary Table 1).
- 25 The EMPA analysis of FMNH-beats were performed using a JEOL 8200 electron microprobe 26 (WDS: 15 kV; 5 nA; beam defocused to 20 µm) interfaced with the Probe for EPMA program from Probe 27 Software, Inc. Standards for these analyses were synthetic fayalite (FeK α), Shankland forsterite (MgK α), 28 synthetic Mn2SiO4 (MnKa), synthetic anorthite (AlKa, SiKa, CaKa), Amelia albite (NaKa), Asbestos 29 microcline (KKa), synthetic TiO2 (TiKa), and synthetic Cr2O3 (CrKa). Quantitative elemental 30 microanalyses were processed with the CITZAF correction procedure (Armstrong 1995). Nominal ~85% 31 percent of LiBO₂ is added in Probe Software to correct for matrix effect and achieve near 100% oxide wt% 32 total. The LiBO₂ was later excluded for reporting the composition of FMNH-beats (supplementary Table 33 1).
- 34 As a result of the discrepancies between the analytical results of the same sample, and the unusual 35 element mass ratios (especially the low relative potassium: K/Th, K/La), we performed a separate LA-ICP-36 MS analysis at the University of Bern (Sample-UniBern), which is described in the Main Text, and we 37 include the calibration measurements and 27 spot analyses in the Supplementary Spreadsheet File S1. In 38 addition, we back-calculated the bulk rock chemistry from the modal mineralogy, and obtained a 39 composition that was significantly closer to Sample-UniBern (calculations shown in Supplementary 40 Spreadsheet File S1, and summarized results shown in Supplementary Table 3). Thus, we consider that the 41 results from Sample-UniBern supersede the Sample-FMNH analyses.

| | | | Sample | FM | NH | | | Sample-Un | iBern | |
|-------------------|-----------------|------------------|-----------------|----|----------|---------------|----------------|--------------|---------------|--|
| | | LA-ICP-I | MS | | EPMA Cal | ltech | | LA-ICP- | MS | |
| | n | Mean | $\pm 2\sigma$ | n | Mean | $\pm 2\sigma$ | n | Mean | $\pm 2\sigma$ | |
| SiO ₂ | 24 | 52.56 | 2.78 | 8 | 44.74 | 1.09 | 27 | 47.90 | 1.09 | |
| TiO ₂ | 24 | 0.96 | 0.03 | 8 | 0.45 | 0.75 | 27 | 0.74 | 0.28 | |
| Al_2O_3 | 24 | 8.08 | 1.00 | 8 | 10.16 | 0.87 | 27 | 6.53 | 0.97 | |
| FeO _T | 24 | 16.27 | 4.25 | 8 | 22.32 | 1.72 | 27 | 20.97 | 1.43 | |
| MnO | 24 | 0.50 | 0.03 | 8 | 0.72 | 0.41 | 27 | 0.51 | 0.03 | |
| MgO | 23 | 8.72 | 1.14 | 8 | 11.36 | 0.84 | 27 | 12.27 | 0.74 | |
| CaO | 24 | 10.15 | 1.39 | 8 | 8.66 | 0.45 | 27 | 8.67 | 0.48 | |
| Na ₂ O | 24 | 0.84 | 0.13 | 8 | 0.66 | 0.25 | 27 | 1.30 | 0.18 | |
| K ₂ O | 24 | 0.03 | 0.02 | 8 | 0.02 | 0.05 | 27 | 0.18 | 0.04 | |
| P_2O_5 | 20 | 0.78 | 0.02 | | | | 27 | 0.73 | 0.21 | |
| Li | | | | | | | 27 | 4.34 | 0.50 | |
| Be | 16 | 0.78 | 0.39 | | | | 27 | 0.37 | 0.15 | |
| В | | | | | | | 27 | 3.66 | 0.98 | |
| Cl | 18 | 415.54 | 313.22 | | | | | | | |
| Sc | 20 | 52.04 | 1.22 | | | | 27 | 44.69 | 4.23 | |
| V | 24 | 244.17 | 19.23 | | | | 27 | 232.17 | 41.30 | |
| Cr | 24 | 2555.65 | 200.91 | 8 | 2188.82 | 742.72 | 27 | 2348.05 | 1560.64 | |
| Co | 24 | 45.83 | 4.13 | | | | 27 | 47.00 | 4.04 | |
| Ni | 24 | 143.14 | 30.72 | | | | 27 | 138.03 | 20.90 | |
| Cu | 20 | 28.67 | 31.77 | | | | 27 | 15.44 | 4.62 | |
| Zn | 20 | 42.32 | 8.69 | | | | 27 | 91.22 | 13.44 | |
| Ga | 20 | 15.21 | 1.22 | | | | 27 | 14.79 | 2.52 | |
| Ge | | | | | | | 27 | 0.80 | 0.12 | |
| As | 24 | bdl ^a | nd ^b | | | | 27 | 0.19 | 0.04 | |
| Rb | 22 | 2.35 | 7.26 | | | | 27 | 6.86 | 2.91 | |
| Sr | 24 | 77.31 | 6.72 | | | | 27 | 56.13 | 6.77 | |
| Y | 24 | 19.04 | 2.01 | | | | 27 | 17.55 | 5.46 | |
| Zr | 24 | 79.15 | 9.11 | | | | 27 | 57.27 | 22.97 | |
| Nb | 24 | 5.29 | 0.60 | | | | 27 | 3.84 | 1.80 | |
| Mo | 24 | 3.28 | 0.66 | | | | 27 | 0.13 | 0.04 | |
| Ag | 4 | 0.26 | 0.24 | | | | 27 | 0.01 | 0.01 | |
| Cď | 12 | 0.36 | 0.72 | | | | 26 | 0.04 | 0.02 | |
| In | | 2.2.0 | | | | | 27 | 0.03 | 0.01 | |
| Sn | 23 | 0.71 | 0.95 | | | | 27 | 0.30 | 0.08 | |
| Sb | 17 | 0.72 | 0.88 | | | | 21 | 0.01 | 0.01 | |
| Cs | 22 | 0.28 | 0.50 | | | | 27 | 0.46 | 0.22 | |
| Ba | ${20}$ | 110.09 | 5.52 | | | | $\frac{-}{27}$ | 62.47 | 7.77 | |
| La | $\frac{1}{20}$ | 4 16 | 0.53 | | | | 27 | 2.92 | 1.00 | |
| Ce | 23 | 6 64 | 1 18 | | | | $\frac{2}{27}$ | 6.82 | 2 4 5 | |
| Pr | $\frac{23}{24}$ | 1.06 | 0.36 | | | | $\frac{2}{27}$ | 0.02 | 0.35 | |
| Nd | 24 | 4 81 | 0.30 | | | | 27 | 4 68 | 1 70 | |
| Sm | $\frac{24}{24}$ | 1.01 | 0.77 | | | | $\frac{2}{27}$ | 1 76 | 0.63 | |
| Fu | 23 | 0.82 | 0.72 | | | | $\frac{2}{27}$ | 0.67 | 0.05 | |
| Gd | $\frac{23}{24}$ | 2 96 | 0.27 | | | | $\frac{2}{27}$ | 0.07 7 77 | 0.20 | |
| Th | 23 | 0.64 | 0.00 | | | | $\frac{2}{27}$ | 0.48 | 0.15 | |
| 10 | 45 | 0.0- | 0.47 | | | | <u> </u> | 0.40 | 0.15 | |

Supplementary Table 1. Whole rock chemistry of two samples of NWA 1115. Oxides are reported in wt. %, and individual elements in $\mu g/g$.

| Dy | 23 | 3.74 | 0.64 | 27 | 3.32 | 1.04 |
|-------------------|----|-------|------|----|-------|-------|
| Но | 24 | 0.91 | 0.26 | 27 | 0.68 | 0.21 |
| Er | 23 | 2.29 | 0.55 | 27 | 2.01 | 0.58 |
| Tm | 24 | 0.40 | 0.18 | 27 | 0.26 | 0.07 |
| Yb | 24 | 2.00 | 0.41 | 27 | 1.76 | 0.42 |
| Lu | 20 | 0.41 | 0.17 | 27 | 0.25 | 0.06 |
| Hf | 24 | 2.49 | 0.37 | 27 | 1.69 | 0.60 |
| Та | 24 | 0.39 | 0.27 | 27 | 0.18 | 0.09 |
| W | 24 | 1.97 | 0.84 | 27 | 0.50 | 0.15 |
| Re | 3 | 0.05 | 0.01 | 0 | | |
| Au | 24 | bdl | nd | 0 | - | - |
| Tl | | | | 27 | 0.03 | 0.01 |
| ²⁰⁶ Pb | 14 | 1.26 | 1.42 | 0 | | |
| ²⁰⁷ Pb | 12 | 1.58 | 2.85 | 0 | | |
| ²⁰⁸ Pb | 14 | 0.76 | 0.74 | 27 | 0.70 | 0.33 |
| Bi | 17 | 0.19 | 0.33 | 20 | 0.004 | 0.003 |
| Th | 24 | 0.59 | 0.22 | 27 | 0.51 | 0.14 |
| U | 20 | 0.40 | 0.51 | 27 | 0.13 | 0.02 |
| Mg# | 23 | 58.24 | 3.30 | | | |

^aAt or below the detection limit. Values represent maximum concentration measured.

Supplementary Table 2. Element ratios used for provenance tests. Martian meteorite average ratios from Taylor (2013).

| | FMNH MS | LA-ICP- | Caltech EPMA Uni | | UniBern | LA-ICP-MS | Martian m average | eteorite |
|-------------------------------|------------|---------------|------------------|---------------|---------|---------------|----------------------|------------------|
| | Ratio | $\pm 2\sigma$ | Ratio | $\pm 2\sigma$ | Ratio | $\pm 2\sigma$ | Ratio | $\pm 2\sigma$ |
| Martian meteorite tests | | | | | | | | |
| Fe/Mn | 32.88 | 10.63 | 33.14 | 15.75 | 41.43 | 1.71 | 40.3 | 2.3 |
| K/Th | 464.29 | 308.80 | - | - | 2987.43 | 810.43 | 5300ª | 220 ^a |
| Cl/Th | 694.69 | 546.21 | - | - | - | - | 236.29 | Nd |
| P/Yb | 1694.51 | 457.88 | - | - | 1802.14 | 211.60 | 2065.27 | Nd |
| Ga ppm/Al wt.% | 3.47 | 0.28 | - | - | 4.28 | 0.62 | 4.067 | Nd |
| Na/Al | 0.15 | 0.04 | 0.09 | 0.04 | 0.28 | 0.02 | 0.247 | Nd |
| MgO wt%/Cu ppm | 0.37 | 0.16 | - | - | 0.81 | 0.24 | 0.611 | Nd |
| Shergottite tests | | | | | | | | |

| Rb/La | 0.54 | 1.70 | - | - | 2.38 | 1.05 | 2.9066 | Nd |
|------------------|-------|-------|---|---|--------|--------|--------|----|
| Rb/K | 0.01 | 0.03 | - | - | 0.005 | 0.001 | 0.0047 | Nd |
| Cs/La | 0.07 | 0.11 | - | - | 0.16 | 0.08 | 0.1805 | Nd |
| Weathering tests | | | | | | | | |
| Th/U | 2.05 | 1.91 | - | - | 4.09 | 0.77 | | |
| Sr/Nd | 16.13 | 2.34 | - | - | 12.26 | 3.53 | | |
| Ce/Ce*b | 0.78 | 0.12 | - | - | 1.01 | 0.04 | | |
| K/La | 57.92 | 25.57 | - | - | 526.94 | 154.59 | | |

^aGlobal surface average from the Gamma Ray Spectrometer on Mars Odyssey (Taylor et al. 2006).

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Supplementary Table 3. Back-calculation of the bulk chemical composition of NWA 11115 from the modal mineralogy, using the mean mineral compositions determined using spot analyses with the BSE SEM (see main text). Densities to derive the mass from the mode were obtained from the Handbook of Mineralogy (Anthony et al.). Since minor sulfide and silica phases were not analyzed, they are assumed to be pyrite and quartz for the purposes of recalculating the bulk composition. Slight discrepancies in the sum totals are due to rounding errors. Detailed calculation is found in the Supplementary Spreadsheet File S1.

| | Olivin | Clinopyroxe | Plagioclas | FeCrMnMgAl | Sulfide | Phosphat | Silic | Tota |
|--------------------------------|--------|-------------|------------|------------|---------|----------|-------|-------|
| | e | ne | e | Ti oxides | s | es | a | 1 wt. |
| | | | | | | | | % |
| Normalize | 14.36 | 50.60 | 30.62 | 1.91 | 0.30 | 2.11 | 0.10 | 100 |
| d mode | | | | | | | | |
| Normalize | 16.85 | 52.86 | 25.14 | 2.66 | 0.46 | 1.95 | 0.08 | 100 |
| d mass | | | | | | | | |
| SiO ₂ | 5.84 | 27.27 | 14.03 | 0.01 | nd | nd | 0.08 | 47.2 |
| | | | | | | | | 4 |
| TiO ₂ | nd | 0.12 | bdl | 0.04 | nd | nd | nd | 0.16 |
| Al ₂ O ₃ | nd | 0.81 | 6.81 | 0.18 | nd | <0.01 | nd | 7.81 |
| Cr ₂ O ₃ | nd | 0.21 | nd | 1.43 | nd | nd | nd | 1.64 |
| FeO _T | 6.91 | 11.07 | 0.19 | 0.88 | 0.14 | 0.05 | nd | 19.2 |
| | | | | | | | | 3 |
| MnO | 0.13 | 0.36 | nd | 0.02 | nd | nd | nd | 0.51 |
| MgO | 3.83 | 9.83 | 0.05 | 0.08 | nd | nd | nd | 13.7 |
| | | | | | | | | 9 |

| CaO | 0.04 | 2.78 | 2.49 | < 0.01 | nd | 1.03 | nd | 6.35 |
|-------------------|------|------|------|--------|------|--------|----|------|
| Na ₂ O | nd | bdl | 1.36 | nd | nd | 0.03 | nd | 1.39 |
| K ₂ O | nd | nd | 0.09 | nd | nd | nd | nd | 0.09 |
| Р | 0.01 | bdl | nd | nd | nd | 0.91 | nd | 0.92 |
| S | 0.01 | 0.03 | nd | nd | 0.09 | < 0.01 | nd | 0.13 |

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