1 Geochemistry and petrography of martian meteorite Northwest Africa 11115: A rare earth element-enriched
2 olivine-phyric shergottite closely linked to Northwest Africa 1068
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21 **Abstract**
22 The shergottite family of meteorites shows a remarkable petrographic and geochemical variety, revealing
23 information about mantle processes and basalt formation on Mars. Northwest Africa (NWA) 11115, found in
24 Morocco in 2016, is one of the newest meteorites in this family. We report bulk-rock major and trace element
25 abundances of NWA 11115, bulk oxygen isotope systematics, and the petrography and mineralogy of a thick
26 section, and compare the geochemistry of this recent find to other martian rocks. NWA 11115 is an olivine-
27 phyric shergottite with an enriched rare earth element pattern, and shares similarities with NWA 1068, another
28 enriched olivine-phyric shergottite. The large (< 2.5 mm) olivine phenocrysts are likely to be cumulates, similar
29 to NWA 1068. However, the abundant maskelynite (~30 vol. %) in NWA 11115 places the bulk chemistry
30 somewhat closer to the basaltic shergottites. We suggest that NWA 11115 is genetically linked to NWA 1068,
31 perhaps crystallizing slightly above in the same cumulate pile. NWA 11115 contains one of the lowest K/Th
32 ratios among the martian meteorites (K/Th = 2987 ± 810), and far lower than the surface of Mars (K/Th =
33 5300). Finally, while NWA 11115 contains abundant (~0.4 vol. %) fracture-filling calcite (presumably from
34 hot desert alteration during its terrestrial residence), diagnostic bulk element mass ratios were not indicative
35 of the presence of terrestrial alteration (Th/U $\approx$ 4.09, Sr/Nd $\approx$ 12.26, K/La $\approx$ 526.94, Ce/Ce* $\approx$ 1.01).
36

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.

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.

1.1. Shergottites: a primer

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

Petrographically and mineralogically, the shergottites are broadly divided into the olivine-phyric, poikilitic (formerly lherzolitic), and pyroxene-phyric/basaltic groups (e.g., Goodrich 2002; Papike et al. 2009). The olivine-phyric shergottites (e.g. NWA 2990, Tissint and Yamato 980459) are related by their olivine-porphyritic textures within finer-grained groundmass, with low augite contents, and with chromite in addition to Fe-Ti oxides. The olivine-phyric shergottites represent rocks that crystallized from melt (e.g. Y-980459) or that contain olivine crystal cumulates (Filiberto and Dasgupta 2011; e.g., Usui et al. 2008). The poikilitic shergottites (e.g. Allan Hills 77005 and NWA 2646) are coarse-grained and the most olivine-rich (~30 – 60 vol. % olivine) of the shergottites. They additionally contain pyroxene, chromite and maskelynite, and are likely cumulates (e.g., Goodrich 2002; Papike et al. 2009). On the other hand, the pyroxene-phyric/basaltic

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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 ~10 × 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 × CI

89 chondrite LREE). Finally, the intermediate shergottites are somewhat more enriched in HREE relative to LREE

90 (0.3 < La/Yb < 0.7), and their overall REE abundances are somewhat elevated compared to CI chondrites (1 –

91 10 × CI chondrite REE) (e.g. Papike et al., 2009; Taylor, 2013).

92

2.   ANALYTICAL METHODS

2.1. X-ray computed tomography

95   Before cutting, the complete specimen of NWA 11115 was scanned using X-ray computer tomography

96 (CT) with a GE v|tome|x s 240 scanner at the University of Chicago's PaleoCT lab. X-ray CT enabled us to

97 quantify the porosity of the meteorite and the interconnectivity of the pores. We used a voltage of 190 kV and

98 a current of 150 μA at a voxel size of 30.3 μm; a 0.5 mm Sn filter was used. The total scan time was 6 hours

99 43 minutes. The scan was performed in several segments that were stitched together in the reconstruction. We

100 used the *Fiji* distribution of the *ImageJ* software (Schindelin et al. 2012) to analyze the tomographic dataset.

101 The tomographic reconstruction is available in the electronic appendix.

102

2.2. Mineralogy and petrography using electron microscopy

104   A chip of NWA 1115 was cut using water-free high-purity (Optima™) isopropanol with a low-speed

105 Buehler IsoMet wafering saw outfitted with a thin diamond blade. The chip was embedded in a 1-inch diameter

106 epoxy round (Buehler EpoxiCure® 2; pre-2016 formulation), polished with diamond film and water-free

107 Optima™ isopropanol, and coated with carbon for characterization by electron microscopy. The sample was

108 analyzed at the FMNH with a Zeiss EVO 60 Scanning Electron Microscope (SEM) equipped with an Oxford

109 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 ~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.

119

120   *2.2.1. Bulk composition using LA-ICP-MS*

121

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 μm, and certain elements like Cr and P_2O_5 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

138   *2.2.2. Oxygen isotope systematics using laser fluorination*

139 The oxygen isotopic composition of NWA 11115 was determined by infrared laser-assisted fluorination at the

140 Open University on two aliquots of homogenized powder each weighing ~ 2 mg (Greenwood et al. 2017;

141 Miller et al. 1999) at the Open University. These were loaded into a Ni sample block along with obsidian

142 internal standards. The sample block was then positioned into a two-part chamber, made vacuum tight using a

143 compression seal fitted with a copper gasket and clamped by a quick-release KFX clamp (Greenwood et al.

144 2017; Miller et al. 1999). Following loading, the cell was heated under vacuum for a minimum of 24 hours to

145 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 BrF_5, with the final blank

147   being less than 60 nmol O_2. Sample heating in the presence of BrF_5 was carried out using an integrated 50 W

148   infrared CO_2 laser (10.6 μm) and video system mounted on an X-Y-Z gantry supplied by Photon Machines Inc.

149   (Greenwood et al., 2017). After fluorination, the released O_2 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 NF_2^+ 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 $\delta^{17}O$;

155   ± 0.094 ‰ for $\delta^{18}O$; ± 0.017 ‰ for $\Delta^{17}O$ (2σ) (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

158   our results with other published laser fluorination analyses of martian samples we have calculated $\Delta^{17}O$, which

159   represents the deviation from the terrestrial fractionation line, as $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$.

160

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   ~ 50 %, and plagioclase (as maskelynite) around ~ 30 %. The remainder consists of ~ 0.3 % sulfides, ~ 0.3 %

166   orthopyroxene, ~ 2 % Fe-Ti-Cr-oxides, ~ 2 % phosphates, and trace K-feldspar and silica (Figure 1). Abundant

167   (~ 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.
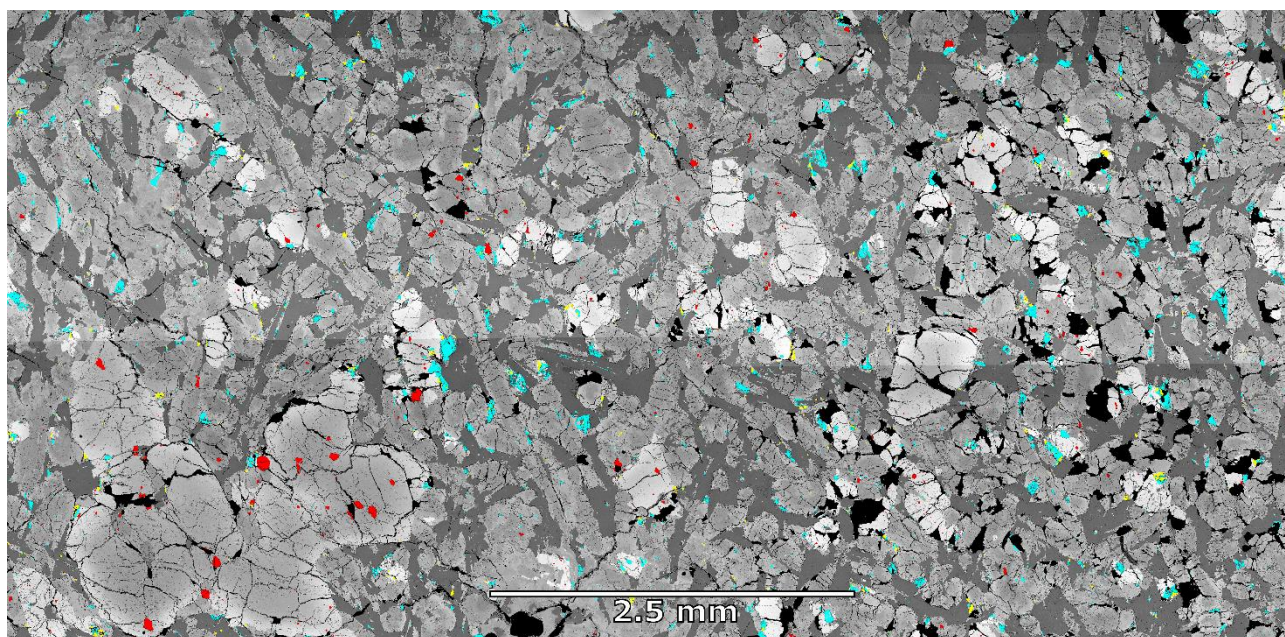
181

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.

182

183

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

| | [a]Olivine | | [b]Pigeonite | | Enstatite | | Augite | | Maskelynite | |
	N = 57		N = 24		N = 8		N = 2		N = 74	
	Wt. %	±1σ	Wt. %	±1σ	Wt. %	±1σ	Wt. %	±1σ	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_2O	nd	-	bdl	-	bdl	-	bdl	-	5.40	0.42
K_2O	nd	-	nd	-	nd	-	nd	-	0.34	0.09
P	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		

6

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	

[a]The compositions of zoned olivine are averaged for modeling bulk mineral abundance. See text for chemical zoning of olivine. [b]See Fig. 3 for compositions of zoned pigeonite. [c]Not determined. [d]Below detection limit. [e]Includes Fe_2O_3.

3.1.1. Olivine

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 (~Fo_{70} to Fo_{45}); smaller olivine grains are much more ferroan (~Fo_{21} to Fo_{35}). Some larger olivine crystals appear to form clumps or glomerophyres consisting of annealed crystals, and each sub-crystal contains its own distinct chemical zonation from core to rims (Figure 2). We address the origin of the olivine crystals in §4.1.
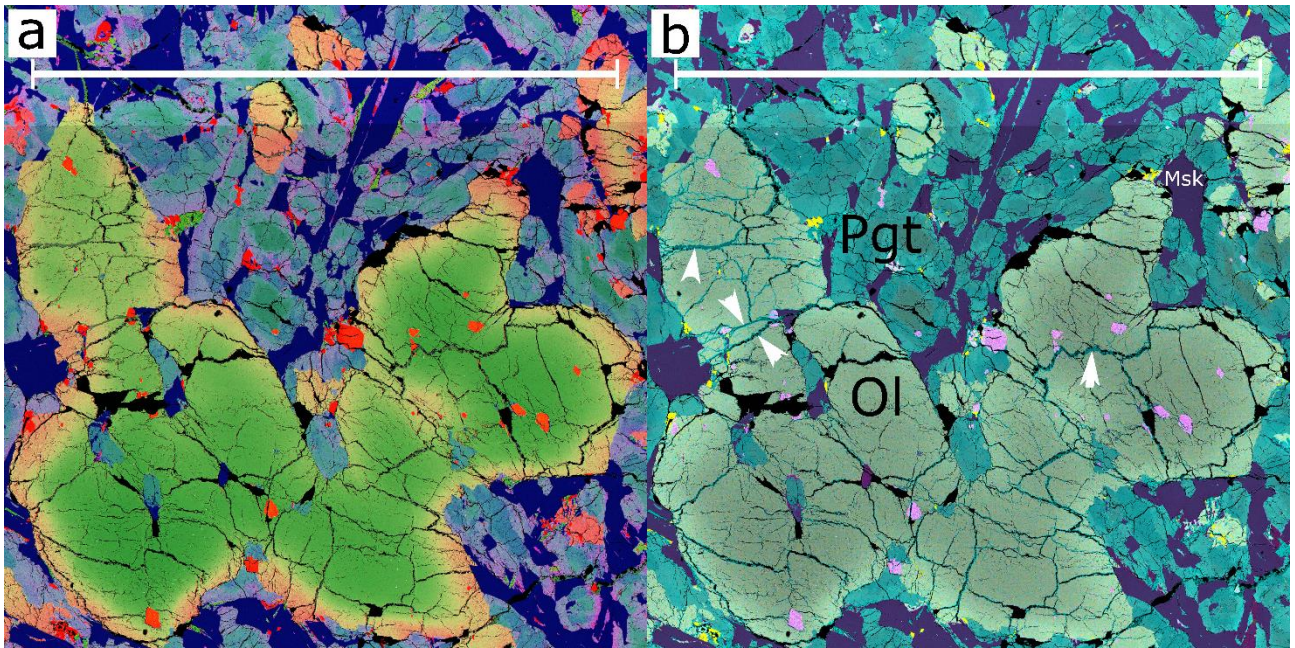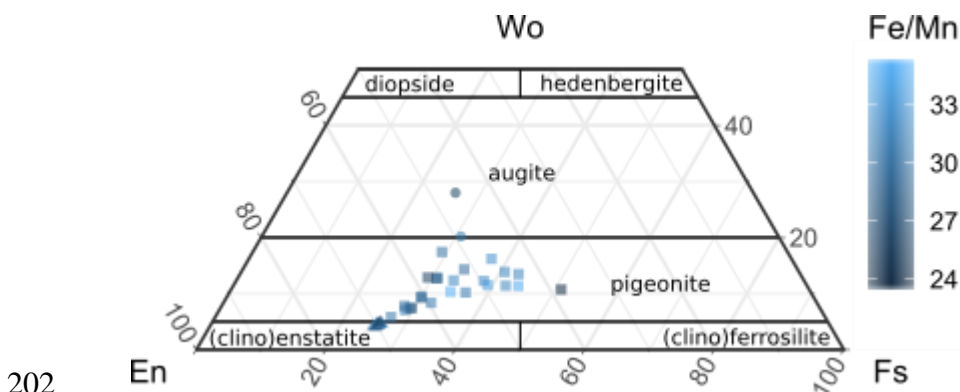

Figure 2. False color composites of an olivine glomerophyre surrounded by maskelynite and pigeonite, and with numerous spinel grains. A) Red = iron, green = magnesium, blue = silicon. B) Cyan = calcium, yellow = sulfur, magenta = aluminum. Abundant calcite (arrows) infills fractures in the olivine phenocrysts,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

3.1.2. Pyroxene

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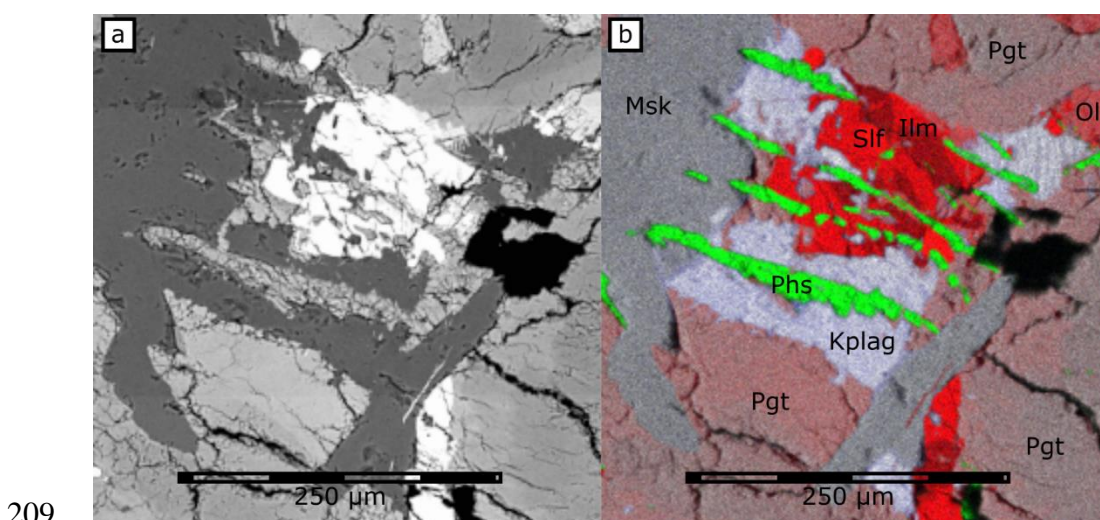
199 core to rim (Figure 1 & Figure 2). Enstatite and augite are also present as accessory grains in the sample.

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

201

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*

204 Plagioclase feldspar in NWA 11115 is found in the form of maskelynite. Most of the plagioclase is K-poor (<

205 0.5 wt%) and does not exhibit substantial compositional variation (Table 1), however, some accessory K-

206 enriched plagioclase does occur (K ≈ 5–10 wt. %; Figure 4). These K-enriched alkali feldspar zones are most

207 often found adjacent to Ca-rich phosphate minerals and Cr-Fe-Ti-oxides (Figure 4).

208

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.

210

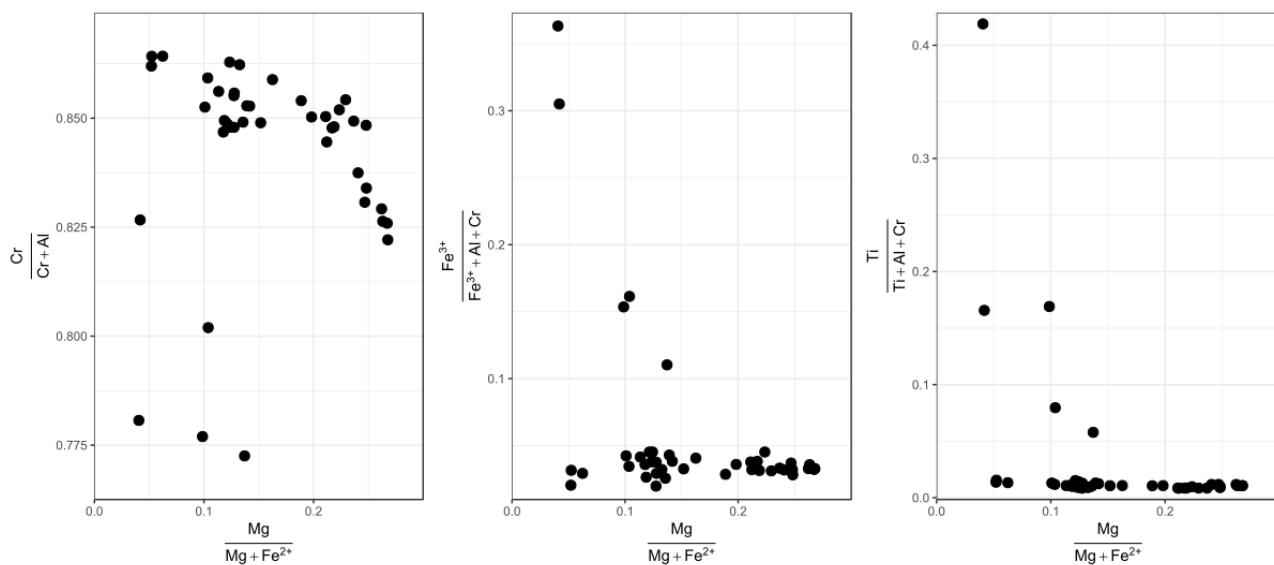8

3.1.1.Iron oxides and sulfides

212	 Spinel minerals are abundant throughout NWA 11115, poikilitically growing in olivine and pyroxene

213	grains, but also occurring separately adjacent to olivine and pyroxene grains. The spinel minerals are

214	intergrown magnesian chromite – hercyinite – ulvöspinel solid solutions (Table 2 and Figure 5), that

215	occasionally also intergrow with sulfides (Figure 4). Individually measured compositions are therefore

216	variable, as for example in their TiO_2 concentration. Spinel grains with higher concentration of magnesium

217	also tend to have higher concentration of aluminum and lower concentration of chromium (Figure 5). Spinels

218	with higher concentration of Ti tend to occur in contact with phosphates and K-rich feldspar (Figure 4).

219

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

	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

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 molar composition[d]			
MgAl$_2$O$_4$[e]	0.02	0.02	0.02	0.03
FeAl$_2$O$_4$[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$_2$O$_4$[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$_2$O$_4$[l]	0.01	0.00	0.01	0.01
Fe$_2$TiO$_4$[m]	0.02	0.01	0.01	0.01

220 [a]Calculated on the basis of stoichiometry, using the method of Droop (1987) implemented in Ferracutti et
221 al. (2015). [b]Below detection limit. [c]Atoms per formula unit. [d]Calculated with the End-Members Generator
222 (Ferracutti et al. 2015), for spinel group minerals with the formula $X^{2+}Y^{3+}{}_2O_4$, for a total charge of 8, normalized
223 here to 1 mol. [e]Spinel. [f]Hercynite. [g]Magnesioferrite. [h]Magnetite. [i]Magnesiochromite. [j]Chromite.
224 [k]Manganochromite. [l]Coulsonite. [m]Ulvöspinel.

225

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

227

228   *3.1.2.Phosphates*

229   Phosphates in NWA 11115 consist primarily of subhedral, elongated (up to ~ 0.6 mm) and fractured

230 merrillite crystals, although minor amounts of chlorine-bearing apatite are also found in the sample (Table 3).

231 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.

Elements	Apatite N = 1 Wt. %	Merrillite N = 25 Wt. %	±1σ
O	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
P	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 (= 100 – total – Cl)	0.29	-	-
	apfu[b]	*apfu*	±1σ
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
P	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

11

∑ +2 and +3 cations	4.64	9.92	0.09

233 ªBelow detection limit. ᵇAtoms per formula unit. ᶜCations are normalized to the ideal number of oxygen atoms

234 per formula unit, i.e. 12 oxygen atoms in apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) and 28 oxygen atoms in merrillite

235 ($Ca_9NaMg(PO_4)_7$).

236

237   *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.

246

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 pocket 1 N = 2		Melt pocket 2 N = 3		Melt pocket 3 N = 1	
	Wt. %	±1σ	Wt. %	±1σ	Wt. %	
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	bdlª	-	0.32	0.09	0.36	
FeO_Tᵇ	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_2O	bdl	-	0.71	0.70	bdl	
K_2O	bdl	-	bdl	-	bdl	
P	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 regression	Mixing ratio	Standard Error	Mixing ratio	Standard Error	Mixing ratio	Standard 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

247 [a]Below detection limit. [b]Total Fe, including FeO and Fe_2O_3.

248

3.1. Bulk-rock geochemistry

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

253 Bivariate Harker diagrams (Figure 6) allow for effective comparison of major element abundances between
254 NWA 11115 and other martian meteorites. The concentration of major oxides in NWA 11115 is consistent with
255 basaltic shergottites, apart from the MgO content, which lies between the average concentration in basaltic
256 shergottites and in olivine-phyric shergottites (Figure 6). The average magnesium number ($100 \times Mg/(Fe +$
257 $Mg)$) of NWA 11115 is Mg# = 57.35. NWA 11115 shows an enriched REE pattern, similar to other enriched
258 shergottites, between NWA 856 and Los Angeles (Figure 7).

259

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 µg/g. See Supplementary Information and Supplementary Spreadsheet File S1 for sidelined FMNH analyses and calibration measurements.*

	Mean	±2σ
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_2O	1.30	0.18
K_2O	0.18	0.04
P_2O_5	0.73	0.21
Li	4.34	0.50

Be	0.37	0.15
B	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
Ho	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
Tl	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

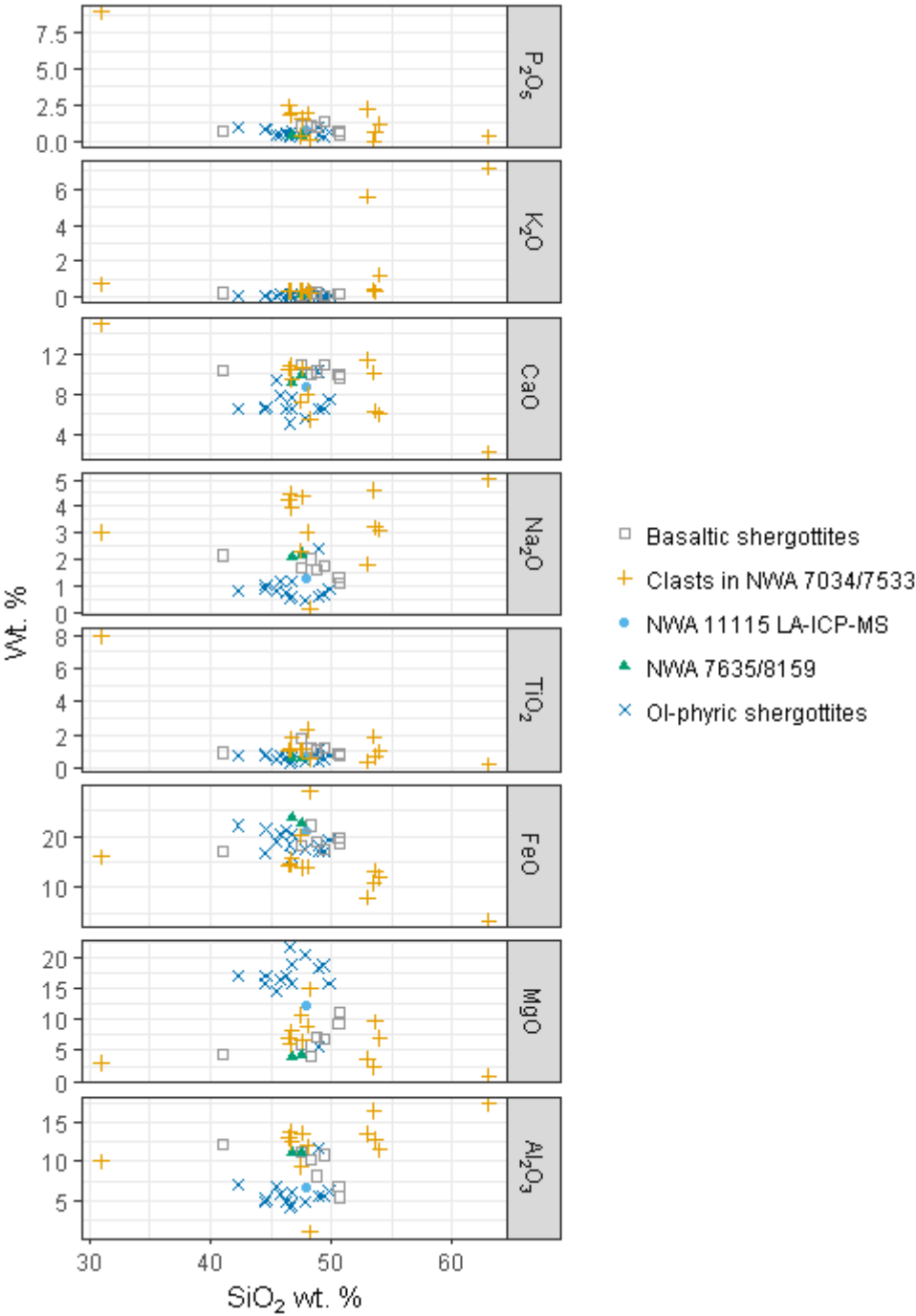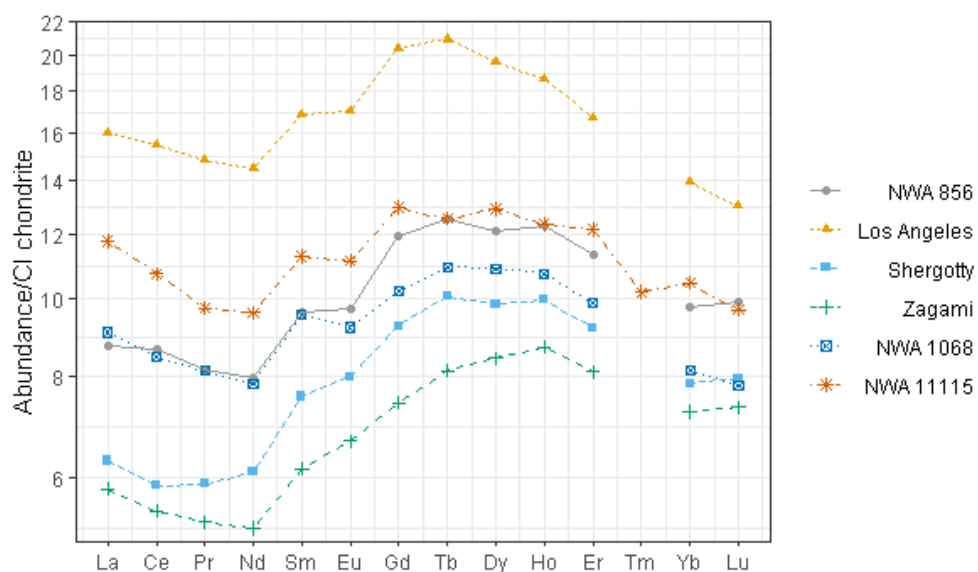260   [a]At or below the detection limit. Values represent maximum concentration measured.

261

262

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).

263

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).

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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 Δ^{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.

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).

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

	Sample-UniBern		Martian meteorite mean	
	Ratio	±2σ	Ratio	±2σ
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]	220[a]
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/U	4.09	0.77	>0.2 (unweathered) <0.2 (weathered)	
Sr/Nd	12.26	3.53		
Ce/Ce*[b]	1.01	0.04	< 1 (leached) > 1 (oxidized or enriched)	
K/La	526.94	154.59		

286 [a]Global surface average from the Gamma Ray Spectrometer on Mars Odyssey (Taylor et al. 2006).

287 [b]CI chondrite Ce abundance from Dauphas and Pourmand (2015).

288

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 Al_2O_3 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
297 vs. K relationship (Figure 10), but on the other hand, it is more in line with the basaltic shergottites, when
298 comparing the relationship between MgO and Al_2O_3 (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 Al_2O_3) or mantle metasomatism (increasing K; Schmidt et al. 2014). However, this is at odds with the
301 moderately high bulk SiO_2 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.

20

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

308   higher SiO_2 and lower MgO content of NWA 11115 (SiO_2 = 45.78 wt. % and MgO ≈ 16.64 wt. % for NWA

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 SiO_2 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 Al_2O_3; 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

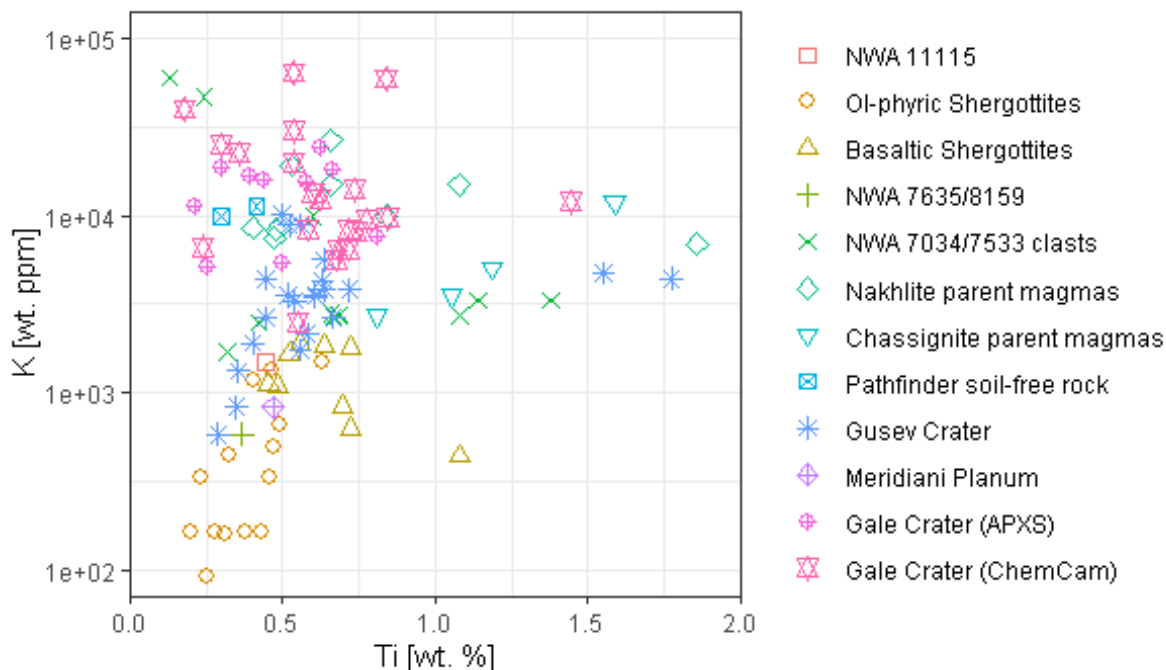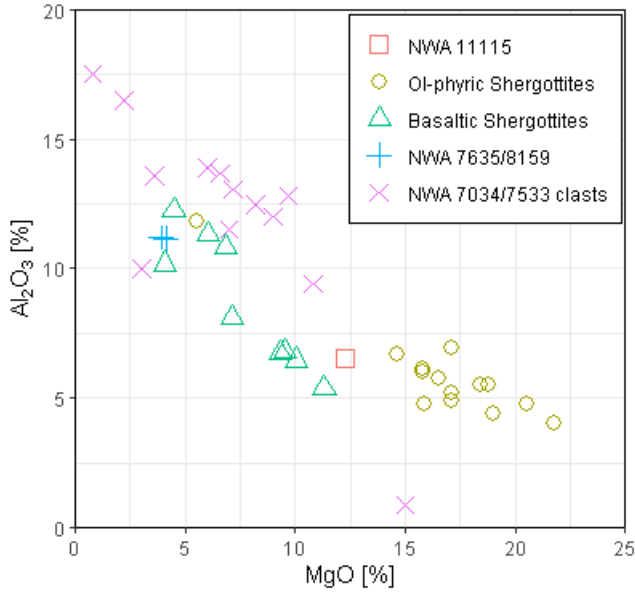324   and pyroxene grains where melt pockets are found.

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.

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Figure 11. Bulk MgO wt. % vs. bulk Al₂O₃ 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
335 1991, 1993), which either causes the removal of Ce^{3+} by dissolution of REE-rich phases (e.g. Ca-phosphates),
336 or oxidizes the relatively soluble Ce^{3+} to relatively insoluble Ce^{4+}, thereby enriching Ce in the sample relative
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):

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

339 where Ce_N, La_N, and Pr_N are the concentrations of these REE elements in the sample normalized to the
340 concentrations of these in CI chondrites. (We use the CI chondrite values reported in Dauphas and Pourmand
341 (2015).)
342 By these measures, NWA 11115 is, if at all, only slightly affected by terrestrial weathering: the Th/U ratio is
343 near-chondritic, the relatively high Sr is tracked by high Nd, and the Ce/Ce* ratio is close to 1 (Table 6). In
344 addition, the bulk oxygen isotopes place the meteorite far from the terrestrial fractionation line (Figure 9).
345 However, the meteorite clearly contains an abundance of large fractures infilled with calcite (e.g. Figure 2) and

22

346 other secondary phases, so the discrepancy is puzzling. A possible explanation is that the alteration was largely
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 CO_2 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 SiO_2 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

390

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