

# Crustal differentiation in the early solar system: clues from the unique achondrite Northwest Africa 7325 (NWA 7325)

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1	Crustal differentiation in the early solar
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3	Northwest Africa 7325 (NWA 7325).
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5	By
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#### Abstract

27 The unique achondrite NWA 7325 is an unusual olivine gabbro composed chiefly of calcic plagioclase (An<sub>85-93</sub>), diopsidic pyroxene (En<sub>50,1-54,0</sub> Wo<sub>44,8-49,3</sub> Fs<sub>0,6-1,3</sub>), and forsteritic olivine (Fo<sub>97</sub>). It 28 29 is Al and Mg-rich and Fe and Na-poor and displays very low concentrations of incompatible trace elements, much below 0.3 x CI abundances for many of them. It is also characterized by huge Eu and 30 31 Sr anomalies (Eu/Eu\*=65, Sr<sub>n</sub>/Ce<sub>n</sub>=240). Although the O isotopic composition of NWA 7325 and some ureilites (those with olivine cores in the range  $Fo_{75}$  to  $Fo_{88}$ ) are similar, a genetic relationship 32 33 between them is unlikely due to the Fe-poor composition of NWA 7325. It is almost certainly derived from a distinct planetesimal, not previously sampled by other achondrites. The low Na/Al, Ga/Al, 34 35 Zn/Al ratios as well as the low K, Rb and Cs shown by NWA 7325, suggest a volatile-depleted parent body. This unique gabbro is demonstrably a cumulate, but the composition of its parental melt cannot 36 be precisely assessed. However, the liquid from which NWA 7325 crystallized would have been very 37 poor in incompatible trace elements (Yb in the range of 0.25 to 1.5 x CI abundance) with a very large 38 39 positive Eu anomaly. Such a melt cannot be the product of the early magmatic activity on a small 40 parent body. Instead, we propose that the parental melt to NWA 7325 formed as a consequence of the total melting of an ancient gabbroic lithology, possibly upon impact, in agreement with the systematics 41 of <sup>26</sup>Al-<sup>26</sup>Mg. Based on recent dating, the crustal material that was parental to NWA 7325 must have 42 43 been older than 4562.8 Ma, and formed possibly  $\approx$ 4566 Ma ago. If this scenario is correct, NWA 7325 44 provides evidence of one of the earliest crusts on a differentiated body so far studied.

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## 50 1. Introduction

Achondrites are relatively rare extraterrestrial samples, which comprise only about 4 % of all the recovered meteorites (Meteoritical Bulletin database). Most of them originated from small differentiated bodies, while others were ejected from Mars, or the Moon, and so complement the sampling undertaken during the Apollo and Luna programs. As a result, achondrites have a high scientific value and, therefore, potentially can provide a unique insight into the processes that operated on a variety of differentiated bodies in the early solar system.

57 The number of parent bodies sampled by achondrites is the subject of ongoing debate. About 58 95 % of these meteorites originated from only two bodies: 4-Vesta (the howardites, eucrites and diogenites, ca. 1500 meteorites, 75 % of all achondrites) and the now-disrupted ureilite parent body 59 (ca. 400 meteorites, 20 % of all achondrites). Mars, the Moon and a handful of smaller bodies are the 60 61 sources of the remaining achondrites. Some of them form distinct groups based on their petrographic 62 and isotopic features, such as the aubrites, the angrites or the brachinites (see recent reviews by Keil, 63 2010, 2012, 2014). Others, as exemplified by Northwest Africa 011 (NWA 011, Yamaguchi et al., 2002), are ungrouped and consequently unique samples of unidentified differentiated bodies. While it 64 65 is more likely that these unique achondrites originated from one of the many planetesimals that 66 differentiated during the first few million years of solar system history, the possibility that we have in 67 our collections an achondrite from Mercury (e.g., Love and Keil, 1995) cannot be wholly discounted. Such a rock would not only provide essential constraints for models of the differentiation of this 68 planet, but for the chemical structure of the inner solar system too. 69

The recent discovery of Northwest Africa 7325 (NWA 7325) and its pairing (NWA 8014 and 8486) was stimulating. Thirty seven fragments totaling ca. 600 g, of an unusual achondrite displaying a distinctive green fusion crust (Fig. 1a), were collected near Bir el Abbas, Morocco. Irving et al. (2013) were the first to study this meteorite and to show that it consists of a unique gabbroic lithology. They compared its major element composition to that of Mercury's surface, as determined by the MESSENGER spacecraft (Weider et al., 2012), and suggested that this meteorite could have 76 originated from this planet. Subsequently, this rock has been extensively studied by different teams 77 using a variety of techniques (Irving et al., 2013; Amelin et al., 2013; Bischoff et al., 2013; Sanborn et 78 al., 2013; Dunlap et al., 2014; El Goresy et al., 2014; Goodrich et al., 2014; Jabeen et al., 2014; Kita et 79 al., 2014; Sutton et al., 2014; Weber et al., 2014, 2015; Archer et al., 2015). Although a mercurian origin is not currently favored by most of these studies, this rock remains fascinating and scientifically 80 important by virtue of its distinct petrographic and geochemical features. Here we report new 81 82 chemical, mineralogical and stable isotope (oxygen, carbon and nitrogen) results that provide 83 important evidence relevant to the origin of this unique meteorite.

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## **2. Samples and analytical techniques**

86 Two samples of NWA 7325 were available for bulk rock chemical analysis: a clean chip of the 87 interior of the meteorite (600 mg, fragment of the same slice used for the thick section), and a sample of cutting dust recovered using distilled water during cutting of the stones by S. Ralew, the owner of 88 89 the meteorite. In addition, two low-Ti gabbroic pebbles from Vaca Muerta were selected for 90 comparison, from the mesosiderite samples studied previously by Greenwood et al. (2006). 91 Petrographic observations and quantitative chemical analyses of the main phases of the NWA 7325 achondrite were made on a polished thick section  $(1 \text{ cm}^2)$  prepared from a slice obtained from S. 92 Ralew. Cameca SX100 electron microprobe analyses at Service Commun "Microsonde Ouest" 93 94 (Plouzané) were obtained at 15 kV accelerating voltage with a probe current of 12 nA. Minerals [wollastonite (Si, Ca), orthoclase (K), albite (Na), apatite (P)], oxide [MnTiO<sub>3</sub> (Mn, Ti)], Al<sub>2</sub>O<sub>3</sub> (Al), 95 Fe<sub>2</sub>O<sub>3</sub> (Fe), Cr<sub>2</sub>O<sub>3</sub> (Cr)], and one sulfide [FeS<sub>2</sub> (S)] were used for calibration. The raw data were 96 97 corrected with the 'PAP' software (Pouchou and Pichoir, 1985).

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99 The Vaca Muerta samples and the NWA 7325 chip were totally powdered using a boron 100 carbide pestle and mortar. Major and trace element concentrations were determined respectively by 101 ICP-AES (inductively coupled plasma-atomic emission spectrometry) and ICP-MS (inductively 102 coupled plasma-mass spectrometry) at Université de Brest (IUEM, Plouzané) using the procedures
103 described by Barrat et al. (2012, 2014). The accuracy of major and trace element concentrations is
104 better than 5% (probably better than 3% for all the REEs) based on various standard and sample
105 duplicates.

Oxygen isotope analyses were carried out at the Open University using an infrared laser 106 107 fluorination system following the methods and procedures of Miller et al. (1999). Analyses were 108 undertaken using a powder prepared from the 600 mg internal sample of NWA 7325. Oxygen was released from 2 mg aliquots by heating in the presence of BrF<sub>5</sub>. After fluorination, the released oxygen 109 gas was purified by passing it through two cryogenic nitrogen traps and over a bed of heated KBr. 110 Oxygen gas was analysed using a MAT 253 dual inlet mass spectrometer. Interference at m/z=33 by 111 the NF<sub>3</sub> fragment ion NF<sup>+</sup> was monitored by performing scans for NF<sub>2</sub><sup>+</sup> on all samples run in this 112 study. In all cases NF<sub>2</sub> was either negligible or absent. Oxygen isotopic analyses are reported in 113 standard  $\delta$  notation, where  $\delta^{18}$ O has been calculated relative to VSMOW (Vienna Standard Mean 114 Ocean Water) as  $\delta^{18}O = [({}^{18}O / {}^{16}O_{sample})/({}^{18}O / {}^{16}O_{VSMOW})-1] \times 1000$  (‰) and similarly for  $\delta^{17}O$  using 115 the <sup>17</sup>O /<sup>16</sup>O ratio.  $\Delta^{17}$ O, which represents the deviation from the terrestrial fractionation line, has been 116 calculated using a linearized format (Miller, 2002): 117

118 
$$\Delta^{17}O = 1000 \ln(1 + \delta^{17}O/1000) - \lambda \ 1000 \ln(1 + \delta^{18}O/1000)$$

119 where  $\lambda = 0.5247$ , which was determined using 47 terrestrial whole-rock and mineral separate samples 120 (Miller et al., 1999; Miller, 2002). Recent levels of precision obtained on the Open University system, 121 as demonstrated by 39 analyses of our internal obsidian standard, were as follows:  $\pm 0.05\%$  for  $\delta^{17}$ O; 122  $\pm 0.09\%$  for  $\delta^{18}$ O;  $\pm 0.02\%$  for  $\Delta^{17}$ O ( $2\sigma$ ).

123 Carbon and nitrogen concentrations and isotopic analyses were obtained by the stepped 124 combustion technique using the multi-element analyzer system "Finesse" (Verchovsky et al., 1998, 125 2003). An aliquot (6.134 mg) of the internal sample of NWA 7325 was heated from 200 to 1400°C 126 with  $100^{\circ}$  increments. The released N and C in the form of N<sub>2</sub> and CO<sub>2</sub> were analyzed simultaneously 127 from the same aliquot. The isotope results are expressed in standard δ notation normalized to air for N
128 and to PDB for C.

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#### 130 **3. Results and discussion**

### 131 3.1. Petrography

132 NWA 7325 has been extensively described in a series of abstracts (Irving et al., 2013; Bischoff 133 et al., 2013; Goodrich et al., 2014; El Goresy et al., 2014). Our observations are in agreement with 134 these earlier studies, and are summarized here. NWA 7325 is a fine to medium grained gabbroic rock 135 with a grain size typically in the range of 0.5-1 mm (Fig. 1). It is unbrecciated, and consists of ~25-30 vol% diopsidic pyroxenes, ~15 vol% olivine grains surrounded or poikilitically enclosed by 136 plagioclase (~55-60 vol%), with accessory iron sulfides (1 vol%), and sparse ferrochromite, metal 137 138 grains and rare eskolaite associated with iron sulfide. El Goresy et al. (2014) report the occurrence of 139 Ca sulfates that they interpret as totally weathered grains of oldhamite. However, like the vast 140 majority of Saharan finds, NWA 7325 contains cracks filled with secondary carbonates. Rather than 141 being formed by the terrestrial alteration of oldhamite, we believe that the Ca sulfates in NWA 7325 are more likely to represent normal hot desert weathering products. 142

Major element compositions of the main phases are reported in Table 1. Coarse-grained plagioclase is calcic (An<sub>85-93</sub>), and contains traces of MgO (=0.13-0.45 wt%). Ca-pyroxene is homogeneous and extremely magnesian (En<sub>50.1-54.0</sub> Wo<sub>44.8-49.3</sub> Fs<sub>0.6-1.3</sub>, Mg/(Fe+Mg)= 0.975-0.983, n=58). Olivine (Fo<sub>97-97.3</sub>, n=51) is in equilibrium with pyroxene (e.g., Perkins and Vielzeuf, 1992). Fesulfide is Cr-rich (Cr = 2.2-6 wt%) and contains lamellas of daubréelite.

Irving et al. (2013) noted that the plagioclase in NWA 7325 is finely mottled, and much less birefringent than normal. It contains clusters of tiny grains of troilite and metal. They suggested that the plagioclase has been totally melted, possibly as a result of shock, and reacted locally with olivine to generate secondary diopside. This view has been challenged by Bischoff et al. (2013). They observed plagioclase-rich veins and occasionally  $SiO_2$ -normative mesostases around mafic minerals and within Ca-pyroxenes, which could have been formed upon shock. However, they pointed out that olivine is only very weakly shocked (stage S2), suggesting that the shock pressure suffered by NWA 7325 was certainly not strong enough to melt it extensively.

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## 157 3.2. Geochemistry

#### 158 3.2.1. Major and trace element.

The major element composition of the cutting dust (Table 2) is very similar to the results obtained at University of Alberta on a distinct sample of cutting dust (Irving et al., 2013). NWA 7325 is a basic rock, rich in MgO and Al<sub>2</sub>O<sub>3</sub>, and poor in Fe, Mn and alkalis (Na<sub>2</sub>O = 0.6 wt%). Using the average compositions of the main phases, it corresponds to an assemblage of about 55 wt% plagioclase, 32 wt% pyroxene, 10 wt% olivine and traces of sulfides and secondary calcite, in agreement with phase proportions estimated from the polished sections (see above).

165 Despite the similarity of their major element compositions, the trace element abundances of the two cutting dust samples (this study and Irving et al., 2013) are different, and display some 166 167 significant discrepancies (Table 3 and Fig. 2 and 3). Both samples are poor in incompatible lithophile elements (REEs except Eu  $< 2 \times CI$ ), light REE enriched (La<sub>n</sub>/Sm<sub>n</sub> = 1.95 - 2.90) with striking positive 168 169 Eu anomalies (Eu/Eu $^*$  = 16.1 – 35.2), but our sample contains respectively about 2x more light REEs, 170 and half the Th content reported by Irving et al. (2013). Furthermore, the Irving et al. (2013) sample displays markedly high Nb and Hf abundances compared to our analysis. A number of possible 171 explanations might account for these differences: i) contamination during the cutting of the meteorite 172 by handling and by the saw blade, ii) different proportions of soil materials which were adhering to the 173 174 surface of the stones (see Fig. 1a), and, iii) different contributions from secondary phases (Fe-oxides, carbonates and sulfates) along surfaces crossed by the saw blade. The low abundance of incompatible 175 176 lithophile elements (e.g., the light REEs, Th, U, Rb and Cs) makes them extremely sensitive to terrestrial contamination, which could have taken place subsequent to its landing on the desert soil, and/or by handling during the recovery and sample preparation. The soil of the strewnfield has not been analyzed, but its Th and REE abundances are probably similar to those of the upper continental crust average. Such a soil [as illustrated by the soil of Tatahouine (Barrat et al., 1999)] can contain ca. 100 times more La and Th than the cutting dust. A slight contamination by soil could be undetectable with major elements, but have a huge impact on the abundances of many trace elements.

183 It is clear from the preceding section that the trace element composition of NWA 7325 should 184 be determined using material from clean interior chips. We prepared one such fraction using a 185 fragment weighing 600 mg. Its major element abundances deviate just slightly from the cutting dust 186 analyses, except for Fe which is three time less abundant in the chip than in the cutting dust. 187 Furthermore, the cutting dust contains much more Ni, Cu, Zn W and Pb than the interior chips, which 188 most likely result from contamination by the saw blade. We don't know exactly the composition of the 189 saw blade which was used here, but saw blades typically have diamond grit in them that are 190 electroplated to the steel blade with a Ni, Cu or Zn matrix. Therefore, most major element abundances determined using cutting dust would appear to be representative of the whole rock, contrary to the 191 trace element contents which are not reliable and should be rejected (Tables 2 and 3). 192

193 Despite our effort to select a fragment that was as fresh as possible, terrestrial weathering 194 effects cannot be totally avoided. The mineralogical and chemical effects of hot desert weathering are 195 now relatively well understood, and have been previously documented in a range of meteorite types 196 (e.g., Barrat et al., 1999; 2004, 2010; Stelzner et al., 1999; Crozaz et al., 2003). Our interior chip is no 197 exception. As shown in Figures 2 and 3, it displays a high Ba abundance, a high U/Th ratio (= 1.1), 198 and a positive Ce anomaly (Ce/Ce\* = 1.25). Such features have been repeatedly observed in weathered 199 Saharan finds, and it is not necessary to repeat here a discussion concerning their origin. Although 200 Saharan finds display often high Sr abundances, the positive Sr anomaly exhibited by NWA 7325 is 201 probably, like the Eu anomaly, a primary feature attributable to plagioclase.

NWA 7325 contains low but significant amounts of Ni (= 57  $\mu$ g/g) and Co (=23  $\mu$ g/g), probably hosted by minute grains of metal (Table 3). It is poor in Zn, Cu and Pb. Its low lithophile element abundances are well illustrated by the CI- normalized trace element patterns (Fig. 2 and 3). Except for Sc, Ba, U, Sr and Eu, all the lithophile trace elements display concentration < 0.3 x CI. Furthermore, the trace element patterns exhibit Cs, Rb, Zr, and Hf depletions. Contrary to the results for the cutting dust, the interior fragment is light-REE depleted (La<sub>n</sub>/Sm<sub>n</sub> = 0.70), and displays large positive Eu and Sr anomalies (Eu/Eu\*= 65, Sr<sub>n</sub>/Ce<sub>n</sub>= 240).

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#### 211 3.2.2. Oxygen isotopes.

The bulk oxygen isotopic composition of NWA 7325 was determined in duplicate using the powder 212 made with the interior fragment. The average of the two analyses was:  $\delta^{17}O = 3.33 \pm 0.09 \%$ ,  $\delta^{18}O =$ 213  $8.10 \pm 0.18$  ‰,  $\Delta^{17}O = -0.91 \pm 0.01$  ‰ (errors  $\pm 1\sigma$ ). Our new analysis of NWA 7325 plots on the 214 CCAM line in Fig. 4, within the ureilite field. Three individual analyses of NWA 7325 by Irving et al. 215 (2013) have somewhat divergent compositions, with one plotting close to the result reported here. 216 217 Jabeen et al. (2014) give oxygen isotope analyses for plagioclase and pyroxene mineral separates from 218 NWA 7325 that are displaced from one another by approximately 2 ‰ along a mass fractionation line 219 (Fig. 4). The mean plagioclase analysis (n=4) of Jabeen et al. (2014) plots close to our bulk value for 220 NWA 7325. However, in view of the significant proportion of pyroxene in NWA 7325 (20-30 %, 221 section 3.1) the analyses of Jabeen suggest that, had they determined a bulk composition for the meteorite, this would probably have been shifted to somewhat lower  $\delta^{18}$ O values compared to our 222 223 analysis.

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225 3.2.3. Carbon and nitrogen isotopes.

The results for C and N are presented in table 4 and Figure. 5. Carbon displays a bimodal release with peaks in the range 200-400°C and 500-700°C. The low temperature peak is due to the terrestrial contamination associated with both weathering during the residence of the meteorite on the Earth's surface and laboratory handling and has a characteristic carbon isotopic composition ( $\delta^{13}C$ = -27 to -29‰). The second peak seems to represent a terrestrial carbonate as indicated both by the release temperature corresponding to that for decomposition of CaCO<sub>3</sub> and the isotopic composition with  $\delta^{13}C$  = -1 to 3‰. This interpretation is consistent with the petrographic data (see section 3.1).

Most of nitrogen is released at low T (200-700°C) and appears to predominantly reflect terrestrial contamination. Isotopically it is relatively heavy and has a comparatively high (~0.1) C/N ratio that also points to terrestrial organic contamination. The extension of the low T peak of nitrogen to 700°C suggests that a part of the nitrogen is associated with the secondary carbonate.

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## 3.3. NWA 7325, a unique achondrite.

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#### 240 3.3.1. What is the parent body of NWA 7325?

241 As pointed out by Irving et al. (2013), various major element ratios (e.g., Al/Si and Mg/Si) determined from NWA 7325 are within the range of values measured on Mercury's surface by remote 242 243 sensing observations (Weider et al., 2012). However, the suggestion that NWA 7325 may represent a 244 sample of Mercury's crust (Irving et al., 2013) has been challenged on the basis of dating evidence. 245 Amelin et al. (2013) obtained a Pb-isotopic age for NWA 7325 of  $4562.5 \pm 4.4$  Ma. This very old age was subsequently confirmed by Dunlap et al. (2014), who obtained an Al-Mg age of  $4562.8 \pm 0.3$  Ma. 246 247 Both teams pointed out that NWA 7325 crystallized at the same time as angrites and some other achondrites, and seems too old to be a sample of the differentiated crust of a planetary-sized body. 248 249 Therefore, a mercurian origin appears to be untenable, and instead it seems more likely that NWA 250 7325 originated from one of the planetesimals that formed during the first millions of years after the 251 formation of refractory inclusions.

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Achondrites display a wide range of mineralogical compositions (e.g., Mittlefehldt et al., 1998).
Even if these rocks sampled a limited number of differentiated bodies, they formed under a variety of

conditions, and illustrate, at least partially, the diversity of primitive materials and conditions present 255 256 in the early Solar System (i.e., highly reduced conditions for aubrites, a volatile-depleted body and 257 more oxidized conditions for angrites, C-rich body with ureilites...). Despite this large mineralogical 258 variability, achondrites displaying highly magnesian silicates and calcic plagioclases are exceptional. Only a unique mm-sized troctolitic clast found in the polymict ureilite Dar al Gani 319 displays phase 259 compositions similar to NWA 7325 (plagioclase An<sub>87-89</sub>, olivine Fo<sub>93</sub>, Ikeda et al., 2000; Kita et al., 260 261 2004; Goodrich et al., 2014). Although the O-isotopic composition of NWA 7325 is in the range of the ureilites (Fig. 4), two important lines of evidence preclude these meteorites originating from the same 262 263 body:

(i) Olivine cores in ureilites display a wide range of compositions which are correlated with the O isotopic composition of the bulk rocks (Clayton and Mayeda, 1996). If NWA 7325 formed from an ureilitic source, the latter would necessarily be among the most Mg-rich ureilites, which display the lowest  $\Delta^{17}$ O values (< -2 ‰), inconsistent with the  $\Delta^{17}$ O value of NWA 7325 (Fig. 6).

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269 (ii) While ureilites display a restricted range of  $\varepsilon^{54}$ Cr values close to -0.9 (e.g., Yamakawa et al., 270 2010), NWA 7325 has a distinct  $\varepsilon^{54}$ Cr value of -0.55 ± 0.08, precluding this meteorite originating from 271 the ureilite parent body (Sanborn et al., 2013).

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Thus, NWA 7325 is a unique achondrite with distinctive geochemical and isotopic features. It 273 274 certainly originated from a parent body unsampled by other achondrites. In Figure 7, we compare the 275 Ga/Al, Zn/Al and Na/Al ratios in NWA 7325 (analyses from the interior chip, not the cutting dust samples) with other well-characterized achondrites. Unlike the martian achondrites, the ureilitic 276 277 (ALM-A) and brachinitic (GRA-06) melts, NWA 7325 displays low Na/Al, Ga/Al and Zn/Al and plots 278 near or in the fields of rocks from the Moon and Vesta, suggesting a volatile-depleted parent body. This inference is strengthened by the very low K, Rb and Cs abundances shown by the NWA 7325 279 280 chip (Table 3).

Discussing the petrology of a gabbroic rock that is the sole sample we have at present from an unknown parent body is a challenging task. The huge positive Eu anomaly displayed by NWA 7325 is unambiguously related to its abundant plagioclases and points to reduced conditions (e.g., Drake and Weill, 1975), in agreement with the occurrence of traces of metal, Cr-rich sulfides. Indeed, the valences of Cr, Ti, V in olivine and pyroxene determined by XANES spectroscopy suggest crystallization conditions close to the Cr-CrO buffer (i.e. fO<sub>2</sub> close to IW-4, Sutton et al., 2014).

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290 Gabbroic rocks displaying positive Eu anomalies are widely considered as cumulates. NWA 291 7325 is no exception (e.g., Irving et al., 2013), but we emphasize that this interpretation is not unique. 292 Significant positive Eu anomalies can be generated in non-cumulative basaltic rocks by partial 293 melting, for example during short duration reheating events (Yamaguchi et al., 2009; 2013). Larger 294 degrees of melting of a basaltic or gabbroic lithology can produce gabbroic restites displaying very 295 low incompatible trace element abundances and huge positive anomalies. Previous studies have emphasized the complex thermal history of NWA 7325, and shown that its texture could be explained 296 297 by remelting (e.g., Bischoff et al., 2013). Thus, the possibility that NWA 7325 could be a restite merits 298 further consideration.

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300 Partial melting has been previously proposed to explain the very low REE abundances and very large Eu anomalies displayed by some gabbroic pebbles found in mesosiderites (e.g., Rubin and 301 302 Mittlefehldt, 1992). We analyzed for comparison two such pebbles from Vaca Muerta (Table 2 and 303 Figures 2 and 3). These meteorites are finds from the Atacama Desert. They display some anomalies that are certainly the result of terrestrial weathering, and that do not require further consideration here, 304 305 i.e. positive Ce anomalies, sometimes high U/Th ratios and high Pb abundances, etc... Interestingly, 306 these two pebbles display at first glance the same level of incompatible trace element concentrations 307 and the same large Sr and Eu anomalies as NWA 7325. However, their REE patterns display marked 308 heavy-REE enrichments ( $Gd_n/Lu_n = 0.14-0.43$ ) which are well explained by the loss of a partial melt 309 (e.g., Yamaguchi et al., 2009). The REE pattern of the NWA 7325 chip does not exhibit such an enrichment ( $Gd_n/Lu_n = 2.92$ ). We conclude that NWA 7325 is probably not restitic, although we note that this inference is model dependent (i.e., composition of the melted lithology).

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If NWA 7325 is a cumulate, what can we infer about the composition of its parental melt 313 based on its petrography and major and trace element abundances? It was certainly "basaltic", not 314 SiO<sub>2</sub>-saturated (crystallization of olivine), and Ca-rich (diopsidic pyroxene and calcic plagioclase). It 315 316 was certainly Na-poor (calcic plagioclase) and of course displayed a very low FeO/MgO in order to 317 explain the very high Mg/(Fe+Mg) ratios of the olivines and pyroxenes. Moreover, NWA 7325 318 displays very low abundances of incompatible trace elements. Its parental melt was certainly very poor 319 in these elements. While it is not possible to precisely constrain its trace element abundances, some 320 very simple assumptions allow us to qualitatively evaluate some of its features. Partition coefficients 321 for Yb or Lu in diopside are about 10 times larger than those for plagioclase or olivine (e.g., McKay et 322 al., 1989; Schosnig and Hoffer, 1998). Consequently, in a cumulate like NWA 7325, made essentially of plagioclase, diopsidic pyroxene and olivine, the pyroxene controls the budget of heavy REEs. 323 324 Assuming that the NWA 7325 chip contained about 33 wt% pyroxene, the Yb or Lu concentrations in this mineral are probably  $\approx 0.15$  x CI abundances. Partition coefficients of Yb for diopside at low 325 326 pressure range from 0.1 and 0.6 (Schosnig and Hoffer, 1998, and references therein) suggesting Yb or 327 Lu abundances in the range of 0.25 to 1.5 x CI abundances only in the parental melt. Furthermore, the 328 shape of its REE pattern was probably not chondritic. Again, since clinopyroxene controls the heavy REE abundances in NWA 7325, the Gd-Lu part of the REE pattern is chiefly controlled by its partition 329 330 coefficients and the  $(Gd/Lu)_n$  of the parental melt. Because  $(D_{Gd}/D_{Lu})_{cpx}$  is  $\approx 1$  (e.g., Schosnig and 331 Hoffer, 1998), (Gd/Lu)<sub>n</sub> ratios close to 1 are expected for pure cumulates formed from a chondritic 332 melt. This inference remains valid even if the cumulates contain some trapped melt. As a consequence, 333 the high  $(Gd/Lu)_n$  ratio (=2.92) displayed by the NWA 7325 chip is inconsistent with a parental melt displaying a flat REE pattern. The parental melt to NWA 7325 must therefore have had a fractionated 334 REE pattern with  $(Gd/Lu)_n$  ratio > 1, and probably  $\approx$  3. Similar lines of reasoning are possible for Eu. 335 Partition coefficients for Eu in plagioclase are much larger than those in pyroxene or olivine (e.g., 336 McKay et al., 1989; Schosnig and Hoffer, 1998). Therefore, the budget of Eu in the rock is strongly 337

338 controlled by plagioclase. Assuming that the NWA 7325 chip contained about 53 wt% plagioclase, the Eu concentration in this phase is  $\approx 16 \text{ x CI}$  abundance. Partition coefficients for Eu in plagioclase are 339 340 not only dependent on the composition of the melt but are also strongly sensitive to the oxygen fugacity (e.g., McKay, 1989). For the purpose of calculation, partition coefficients for Eu in calcic 341 plagioclase at low fO<sub>2</sub> for a basaltic melt are assumed to range from 0.7 to 1.1 as suggested by McKay 342 (1989), and in agreement with the recent experimental results obtained by Rapp et al. (2015). The Eu 343 344 concentration of the parental melt was probably in the range of 14 to 23 x CI abundances. Even if we take into account the enrichment in middle REEs of the parental melt (i.e., the (Gd/Yb)<sub>n</sub> or the 345 (Gd/Lu)<sub>n</sub> ratios), its level of concentration of Eu is very high compared to the heavy-REEs. It comes as 346 347 an unavoidable conclusion that the parental melt of NWA 7325 certainly displayed a very large positive Eu anomaly ( $Eu_n/Yb_n > 10$ , probably  $Eu_n/Gd_n > 3$ ) that is difficult to estimate accurately. 348

A melt with such a large positive Eu is very unlikely to be the direct product of the early magmatic activity on a planetesimal. On the other hand, gabbros formed in reduced conditions can display low incompatible trace element abundances and large positive Eu, as exemplified by the cumulate eucrites. Total melting of such rocks could produce melts with these features. It is tempting to propose that NWA 7325 is a cumulate derived from the crystallization of such a melt, with the melting of its protolith possibly produced by an energetic impact.

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356 Recent data for NWA 7325 allow us to further evaluate this hypothesis. Highly Siderophile 357 Elements (HSEs) are sensitive tracers of chondritic contributions in impact melts and impactites. Two 358 samples were analyzed by Archer et al. (2015). Their abundances differ from one another by almost 359 one order of magnitude, and demonstrate that the HSE carriers are heterogeneously distributed in the 360 bulk rock. The sample displaying the highest abundances shows a chondritic distribution of HFEs, in 361 agreement with a possible projectile contribution (it contains about 0.9 ng/g Ir, suggesting the addition of  $\approx 0.2$  wt% of chondritic material). Archer et al. (2015) suggested that this chondritic signature was 362 introduced into the rock after crystallization during late-stage impacts. Because NWA 7325 is 363 unbrecciated, this explanation is unlikely. Alternatively, a chondritic component could have been 364 introduced into the NWA 7325 parental melt during its crystallization. One possibility is that NWA 365

366 7325 became contaminated through interaction with regolith material. The parental melt could have 367 inefficiently assimilated regolith containing chondritic debris. However, as pointed out by Archer et al. 368 (2015), an assimilation process that only partially affected the rock, is difficult to envisage. Instead, a 369 heterogeneously distributed chondritic signature in NWA 7325 is best explained if this meteorite was 370 derived from the crystallization of an impact melt.

Moreover, the systematics of <sup>26</sup>Al-<sup>26</sup>Mg further strengthens the hypothesis that NWA 7325 371 formed by impact-melting of gabbroic material. The Al-Mg internal isochron obtained previously by 372 Dunlap et al. (2014) for NWA 7325 has a well-resolved positive intercept ( $\delta^{26}Mg_0^*$ ) of 0.095 ± 0.011 373 ‰, and lies well above the bulk chondritic value (Al/Mg  $\approx 0.1$  and  $\delta^{26}$ Mg\*  $\approx 0$  ‰). As noted by 374 Dunlap et al. (2014), this high  $\delta^{26}Mg_0^*$  could imply a non-chondritic initial composition for the 375 parental body. Alternatively, the source material for this achondrite may have evolved with a highly 376 377 superchondritic Al/Mg ratio early in the history of the solar system prior to the heating event that formed the melt that was parental to NWA 7325. Gabbros and plagioclase-rich cumulates are Al-rich 378 379 compared to chondrites, and exhibit highly superchondritic Al/Mg ratios. The impact-melting hypothesis of this kind of rock offers a straightforward explanation for the distinctly high  $\delta^{26}Mg_0^*$  of 380 NWA 7325 (Fig. 8). Moreover, assuming that the parental melt of NWA 7325 formed by impact 381 melting of a gabbroic target 4.5628 Ga ago, we can place some constraints on the formation age of its 382 protolith. Unfortunately, the <sup>27</sup>Al/<sup>24</sup>Mg ratio of the parental melt of NWA 7325 is not known. Because 383 NWA 7325 is a plagioclase rich cumulate, its parental melt displayed probably a lower Al abundance 384 385 than the whole rock, but it is not possible to assess neither its Mg concentration nor its Al/Mg ratio. In 386 the case of eucrites, the Al/Mg ratios of cumulate and basaltic eucrites are similar. Although these 387 rocks are probably not perfect analogs of NWA 7325, we can reasonably propose that the situation was comparable for NWA 7325 and its parental melt. For the purpose of calculation, we used the 388 whole rock  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  ratio (= 1.56) and we obtained an intercept with the solar system growth curve at 389 390 about 4566 Ma. A lower Al/Mg ratio would point to an older model age, and conversely younger 391 model ages are obtained with higher Al/Mg ratios, but variations of 25 % around the Al/Mg ratio of 392 the whole rock do not alter this estimation (Fig. 9). Although only indicative, our calculations show

that remelting of a very old gabbroic lithology can perfectly explain the high  $\delta^{26}Mg_{0}^{*}$  of NWA 7325. Thus, NWA 7325 provides evidence of one of the earliest crusts on a differentiated body so far studied. We note that the NWA 7325 protolith could be practically contemporaneous to Asuka 881394, which formed 4566.5 ± 0.2 Ma ago on a distinct parent body (Wadhwa et al., 2009).

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#### 398 4. Conclusions

Two important conclusions emerge from this study. The first one is methodological. While it 399 400 is often very difficult to obtain representative samples of rare meteorites, the use of cutting dust should be avoided, at least for the trace element analyses. Secondly, our data confirm that NWA 7325 is a 401 new type of achondrite that originated from a parent body not previously sampled by the other 402 meteorites. Despite their similar oxygen isotope compositions, a number of lines of evidence preclude 403 a relationship between NWA 7325 and the ureilites. NWA 7325 is a gabbroic rock that displays 404 distinct phase compositions, notably highly magnesian pyroxenes and olivine. Its chemical 405 406 composition suggests that it formed from an unusual melt characterized by very low incompatible 407 trace element abundances and a very large positive Eu anomaly. We propose that this melt formed by the remelting of an ancient gabbroic lithology, possibly upon impact, in agreement with the HSE 408 abundances, and the systematics of <sup>26</sup>Al-<sup>26</sup>Mg. Based on recent dating, the crustal material that was 409 410 parental to NWA 7325 must have been older than 4562.8 Ma. Thus, NWA 7325 provides evidence of one of the earliest crusts on a differentiated body so far studied and indicates how such materials were 411 412 rapidly recycled.

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Table 1. Average compositions of main phases in NWA 7325 (in wt%).

	n	SiO <sub>2</sub>	TiO <sub>2</sub>	$Al_2O_3$	Cr <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Total	endmembers
plagio. pyrox. olivine	71 58 51	45.25 52.68 42.25	< 0.03 0.04 < 0.03	34.14 2.93 0.04	< 0.03 1.03 0.37	0.07 0.73 2.81	< 0.03 0.05 0.07	0.29 18.88 54.38	18.11 22.54 0.35	1.18 0.16 < 0.03	< 0.03 < 0.03 < 0.03	99.07 99.04 100.25	$\begin{array}{l} An_{89,4}Ab_{10.5} \\ En_{53.2}Wo_{45.6}Fs_{1.2} \\ Fo_{97.2} \end{array}$
		Si	Ti	Al	Cr	Fe	Mn	Mg	Ca	Na	S	Total	-
sulfide 606	13	0.04	< 0.03	< 0.03	3.57	59.62	< 0.03	0.01	0.15	< 0.03	37.64	101.19	

Table 2. Major element compositions of NWA 7325 and two low-Ti Vaca Muerta pebbles (in wt%, \*:
SiO<sub>2</sub> calculated by difference). Data given by Irving et al. (2013) obtained at University of
Alberta, are shown for comparison.

		NWA 7325	Vaca Muerta		
	cutting	dust	chip	VM3	VM4
Lab.	U. Alberta	Brest	Brest	Brest	Brest
$SiO_2$	47.09	48.04	(46.4*)	(50.0*)	(46.0*)
TiO <sub>2</sub>	0.01	0.05	0.03	0.04	0.06
$Al_2O_3$	18.6	18.91	17.83	9.65	13.14
$Cr_2O_3$	0.40	0.44	0.54	0.36	0.35
FeO	1.57	1.87	0.57	19.72	19.74
MnO	0.03	0.04	0.03	0.60	0.58
MgO	12.13	12.18	13.84	10.84	9.69
CaO	17.94	18.37	20.15	8.30	10.05
Na <sub>2</sub> O	0.60	0.65	0.63	0.17	0.27
$K_2O$	0.01	0.03	< 0.01	0.03	0.02
$P_2O_5$	0.02	0.03	0.04	0.30	0.12
total	98.40	100.61	100.00*	100.00*	100.00*

		NWA 7325		Vaca Muerta		
	cutting	dust	chip	VM3	VM4	
Lab.	U. Alberta	Brest	Brest	Brest	Brest	
Li	0.53	0.93	0.32	3.86	4.22	
Be		0.028	0.002	0.010	0.021	
P <sub>2</sub> O <sub>5</sub> wt%	0.02	0.043	0.024			
K	83	281	23			
Sc		19.64	24.18	29.38	25.41	
Ti		239	106	215	361	
V		190	249	83.8	85.3	
Mn	230	260	254	4246	4097	
Co		21.7	23.5	53.1	38.0	
Ni	78	164	57	1278	716	
Cu		264	6.76	13.6	14.2	
Zn		330	5.23	1.97	1.01	
Ga		8.32	8.65	1.36	1.58	
Rb	0.37	0.86	0.055	0.14	0.18	
Sr	198	195	189	37.0	54.9	
Y		0.566	0.152	0.064	0.210	
Zr	1.3	1.68	0.080	0.98	0.18	
Nb	2.5	0.208	0.026	0.12	0.12	
Cs		0.043	0.004	0.010	0.009	
Ba	61	67.92	14.92	2.48	1.59	
La	0.15	0.421	0.0188	0.0585	0.101	
Ce	0.34	0.927	0.0612	0.179	0.279	
Pr		0.109	0.00755	0.0201	0.0328	
Nd	0.16	0.430	0.0413	0.0801	0.127	
Sm	0.05	0.0944	0.0175	0.0165	0.0185	
Eu	0.58	0.532	0.499	0.176	0.286	
Gd	0.05	0.107	0.0308	0.0124	0.0145	
Tb		0.0165	0.00484	0.00192	0.00286	
Dy		0.0978	0.0302	0.0117	0.0243	
Ho		0.0191	0.00573	0.00272	0.00764	
Er		0.0521	0.0133	0.00855	0.0315	
Yb		0.0452	0.00985	0.0174	0.0658	
Lu		0.00635	0.00126	0.00348	0.0125	
Hf	0.44	0.049	0.00340	0.0165	0.0035	
Та		0.0170	0.0009	0.011	0.009	
W		0.112	< 0.001	0.020	< 0.001	
Pb		3.91	0.027	2.64	0.19	
Th	0.27	0.112	0.00901	0.00661	0.0107	
U		0.0409	0.00987	0.00591	0.00295	

615	Table 3. Trace element	abundances in NWA	7325 and in two low-Ti	i Vaca Muerta pebble	s (in $\mu g/g$ ).

617	Table 4.	Nitrogen and	Carbon isotope	e results. The	e sample v	weight was	6.143 mg.
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T (°C)	C (ng)	$\delta^{13}$ C (‰)	±	N (ng)	$\delta^{15}N$ (‰)	<u>+</u>
200	151	-28.8	0.1	1.82	-4.7	1.4
300	1081	-28.7	0.2	117.7	10.6	0.2
400	533	-27.5	0.2	28.31	4.8	0.2
500	479	-22.2	0.2	23.63	5.5	0.3
600	2241	1.2	0.2	15.53	2.6	0.3
700	2542	3.0	0.2	13.84	3.0	0.4
800	71	-12.6	0.1	3.35	1.1	0.9
900	18	-14.4	0.2	2.17	11.9	1.3
1000	43	-13.1	0.5	0.86	16.5	2.1
1100	8	-16.9	0.2	0.52	-3.1	3.5
1200	15	-22.7	0.2	0.53	11.0	4.1
1300	9	-23.9	0.1	0.42	11.3	5.2
1400	39	-24.9	0.2	0.89	42.5	2.4
	7237	-7.4		210.6	8.0	



Figure 1. a: one of the largest NWA 7325 stones; notice the distinctive green fusion crust and the soil
materials adhering to the stone; the size of the cube is 1 cm; b: slice of NWA 7325 showing its

- 628 unbrecciated structure; c: crossed polarized light image of a thin section showing the gabbroic texture.
- 629 (Pictures a and b, courtesy of Stefan Ralew, picture c, courtesy of John Kashuba).



Figure 2. REE patterns of NWA 7325 and two low-Ti gabbros from the Vaca Muerta mesosiderite.

634 The reference CI chondrite is from Barrat et al. (2012).

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Figure 3. CI normalized multi-element patterns for NWA 7325 and two low-Ti gabbros from the VacaMuerta mesosiderite. The reference CI chondrite is from Barrat et al. (2012).



Figure 4. Oxygen isotope composition of NWA 7325 (Irving et al., 2013; Jabeen et al., 2014 and this
work) compared with ureilites (Clayton and Mayeda, 1996) and other achondrites (Greenwood et al.
2012, 2014 and references therein). MGP, main-group pallasites; HEDs, howardites, eucrites,
diogenites; TFL, terrestrial fractionation line; CCAM, the carbonaceous chondrite anhydrous mineral
line (Clayton and Mayeda, 1999); Px, pyroxene; Pl, plagioclase.



Figure 5. a: Carbon stepwise combustion results for NWA 7325; b: Nitrogen stepwise combustion resultsfor NWA 7325.



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659 Figure 6. Plot of  $\Delta^{17}$ O in the bulk rocks *vs.* olivine core compositions for ureilites (data from Clayton and 660 Mayeda (1996), Downes et al. (2008), Singletary and Grove (2003), Goodrich et al. (2006, 2014) and references 661 therein) and NWA 7425 (Irving et al., 2013 and this work, same symbols as Fig. 3).



Figure 7. Ga/Al, and Zn/Al vs. Na/Al plots comparing NWA 7325 (chip) and the two Vaca Muerta
Pebbles (VM) with main types of achondrites (fields and data from Warren et al. (2013), Yamaguchi
et al. (2002), Day et al. (2012) and Bischoff et al. (2014)). APB, angrite parent body.



Figure 8. The Mg isotopic composition of NWA 7325 (Dunlap et al., 2014) compared to the theoretical evolution of the Mg isotopic composition of the solar system (calculated for a chondritic  $^{27}$ Al/<sup>24</sup>Mg ratio of 0.101, a ( $^{26}$ Al/<sup>27</sup>Al)<sub>0</sub> of 5.23 x 10<sup>-5</sup>, and a  $\delta^{26}$ Mg\*<sub>0</sub> of -0.034 ‰ (Jacobsen et al., 2008)).



Figure 9. Model age of the protolith of NWA 7325 vs.  ${}^{27}\text{Al}/{}^{24}\text{Mg}$  of its parental melt. Assuming that the parental melt and the whole rock have the same Al/Mg ratios ( ${}^{27}\text{Al}/{}^{24}\text{Mg}$ = 1.56), an intercept with the solar system growth curve at about 4566 Ma is obtained.