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

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By

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Abstract

The unique achondrite NWA 7325 is an unusual olivine gabbro composed chiefly of calcic plagioclase (An_{85-93}), diopsidic pyroxene ($En_{50.1-54.0}$ $Wo_{44.8-49.3}$ $Fs_{0.6-1.3}$), and forsteritic olivine (Fo_{97}). It 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 Sr anomalies (Eu/Eu*=65, Sr_n/Ce_n=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 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, 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 be precisely assessed. However, the liquid from which NWA 7325 crystallized would have been very poor in incompatible trace elements (Yb in the range of 0.25 to 1.5 x CI abundance) with a very large positive Eu anomaly. Such a melt cannot be the product of the early magmatic activity on a small 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 of ^{26}Al-^{26}Mg. Based on recent dating, the crustal material that was parental to NWA 7325 must have been older than 4562.8 Ma, and formed possibly ≈4566 Ma ago. If this scenario is correct, NWA 7325 provides evidence of one of the earliest crusts on a differentiated body so far studied.

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.

The number of parent bodies sampled by achondrites is the subject of ongoing debate. About 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 (ca. 400 meteorites, 20 % of all achondrites). Mars, the Moon and a handful of smaller bodies are the sources of the remaining achondrites. Some of them form distinct groups based on their petrographic and isotopic features, such as the aubrites, the angrites or the brachinites (see recent reviews by Keil, 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 is more likely that these unique achondrites originated from one of the many planetesimals that differentiated during the first few million years of solar system history, the possibility that we have in 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 planet, but for the chemical structure of the inner solar system too.

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

originated from this planet. Subsequently, this rock has been extensively studied by different teams using a variety of techniques (Irving et al., 2013; Amelin et al., 2013; Bischoff et al., 2013; Sanborn et al., 2013; Dunlap et al., 2014; El Goresy et al., 2014; Goodrich et al., 2014; Jabeen et al., 2014; Kita et 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 important by virtue of its distinct petrographic and geochemical features. Here we report new chemical, mineralogical and stable isotope (oxygen, carbon and nitrogen) results that provide important evidence relevant to the origin of this unique meteorite.

2. Samples and analytical techniques

Two samples of NWA 7325 were available for bulk rock chemical analysis: a clean chip of the 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 the meteorite. In addition, two low-Ti gabbroic pebbles from Vaca Muerta were selected for comparison, from the mesosiderite samples studied previously by Greenwood et al. (2006). Petrographic observations and quantitative chemical analyses of the main phases of the NWA 7325 achondrite were made on a polished thick section (1 cm^2) prepared from a slice obtained from S. Ralew. Cameca SX100 electron microprobe analyses at Service Commun "Microsonde Ouest" (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 [$MnTiO_3$ (Mn, Ti)], Al_2O_3 (Al), Fe_2O_3 (Fe), Cr_2O_3 (Cr)], and one sulfide [FeS_2 (S)] were used for calibration. The raw data were corrected with the 'PAP' software (Pouchou and Pichoir, 1985).

The Vaca Muerta samples and the NWA 7325 chip were totally powdered using a boron carbide pestle and mortar. Major and trace element concentrations were determined respectively by ICP-AES (inductively coupled plasma-atomic emission spectrometry) and ICP-MS (inductively

coupled plasma-mass spectrometry) at Université de Brest (IUEM, Plouzané) using the procedures described by Barrat et al. (2012, 2014). The accuracy of major and trace element concentrations is better than 5% (probably better than 3% for all the REEs) based on various standard and sample duplicates.

Oxygen isotope analyses were carried out at the Open University using an infrared laser fluorination system following the methods and procedures of Miller et al. (1999). Analyses were 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_5. After fluorination, the released oxygen gas was purified by passing it through two cryogenic nitrogen traps and over a bed of heated KBr. Oxygen gas was analysed using a MAT 253 dual inlet mass spectrometer. Interference at m/z=33 by the NF_3 fragment ion NF^+ was monitored by performing scans for NF_2^+ on all samples run in this study. In all cases NF_2 was either negligible or absent. Oxygen isotopic analyses are reported in standard δ notation, where $\delta^{18}O$ has been calculated relative to VSMOW (Vienna Standard Mean 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 the $^{17}O/^{16}O$ ratio. $\Delta^{17}O$, which represents the deviation from the terrestrial fractionation line, has been calculated using a linearized format (Miller, 2002):

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

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

Carbon and nitrogen concentrations and isotopic analyses were obtained by the stepped combustion technique using the multi-element analyzer system "Finesse" (Verchovsky et al., 1998, 2003). An aliquot (6.134 mg) of the internal sample of NWA 7325 was heated from 200 to 1400°C with 100° increments. The released N and C in the form of N_2 and CO_2 were analyzed simultaneously

from the same aliquot. The isotope results are expressed in standard δ notation normalized to air for N and to PDB for C.

3. Results and discussion

3.1. Petrography

NWA 7325 has been extensively described in a series of abstracts (Irving et al., 2013; Bischoff et al., 2013; Goodrich et al., 2014; El Goresy et al., 2014). Our observations are in agreement with these earlier studies, and are summarized here. NWA 7325 is a fine to medium grained gabbroic rock 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 plagioclase (~55-60 vol%), with accessory iron sulfides (1 vol%), and sparse ferrochromite, metal grains and rare eskolaite associated with iron sulfide. El Goresy et al. (2014) report the occurrence of Ca sulfates that they interpret as totally weathered grains of oldhamite. However, like the vast majority of Saharan finds, NWA 7325 contains cracks filled with secondary carbonates. Rather than 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.

Major element compositions of the main phases are reported in Table 1. Coarse-grained plagioclase is calcic (An_{85-93}), and contains traces of MgO (=0.13-0.45 wt%). Ca-pyroxene is homogeneous and extremely magnesian ($En_{50.1-54.0}$ $Wo_{44.8-49.3}$ $Fs_{0.6-1.3}$, Mg/(Fe+Mg)= 0.975-0.983, n=58). Olivine ($Fo_{97-97.3}$, n=51) is in equilibrium with pyroxene (e.g., Perkins and Vielzeuf, 1992). Fe-sulfide 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.

3.2. Geochemistry

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_2O_3, and poor in Fe, Mn and alkalis (Na_2O = 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).

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 significant discrepancies (Table 3 and Fig. 2 and 3). Both samples are poor in incompatible lithophile elements (REEs except Eu < 2 x CI), light REE enriched (La_n/Sm_n = 1.95 – 2.90) with striking positive Eu anomalies (Eu/Eu* = 16.1 – 35.2), but our sample contains respectively about 2x more light REEs, 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 explanations might account for these differences: i) contamination during the cutting of the meteorite by handling and by the saw blade, ii) different proportions of soil materials which were adhering to the 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 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.

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

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

NWA 7325 contains low but significant amounts of Ni (= 57 µg/g) and Co (=23 µg/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_n/Sm_n = 0.70), and displays large positive Eu and Sr anomalies (Eu/Eu*= 65, Sr_n/Ce_n= 240).

3.2.2. Oxygen isotopes.

The bulk oxygen isotopic composition of NWA 7325 was determined in duplicate using the powder made with the interior fragment. The average of the two analyses was: $\delta^{17}O$ =3.33 ± 0.09 ‰, $\delta^{18}O$ = 8.10 ± 0.18 ‰, $\Delta^{17}O$ = −0.91 ± 0.01 ‰ (errors ± 1σ). Our new analysis of NWA 7325 plots on the CCAM line in Fig. 4, within the ureilite field. Three individual analyses of NWA 7325 by Irving et al. (2013) have somewhat divergent compositions, with one plotting close to the result reported here. Jabeen et al. (2014) give oxygen isotope analyses for plagioclase and pyroxene mineral separates from NWA 7325 that are displaced from one another by approximately 2 ‰ along a mass fractionation line (Fig. 4). The mean plagioclase analysis (n=4) of Jabeen et al. (2014) plots close to our bulk value for NWA 7325. However, in view of the significant proportion of pyroxene in NWA 7325 (20-30 %, 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 analysis.

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 $CaCO_3$ 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.

3.3. NWA 7325, a unique achondrite.

3.3.1. What is the parent body of NWA 7325?

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 sensing observations (Weider et al., 2012). However, the suggestion that NWA 7325 may represent a sample of Mercury's crust (Irving et al., 2013) has been challenged on the basis of dating evidence. Amelin et al. (2013) obtained a Pb-isotopic age for NWA 7325 of 4562.5 ± 4.4 Ma. This very old age was subsequently confirmed by Dunlap et al. (2014), who obtained an Al-Mg age of 4562.8 ± 0.3 Ma. 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. Therefore, a mercurian origin appears to be untenable, and instead it seems more likely that NWA 7325 originated from one of the planetesimals that formed during the first millions of years after the formation of refractory inclusions.

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 in the early Solar System (i.e., highly reduced conditions for aubrites, a volatile-depleted body and more oxidized conditions for angrites, C-rich body with ureilites…). Despite this large mineralogical 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 compositions similar to NWA 7325 (plagioclase An_{87-89}, olivine Fo_{93}, Ikeda et al., 2000; Kita et al., 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 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).

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

Thus, NWA 7325 is a unique achondrite with distinctive geochemical and isotopic features. It certainly originated from a parent body unsampled by other achondrites. In Figure 7, we compare the 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 (ALM-A) and brachinitic (GRA-06) melts, NWA 7325 displays low Na/Al, Ga/Al and Zn/Al and plots 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 chip (Table 3).

3.3.2. Petrology of NWA 7325

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_2 close to IW-4, Sutton et al., 2014).

Gabbroic rocks displaying positive Eu anomalies are widely considered as cumulates. NWA 7325 is no exception (e.g., Irving et al., 2013), but we emphasize that this interpretation is not unique. Significant positive Eu anomalies can be generated in non-cumulative basaltic rocks by partial melting, for example during short duration reheating events (Yamaguchi et al., 2009; 2013). Larger degrees of melting of a basaltic or gabbroic lithology can produce gabbroic restites displaying very 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 by remelting (e.g., Bischoff et al., 2013). Thus, the possibility that NWA 7325 could be a restite merits further consideration.

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 Mittlefehldt, 1992). We analyzed for comparison two such pebbles from Vaca Muerta (Table 2 and 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, i.e. positive Ce anomalies, sometimes high U/Th ratios and high Pb abundances, etc… Interestingly, these two pebbles display at first glance the same level of incompatible trace element concentrations and the same large Sr and Eu anomalies as NWA 7325. However, their REE patterns display marked heavy-REE enrichments (Gd_n/Lu_n = 0.14-0.43) which are well explained by the loss of a partial melt (e.g., Yamaguchi et al., 2009). The REE pattern of the NWA 7325 chip does not exhibit such an

310 enrichment (Gd_n/Lu_n = 2.92). We conclude that NWA 7325 is probably not restitic, although we note
311 that this inference is model dependent (i.e., composition of the melted lithology).
312
313 If NWA 7325 is a cumulate, what can we infer about the composition of its parental melt
314 based on its petrography and major and trace element abundances? It was certainly "basaltic", not
315 SiO_2-saturated (crystallization of olivine), and Ca-rich (diopsidic pyroxene and calcic plagioclase). It
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
323 of plagioclase, diopsidic pyroxene and olivine, the pyroxene controls the budget of heavy REEs.
324 Assuming that the NWA 7325 chip contained about 33 wt% pyroxene, the Yb or Lu concentrations in
325 this mineral are probably ≈ 0.15 x CI abundances. Partition coefficients of Yb for diopside at low
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
329 REE abundances in NWA 7325, the Gd-Lu part of the REE pattern is chiefly controlled by its partition
330 coefficients and the $(Gd/Lu)_n$ of the parental melt. Because $(D_{Gd}/D_{Lu})_{cpx}$ is ≈ 1 (e.g., Schosnig and
331 Hoffer, 1998), $(Gd/Lu)_n$ 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
334 displaying a flat REE pattern. The parental melt to NWA 7325 must therefore have had a fractionated
335 REE pattern with $(Gd/Lu)_n$ ratio > 1, and probably ≈ 3. Similar lines of reasoning are possible for Eu.
336 Partition coefficients for Eu in plagioclase are much larger than those in pyroxene or olivine (e.g.,
337 McKay et al., 1989; Schosnig and Hoffer, 1998). Therefore, the budget of Eu in the rock is strongly

338 controlled by plagioclase. Assuming that the NWA 7325 chip contained about 53 wt% plagioclase, the
339 Eu concentration in this phase is ≈ 16 x CI abundance. Partition coefficients for Eu in plagioclase are
340 not only dependent on the composition of the melt but are also strongly sensitive to the oxygen
341 fugacity (e.g., McKay, 1989). For the purpose of calculation, partition coefficients for Eu in calcic
342 plagioclase at low fO_2 for a basaltic melt are assumed to range from 0.7 to 1.1 as suggested by McKay
343 (1989), and in agreement with the recent experimental results obtained by Rapp et al. (2015). The Eu
344 concentration of the parental melt was probably in the range of 14 to 23 x CI abundances. Even if we
345 take into account the enrichment in middle REEs of the parental melt (i.e., the $(Gd/Yb)_n$ or the
346 $(Gd/Lu)_n$ ratios), its level of concentration of Eu is very high compared to the heavy-REEs. It comes as
347 an unavoidable conclusion that the parental melt of NWA 7325 certainly displayed a very large
348 positive Eu anomaly ($Eu_n/Yb_n > 10$, probably $Eu_n/Gd_n > 3$) that is difficult to estimate accurately.
349 A melt with such a large positive Eu is very unlikely to be the direct product of the early
350 magmatic activity on a planetesimal. On the other hand, gabbros formed in reduced conditions can
351 display low incompatible trace element abundances and large positive Eu, as exemplified by the
352 cumulate eucrites. Total melting of such rocks could produce melts with these features. It is tempting
353 to propose that NWA 7325 is a cumulate derived from the crystallization of such a melt, with the
354 melting of its protolith possibly produced by an energetic impact.
355
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
362 of ≈0.2 wt% of chondritic material). Archer et al. (2015) suggested that this chondritic signature was
363 introduced into the rock after crystallization during late-stage impacts. Because NWA 7325 is
364 unbrecciated, this explanation is unlikely. Alternatively, a chondritic component could have been
365 introduced into the NWA 7325 parental melt during its crystallization. One possibility is that NWA

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

Moreover, the systematics of ^{26}Al-^{26}Mg further strengthens the hypothesis that NWA 7325 formed by impact-melting of gabbroic material. The Al-Mg internal isochron obtained previously by Dunlap et al. (2014) for NWA 7325 has a well-resolved positive intercept ($\delta^{26}Mg_0$*) of 0.095 ± 0.011 ‰, and lies well above the bulk chondritic value (Al/Mg ≈ 0.1 and δ^{26}Mg* ≈ 0 ‰). As noted by Dunlap et al. (2014), this high $\delta^{26}Mg_0$* could imply a non-chondritic initial composition for the parental body. Alternatively, the source material for this achondrite may have evolved with a highly 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 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 NWA 7325 (Fig. 8). Moreover, assuming that the parental melt of NWA 7325 formed by impact melting of a gabbroic target 4.5628 Ga ago, we can place some constraints on the formation age of its protolith. Unfortunately, the ^{27}Al/^{24}Mg ratio of the parental melt of NWA 7325 is not known. Because NWA 7325 is a plagioclase rich cumulate, its parental melt displayed probably a lower Al abundance than the whole rock, but it is not possible to assess neither its Mg concentration nor its Al/Mg ratio. In the case of eucrites, the Al/Mg ratios of cumulate and basaltic eucrites are similar. Although these 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 whole rock ^{27}Al/^{24}Mg ratio (= 1.56) and we obtained an intercept with the solar system growth curve at about 4566 Ma. A lower Al/Mg ratio would point to an older model age, and conversely younger model ages are obtained with higher Al/Mg ratios, but variations of 25 % around the Al/Mg ratio of the whole rock do not alter this estimation (Fig. 9). Although only indicative, our calculations show

393 that remelting of a very old gabbroic lithology can perfectly explain the high $\delta^{26}Mg^*_0$ of NWA 7325.
394 Thus, NWA 7325 provides evidence of one of the earliest crusts on a differentiated body so far
395 studied. We note that the NWA 7325 protolith could be practically contemporaneous to Asuka
396 881394, which formed 4566.5 ± 0.2 Ma ago on a distinct parent body (Wadhwa et al., 2009).
397

398 # 4. Conclusions

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

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

	n	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total	endmembers
plagio.	71	45.25	< 0.03	34.14	< 0.03	0.07	< 0.03	0.29	18.11	1.18	< 0.03	99.07	$An_{89.4}\,Ab_{10.5}$
pyrox.	58	52.68	0.04	2.93	1.03	0.73	0.05	18.88	22.54	0.16	< 0.03	99.04	$En_{53.2}\,Wo_{45.6}\,Fs_{1.2}$
olivine	51	42.25	< 0.03	0.04	0.37	2.81	0.07	54.38	0.35	< 0.03	< 0.03	100.25	$Fo_{97.2}$

		Si	Ti	Al	Cr	Fe	Mn	Mg	Ca	Na	S	Total
sulfide	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_2 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_2	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_2O	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*

615 Table 3. Trace element abundances in NWA 7325 and in two low-Ti Vaca Muerta pebbles (in µg/g).

	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_2O_5 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
Ta		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

616

Table 4. Nitrogen and Carbon isotope results. The sample weight was 6.143 mg.

T (°C)	C (ng)	$\delta^{13}C$ (‰)	±	N (ng)	$\delta^{15}N$ (‰)	±
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	

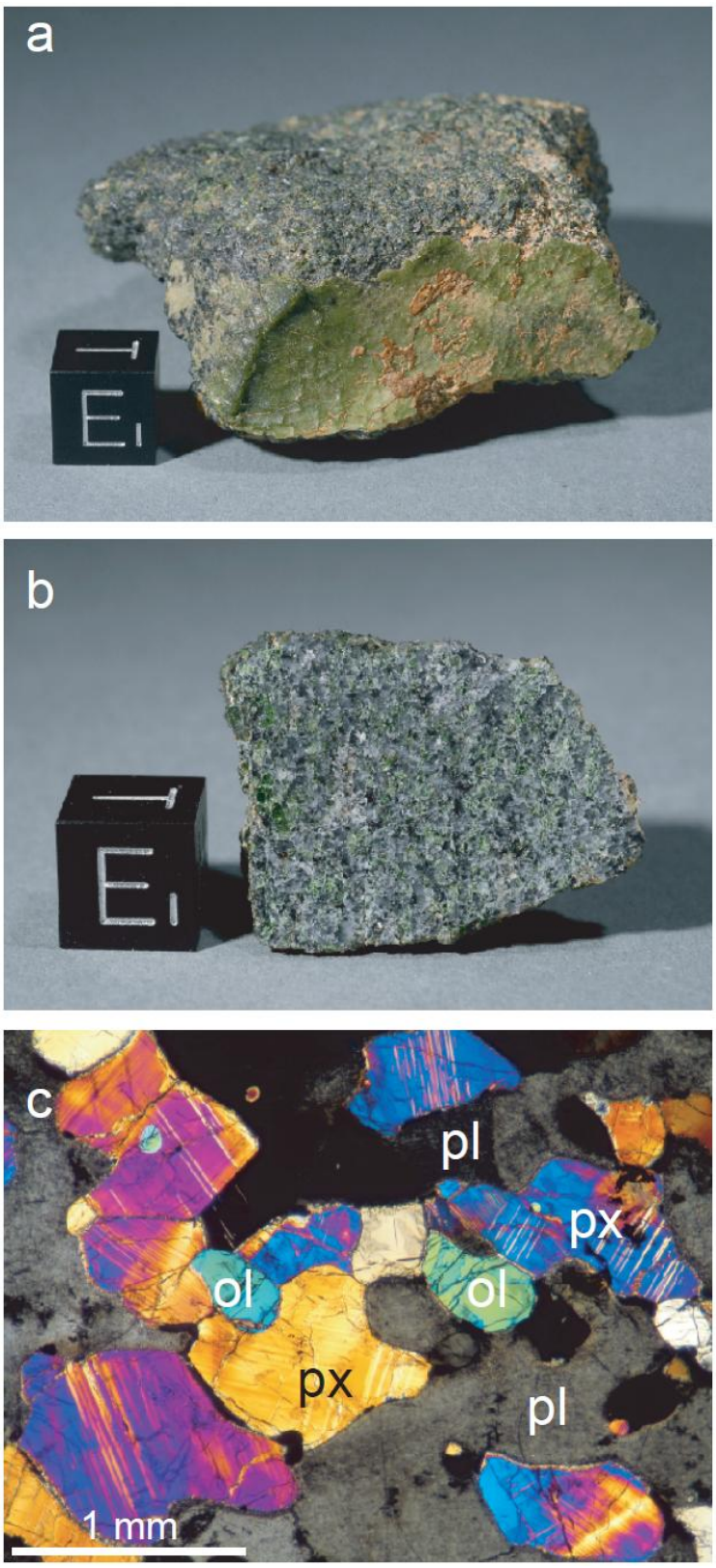

Figure 1. a: one of the largest NWA 7325 stones; notice the distinctive green fusion crust and the soil materials adhering to the stone; the size of the cube is 1 cm; b: slice of NWA 7325 showing its

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).

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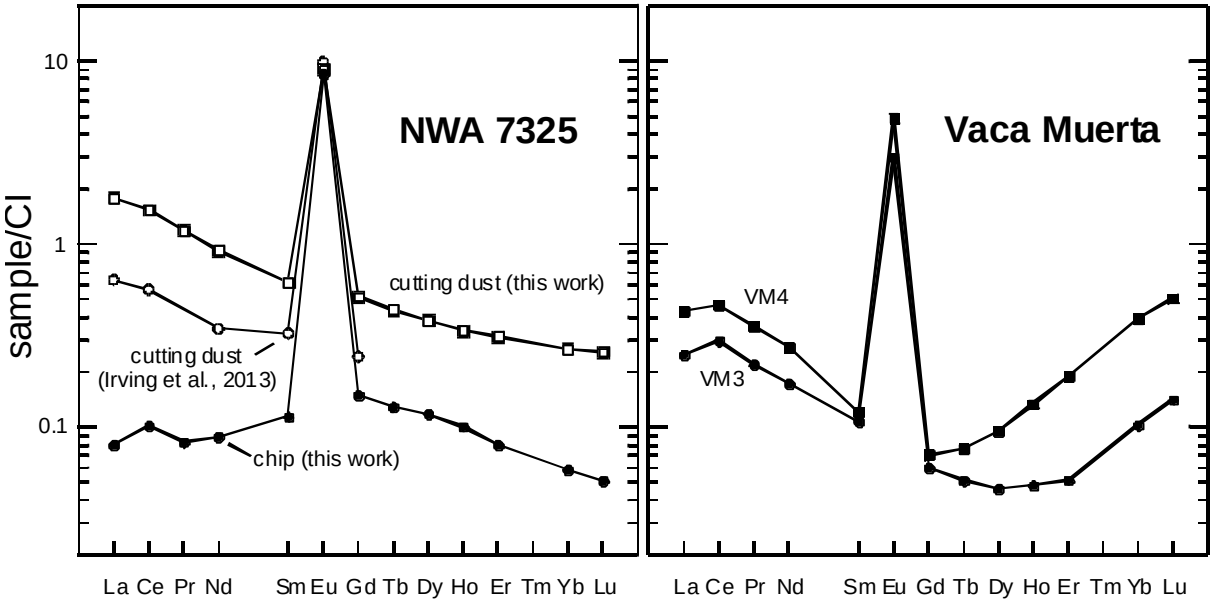

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633 Figure 2. REE patterns of NWA 7325 and two low-Ti gabbros from the Vaca Muerta mesosiderite.
634 The reference CI chondrite is from Barrat et al. (2012).

635

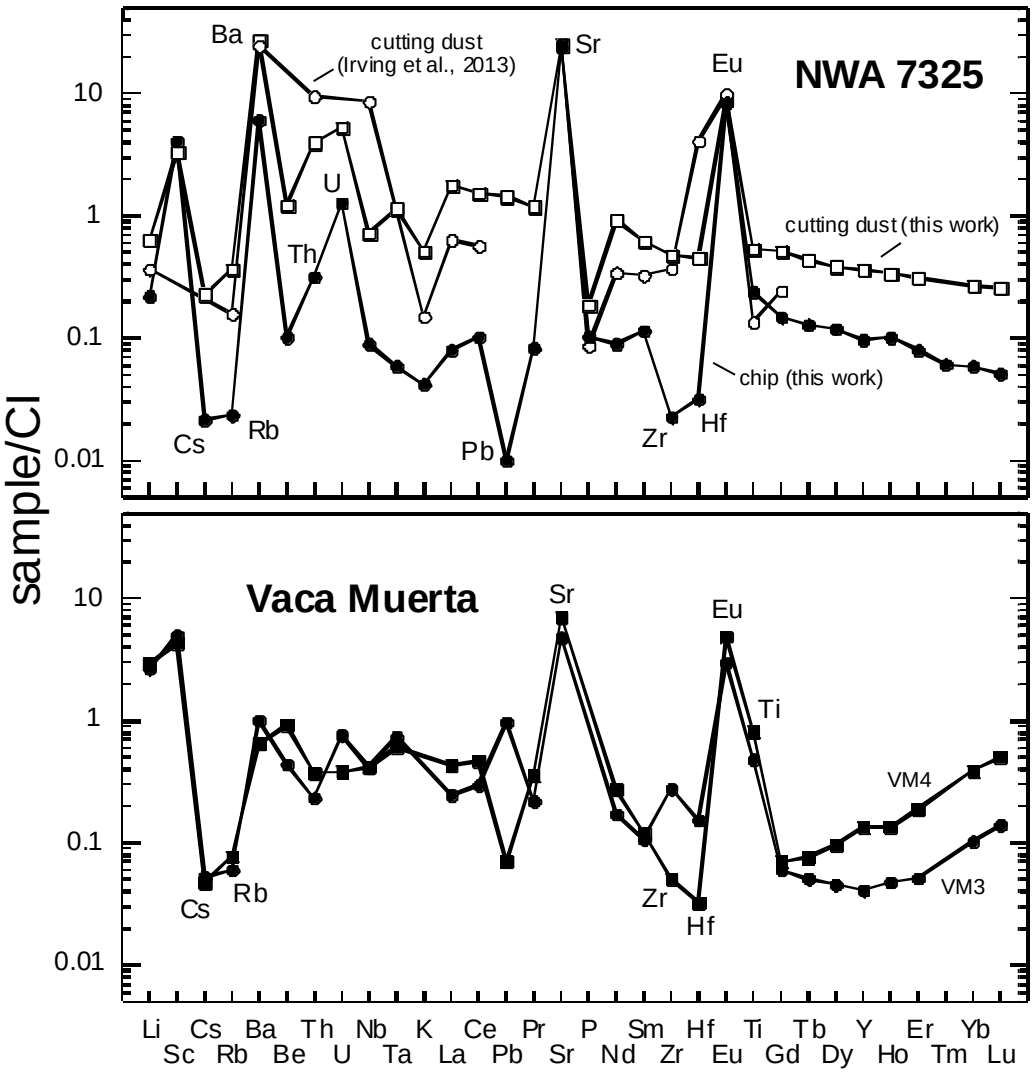
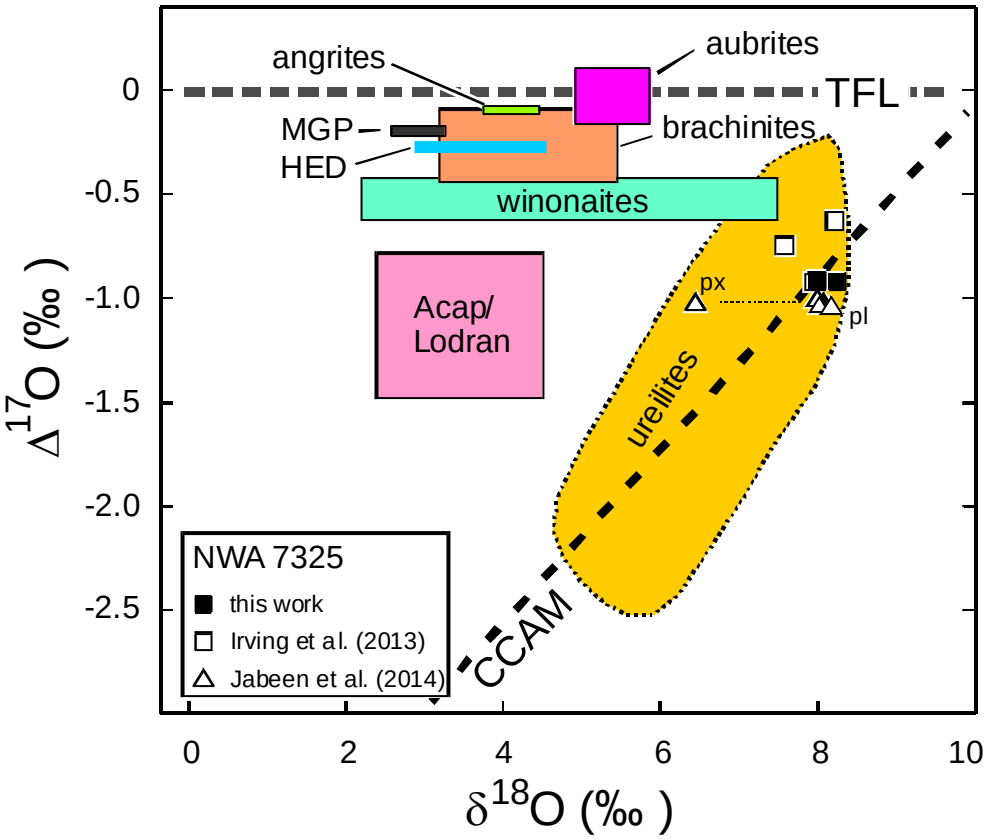


Figure 3. CI normalized multi-element patterns for NWA 7325 and two low-Ti gabbros from the Vaca Muerta mesosiderite. The reference CI chondrite is from Barrat et al. (2012).



644

645 Figure 4. Oxygen isotope composition of NWA 7325 (Irving et al., 2013; Jabeen et al., 2014 and this
646 work) compared with ureilites (Clayton and Mayeda, 1996) and other achondrites (Greenwood et al.
647 2012, 2014 and references therein). MGP, main-group pallasites; HEDs, howardites, eucrites,
648 diogenites; TFL, terrestrial fractionation line; CCAM, the carbonaceous chondrite anhydrous mineral
649 line (Clayton and Mayeda, 1999); Px, pyroxene; Pl, plagioclase.
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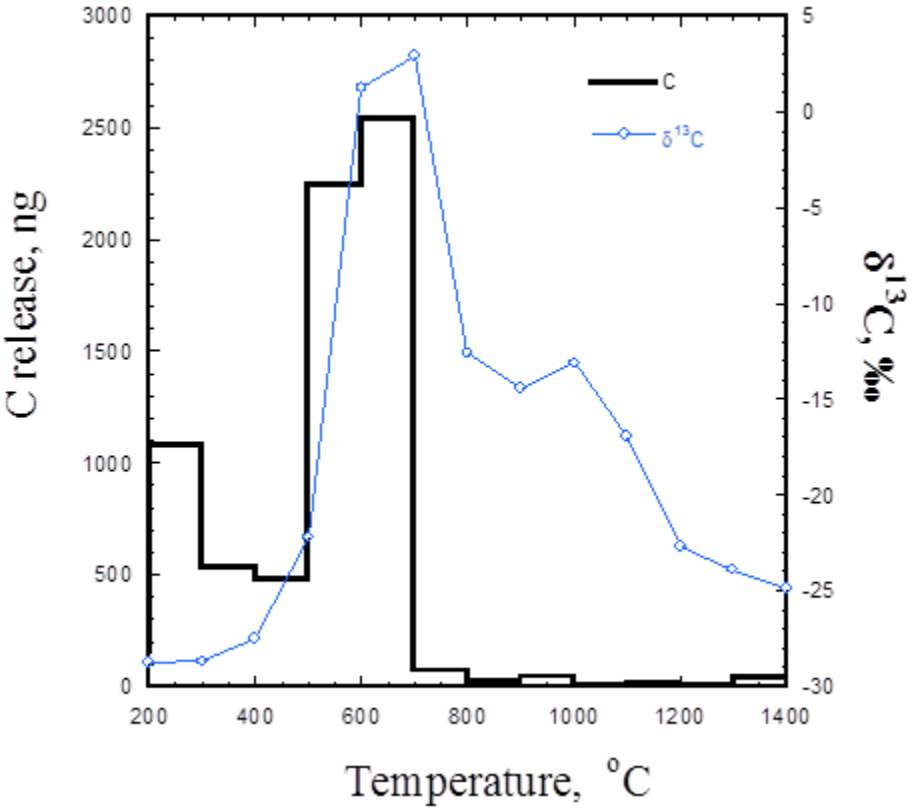

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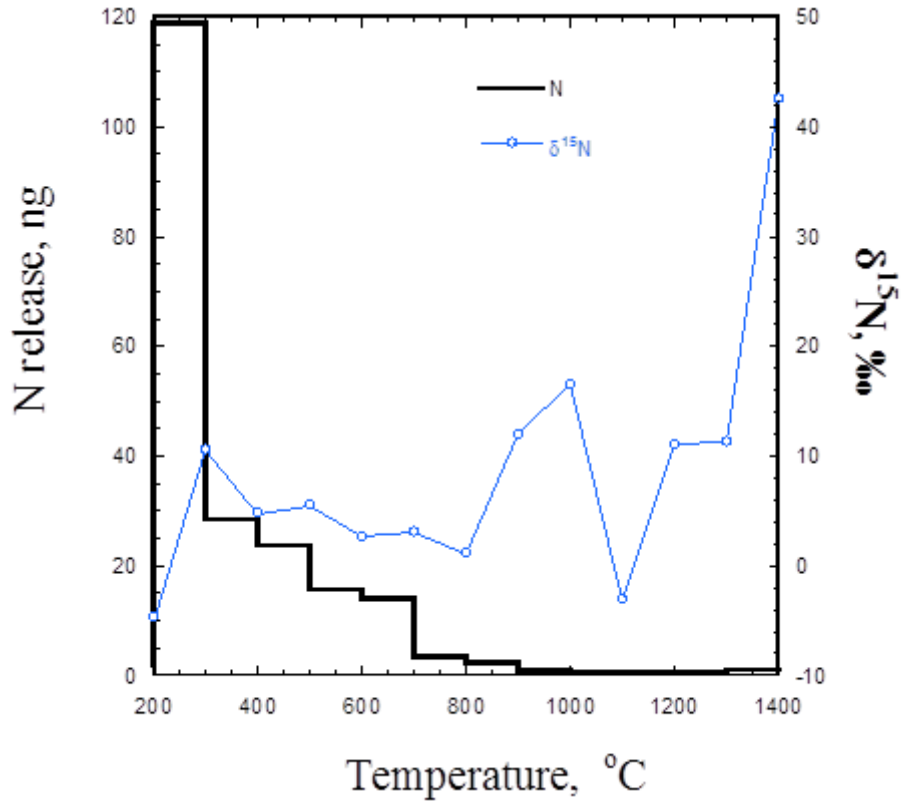

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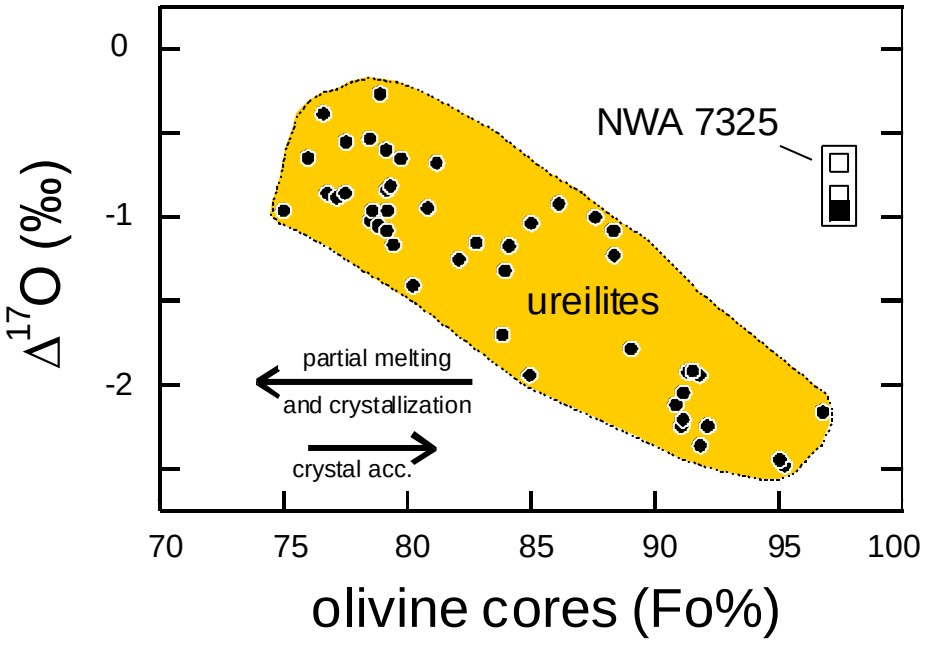
656 Figure 5. a: Carbon stepwise combustion results for NWA 7325; b: Nitrogen stepwise combustion results
657 for NWA 7325.



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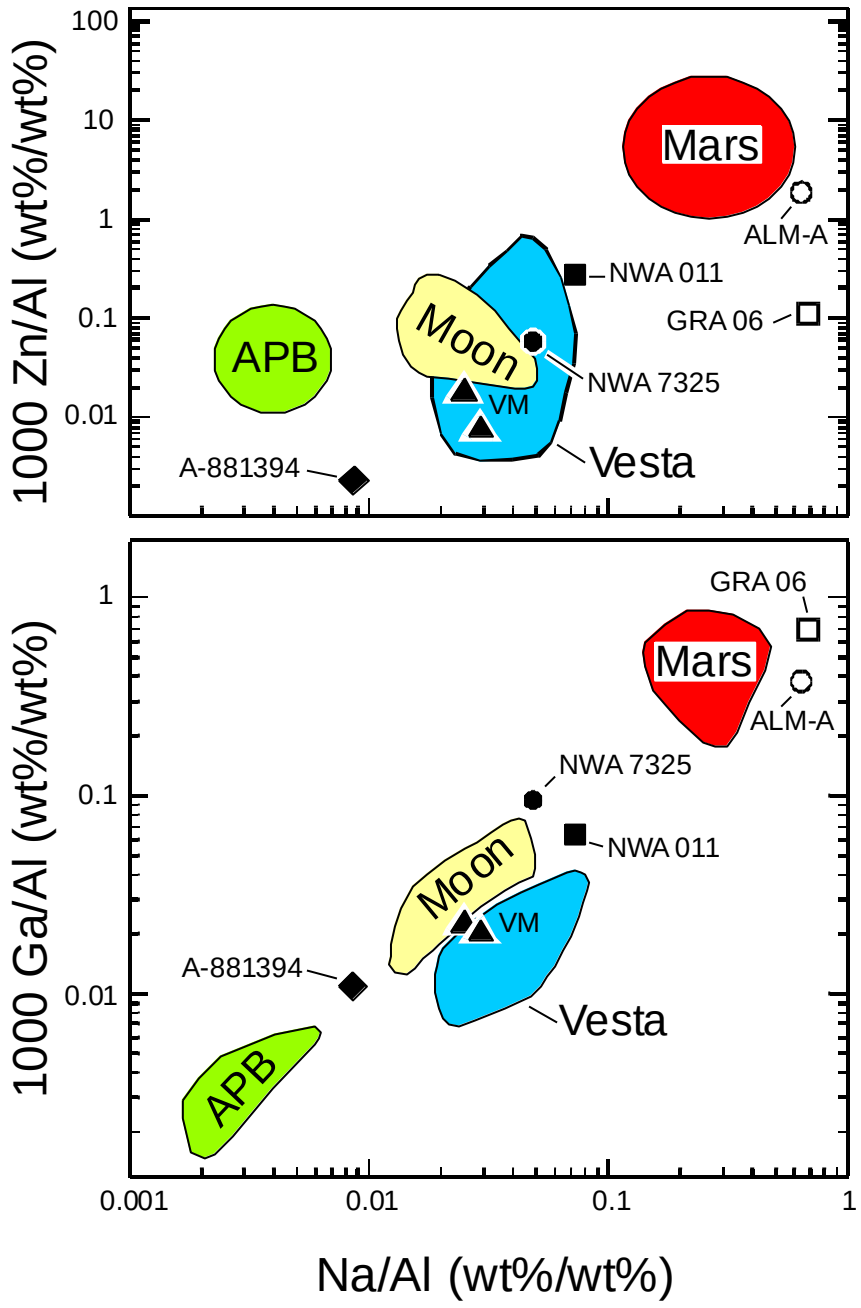
659 Figure 6. Plot of $\Delta^{17}O$ in the bulk rocks *vs.* olivine core compositions for ureilites (data from Clayton and
660 Mayeda (1996), Downes et al. (2008), Singletary and Grove (2003), Goodrich et al. (2006, 2014) and references
661 therein) and NWA 7425 (Irving et al., 2013 and this work, same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



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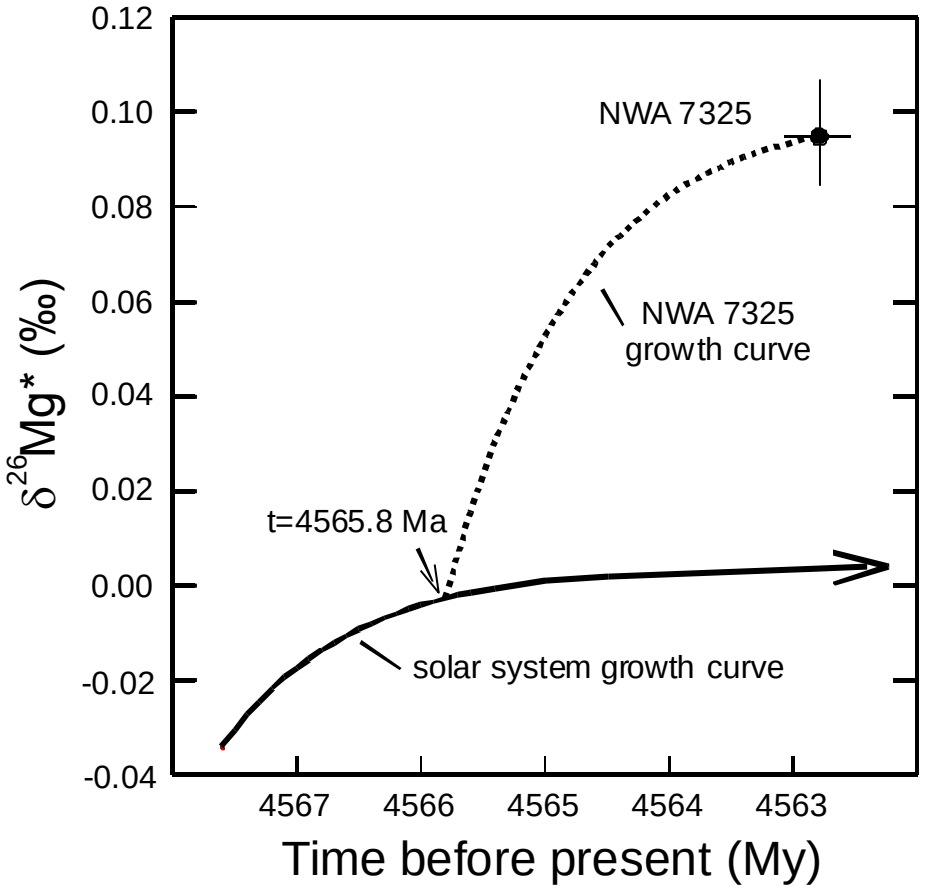

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669 Figure 8. The Mg isotopic composition of NWA 7325 (Dunlap et al., 2014) compared to the
670 theoretical evolution of the Mg isotopic composition of the solar system (calculated for a chondritic
671 $^{27}Al/^{24}Mg$ ratio of 0.101, a $(^{26}Al/^{27}Al)_0$ of 5.23 x 10^{-5}, and a $\delta^{26}Mg^*_0$ of -0.034 ‰ (Jacobsen et al.,
672 2008)).

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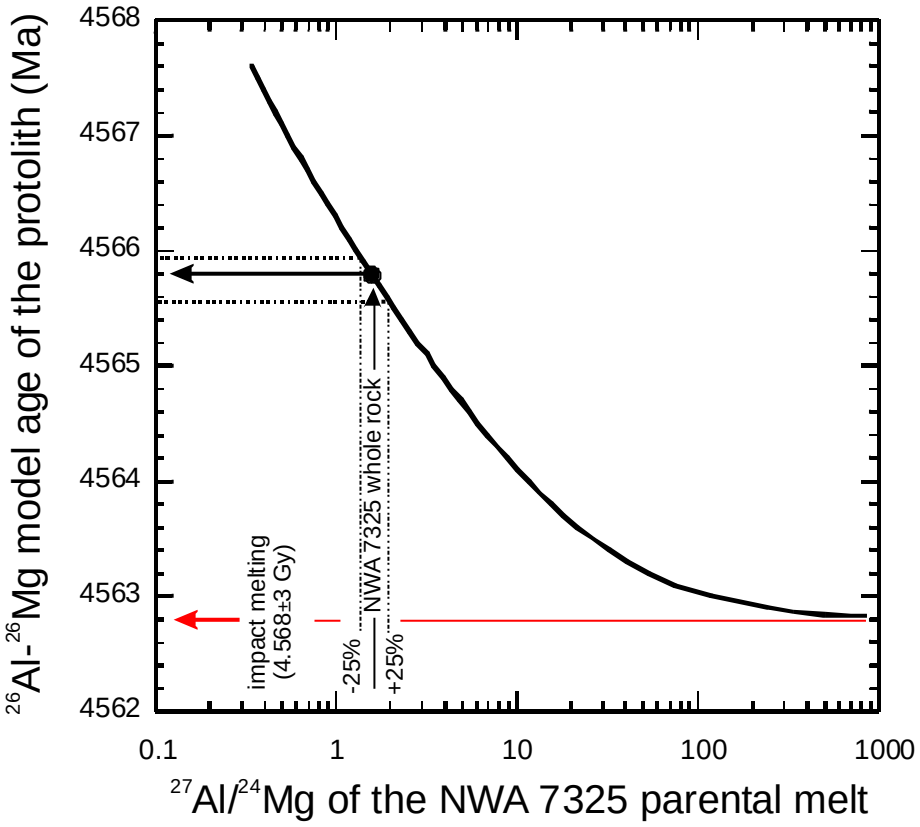

Figure 9. Model age of the protolith of NWA 7325 vs. ^{27}Al/^{24}Mg of its parental melt. Assuming that the parental melt and the whole rock have the same Al/Mg ratios (^{27}Al/^{24}Mg= 1.56), an intercept with the solar system growth curve at about 4566 Ma is obtained.