Carbon isotopic variation in ureilites: Evidence for an early, volatile-rich Inner Solar System

Barrat Jean-Alix [1, 2, *], Sansjofre Pierre [1, 2], Yamaguchi Akira [3, 4], Greenwood Richard C. [5], Gillet Philippe [6]

[1] Univ Bretagne Occidentale, UMR CNRS 6538, Lab Geosci Ocean, Pl Nicolas Copernic, F-29280 Plouzane, France.
[2] Inst Univ Europeen Mer, Pl Nicolas Copernic, F-29280 Plouzane, France.
[3] Natl Inst Polar Res, Tachikawa, Tokyo 1908518, Japan.
[4] Grad Univ Adv Sci, Sch Multidisciplinary Sci, Dept Polar Sci, Tachikawa, Tokyo 1908518, Japan.
[5] Open Univ, Sch Phys Sci, Planetary & Space Sci, Walton Hall, Milton Keynes MK7 6AA, Bucks, England.
[6] Ecole Polytech Federate Lausanne, Inst Condensed Matter Phys, EPSL, Stn 3, CH-1015 Lausanne, Switzerland.

* Corresponding author : Jean-Alix Barrat, email address : barrat@univ-brest.fr

Abstract :

We analyzed the C isotopic compositions of 32 unbrecciated ureilites, which represent mantle debris from a now disrupted, C-rich, differentiated body. The $\delta 13C$ values of their C fractions range from −8.48 to +0.11‰. The correlations obtained between $\delta 13C$, $\delta 18O$ and $\Delta 17O$ values and the compositions of the olivine cores, indicate that the ureilite parent body (UPB) accreted from two reservoirs displaying distinct O and C isotopic compositions. The range of Fe/Mg ratios shown by its mantle was not the result of melting processes involving reduction with C ("smelting"), but was chiefly inherited from the mixing of these two components. Because smelting reactions are pressure-dependent, this result has strong implications for the size of the UPB, and points to a large parent body, at least 690 km in diameter. It demonstrates that C-rich primitive matter distinct from that represented by carbonaceous chondrites was present in some areas of the early inner Solar System, and could have contributed to the growth of the terrestrial planets. We speculate that differentiated, C-rich bodies, or debris produced by their disruption, were an additional source of volatiles during the later accretion stages of the rocky planets, including Earth.

Highlights

► $\delta^{13}C$ in ureilites correlate with the Fe/Mg ratios of the cores of their olivines. ► The ureilitic mantle has recorded the involvement of two C-rich reservoirs. ► The UPB's diameter was larger than 690 km. ► C-rich matter, unlike carbonaceous chondrites, was present in the inner Solar System.

Keywords : carbon isotopes, ureilite, planetary differentiation, volatiles

1. Introduction

The origin of volatiles in the inner Solar System, including Earth, remains controversial. It is widely held that water and other volatiles were delivered late in the development of the terrestrial planets (Marty, 2012; Alexander et al., 2012; Rubie et al., 2015). An alternative view suggests that the inner planets accreted volatile-rich, so that phases such as water and other light elements, vital to the origin of life, were mainly indigenous (Halliday, 2013). Here we look at the origin of the ureilites, C-rich meteorites from a single differentiated body (Downes et al., 2005) that formed in the inner Solar System (Yamakawa et al., 2010; Warren, 2011; Barrat et al., 2016a; Budde et al., 2017), and hence are potentially representative of some of the materials from which the terrestrial planets accreted.

The ureilites are peridotites that constitute the largest sampling of the mantle of a body other than the Earth and so provide a unique opportunity to constrain the differentiation processes that took place within a protoplanet. Geochemical studies have shown that the UPB accreted no more than 1.6 My after initial Solar System formation (Budde et al., 2015). It was heated by decay of short-lived isotopes, principally ^{26}Al, resulting in the segregation of a S-rich core (e.g., Warren et al., 2006; Rankenburg et al., 2008; Barrat et al., 2015) and the formation of a trachyandesitic crust (Bischoff et al., 2014; Barrat et al., 2016b). This differentiation event occurred between 3 and 7 My, and was terminated by the catastrophic breakup of the body as the result of a large impact event (Goodrich et al., 2015).

Ureilites are restites formed after extraction of magmas and S-rich metallic melts (e.g., Scott et al., 1993; Warren et al., 2006; Barrat et al., 2016b). They consist chiefly of olivine and pyroxene, and are remarkably rich in C [1-6 wt% (Goodrich et al., 2015), graphite (Fig. 1) and diamond]. Olivines in ureilites have distinctive Mg-rich rims and veins that formed as a result of localized reduction reactions with adjacent C phases. These reactions probably took place during the disruption of the UPB (Miyamoto et al., 1985; Warren and Huber, 2006). Apart from these rims and veins, olivine cores and pyroxene grains are quite uniform in Mg# number [= 100 Mg/(Mg+Fe), atomic] within any individual ureilite sample. However, collectively their overall compositional variation is very large, as shown by the olivine-core Mg#, which ranges from 74 to 97 (Downes et al., 2008). The Fe/Mn ratios and Δ^{17}O values are correlated with this parameter. These variations cannot be explained by igneous

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66 fractionation. Instead, it has been argued that the Mg# range is the result of reduction
67 reactions involving C ("smelting", e.g., Singletary and Grove (2003), Goodrich et al. (2007,
68 2013)) that took place during the differentiation of the UPB, pre-igneous oxidation of metal
69 by H_2O from ice (Sanders et al., 2017) or, alternatively, was inherited from the accreted
70 materials, and preserved despite significant partial melting (Warren and Huber, 2006; Warren,
71 2012).

72   In this paper, we report new high-quality C isotopic data obtained on a large number
73 of unbrecciated ureilites, with the aim of constraining the role of C during the differentiation
74 of the UPB, the size of this body, and finally of discussing the diversity of volatile sources in
75 the inner Solar System.

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2. Samples and analytical procedure

78   We analyzed 32 unpaired meteorites collected in Antarctica and in the Sahara. The
79 details of the samples used in this study, all unbrecciated ureilites, are given in Table 1. Their
80 olivine cores cover nearly the full range of compositions known for these meteorites (Fo =
81 74–97 %). Polymict ureilites have deliberately been excluded from this study, as have
82 samples of the rare ''Hughes'' group ureilites. However, one sample (MET 01085) is not a
83 peridotite, but a pyroxenite devoid of olivine.

84   Samples (0.25 - 1 g) were powdered using a boron-carbide mortar and pestle. About
85 250 mg of powder for each sample was digested on a hot plate heated to 125°C, using
86 sequential mixtures of 10 N HF/14 N HNO_3, 14 N HNO_3 and 6 N HCl. This procedure
87 ensures a perfect dissolution of all the phases, except graphite and diamond, which are not
88 oxidized by these acids at this temperature. The resulting clear solution was carefully pipetted
89 off, and the C residues rinsed twice using ultrapure water and then dried. Our procedure has
90 the advantage of directly removing all terrestrial carbonates and all terrestrial C in the
91 samples. Carbon isotopic compositions were determined at the Pôle Spectrométrie Océan
92 (PSO), Institut Universitaire Européen de la Mer (IUEM, Plouzané, France). 0.1 to 0.2 mg of
93 the C powder was introduced in tin capsules and $\delta^{13}C$ was determined following flash
94 combustion using an EA-IRMS Flash-EA 2000 analyzer coupled to a Thermo Fisher Delta-V
95 Plus mass spectrometer. The oxygen flux was optimized at 240 ml/min for a flash combustion
96 of 15 s, to ensure a complete oxidation of the sample. Isotopic data are reported as parts per
97 thousand deviation (‰) from the Peedee belemnite reference material (PDB): $\delta^{13}C = 1000$
98 $[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1]$. Most measurements were determined in duplicate with an

99   external reproducibility better than 0.2 ‰ (2 σ). An in-house graphite standard (LCgraphite),

100   kindly provided by Pierre Cartigny (IPG, Paris) has been repeatedly analysed during the

101   course of this study in order to check the reproducibility and our calibration. These analyses

102   are in excellent agreement with previous results obtained by the Institut de Physique du
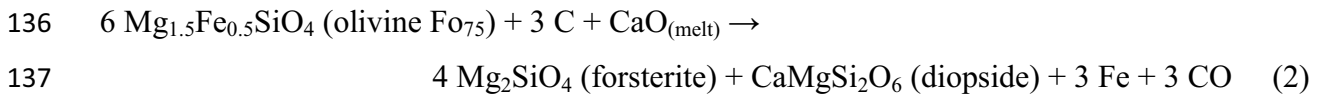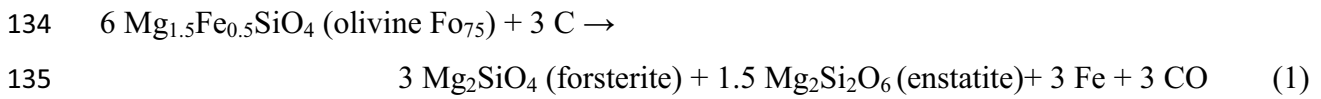
103   Globe, Paris (Table 1).

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105   ## 3. Results and discussion

106   ### 3.1. δ^{13}C systematics and the size of the UPB

107   Ureilitic C yielded δ^{13}C ranging from -8.48 to +0.11 ‰ (Table 1), in agreement with

108   earlier results ranging from -11.1 to ≈+0.5 ‰, (Grady et al., 1985; Grady and Pillinger, 1986;

109   Russell et al., 1993; Smith et al., 2001; Hudon et al., 2004; Downes et al., 2015; Miyahara et

110   al., 2015). Many of our samples (e.g., the Antarctic ureilites found before 2000) were

111   analysed previously, but a comparison with our results is unfortunately not straightforward.

112   Most of the literature results are only available in conference abstracts, with few, if any,

113   details of the analytical procedures used and data sometimes appearing only in figures (e.g.,

114   Hudon et al., 2004). In a δ^{13}C vs. olivine core composition plot, the previous results are

115   scattered and no clear systematic behaviour is apparent (Fig. 2). However, results obtained by

116   Hudon et al. (2004) show that C in ureilites with ferroan olivines have a tendency to be

117   heavier than in those with the most forsteritic olivines. In contrast, our analyses, with the

118   exception of one sample (Elephant Moraine (EET) 83225), fit hyperbolae in δ^{13}C versus

119   olivine core composition plots (Figs. 2-4). The reasons for the spread in the literature data are

120   unclear. Earlier results were mostly obtained by the stepped combustion technique on small

121   whole-rock samples (e.g., Grady et al., 1985). Analytical biases are possible and could mask

122   possible relationships. Alternatively, the spread could be indicative of strong intra-sample

123   heterogeneities in δ^{13}C. However, the sole detailed in-situ study of a ureilitic clast failed to

124   detect large C-isotopic variations (Miyahara et al., 2015), and weakens this possibility.

125   The hyperbolae in δ^{13}C versus olivine core composition plots obtained in this study

126   (Figs. 3-4) provide strong constraints on the differentiation processes of the UPB. These

127   results are pertinent to the three competing processes for the evolution of the UPB: i) was the

128   range in Mg#-values measured in ureilitic olivine cores the result of smelting; (ii) the pre-

129   igneous oxidation of metal by H_2O from ice; or (iii) simply inherited from the accreted

130   materials?

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In the case of smelting, C reacts with silicates containing iron and eventually partially melts, as illustrated by the two following reactions (Singletary and Grove, 2003; Warren and Huber, 2006):

$$6\ Mg_{1.5}Fe_{0.5}SiO_4\ (olivine\ Fo_{75}) + 3\ C \rightarrow$$
$$3\ Mg_2SiO_4\ (forsterite) + 1.5\ Mg_2Si_2O_6\ (enstatite) + 3\ Fe + 3\ CO \qquad (1)$$

$$6\ Mg_{1.5}Fe_{0.5}SiO_4\ (olivine\ Fo_{75}) + 3\ C + CaO_{(melt)} \rightarrow$$
$$4\ Mg_2SiO_4\ (forsterite) + CaMgSi_2O_6\ (diopside) + 3\ Fe + 3\ CO \qquad (2)$$

If redox reactions were involved, they produced not only Mg-rich silicate assemblages but also converted the indigenous solid C to CO gas, which was then lost to space. Such reactions are controlled by the composition of the silicate assemblages (i.e., Mg#), pressure and temperature, and are blocked if the pressures are too high (Warren and Huber, 2006; Warren, 2012). In other words, redox reactions can affect about half the mantle of a 200 km diameter C-rich body, but much lower fractions for larger bodies. Furthermore, to yield internal pressures prohibitive of smelting for the most ferroan ureilitic compositions, the body would have to have been at least 690 km in diameter (Warren and Huber, 2006; Warren, 2012). Thus, if it can be demonstrated that C phases remained stable during partial melting, a strong constraint on the size of the UPB would be provided.

Carbon isotopic compositions are fractionated by redox reactions with CO formation preferentially consuming ^{12}C, the lighter isotope (see Fig. 20 in Chacko et al., 2001). Such reactions are likely to produce residues enriched in ^{13}C. Therefore, C after smelting should display $\delta^{13}C$ equal to or higher than the initial value.

A number of important conclusions emerge from the strong link between the variation in C isotopes and the composition of olivine cores.

Firstly, the importance of the reduction reactions during the breakup of the UPB is highly variable (e.g., Singletary and Grove, 2003), with a full gradation in textures from ureilites displaying olivines with thin forsteritic rims (e.g., Asuka 881931) to ureilites containing Mg-rich olivines displaying rare domains of preserved (i.e., more Fe-rich) cores (e.g., Northwest Africa 2234). The conservation of a well-defined relationship between olivine core and C isotopic compositions indicates that primary C isotope values were unaffected, or not severely modified, during the disruption of the body.

Secondly, it was originally proposed by both Boynton et al. (1976) and Wasson et al. (1976) that C was introduced into ureilites after the main phase of UPB differentiation, or during the disruption of the body. Late addition of C has also been invoked by Day et al.

164 (2017) based on a study of the Antarctic ureilite Miller Range (MIL) 091004. They observed

165 a small area enriched in graphite (34 vol%) in a single polished section (1.35 cm^2), and

166 proposed that it was injected or smeared into the rock after silicate and Fe-Ni-S depletion, by

167 late-stage C-rich fluid/melt infiltration. The composition of this fluid is unspecified.

168 Alternatively, the heterogeneous distribution of graphite at a centimeter scale is possible in

169 ureilites, and can account for the observations made by Day et al. (2017), without invoking C-

170 rich fluids or melts. Also significant is the lack of chemical differences between the silicate

171 phases in the "C-rich lithology" compared to the rest of the sample. MIL 091004 has a

172 regular bulk composition, which is similar to group-B ureilites as defined by Barrat et al.

173 (2016), ruling out hypothetical low degree partial melts as possible metasomatic agents as

174 suggested by Day et al. (2017). A true C-rich veinlet (~4.7 mm x ~0.3 mm in size) containing

175 a complex network of S-rich, Fe-S-rich, Al-rich and Si-rich areas, was described in the

176 Yamato 74130 ureilite (Tomeoka and Takeda, 1990). It demonstrates that, locally, a small

177 amount of C was mobilized. The importance of the mobilization of C into ureilites via melts

178 or fluid, should not be overemphasized: among the hundreds of ureilites examined so far, only

179 this single C-rich veinlet has been described. Furthermore, C-addition by fluids/melts, either

180 before or during the disruption of the body, would have totally erased the hyperbolic

181 relationship between $\delta^{13}C$ and olivine core composition documented in this study and this is

182 clearly not the case. Significantly, among the 32 ureilites we have analyzed, only one sample

183 (EET 83225) does not lie on this trend. A detailed study of this ureilite is clearly warranted in

184 order to understand its potentially anomalous composition.

185   More significantly, C isotopes directly rule out redox reactions during the

186 differentiation of the UPB as the cause of the wide range of silicate compositions. If this had

187 been the case, C in Mg-rich ureilites would have been heavier than in more ferroan rocks. The

188 trends seen in Figures 3 and 4 show just the opposite: the ureilites with the most Mg-rich

189 olivines always display the lowest $\delta^{13}C$ values (< -7 ‰) and consequently the isotopically

190 lightest C.

191   Sanders et al. (2017) have proposed that the UPB accreted as a mixture of nebular ice

192 with high $\Delta^{17}O$, Mg-rich silicates with low $\Delta^{17}O$ and metallic iron, and also assumed that the

193 UPB was large enough that smelting was inhibited. Water from the thawing ice then oxidized

194 the metal and formed secondary FeO-bearing minerals with high $\Delta^{17}O$ values. These

195 secondary phases became incorporated into ureilite silicates during the metamorphism of the

196 body before the onset of the igneous processes. This model can potentially explain the

correlations observed between Fe/Mg, Fe/Mn and O isotopic compositions (Fig. 3). However, the effects of this pre-igneous oxidation processes on the $\delta^{13}C$ values is not obvious. Assuming that this model is correct, the most ferroan ureilites incorporated the highest fractions of the pre-igneous secondary phases, and display the heaviest C isotopic compositions. Thus, an increase of the $\delta^{13}C$ values could be a fingerprint of the oxidation process and of the aqueous alteration of chondrites. However, available data on chondrites do not show such an effect (e.g., see analyses given by Alexander et al., 2012), and weaken the model proposed by Sanders et al. (2017).

The isotopic diversity recorded by ureilites was more likely inherited from the materials that accreted to form the UPB. The chemical, O and C isotopic variations displayed by ureilites are compatible with the involvement of two components which can be constrained using the two arms of the hyperbolic trends. The first (A) displays the heaviest C ($\delta^{13}C \approx 0$ ‰), $\delta^{18}O \approx 8$ ‰, $\Delta^{17}O \approx -0.5$ ‰, and corresponds to the ureilites with the most ferroan olivines (Mg# ≈ 75, Fe/Mn ≈ 50). The isotopic compositions of the second one (B) are $\delta^{13}C \approx -8$ ‰, $\delta^{18}O \approx 5$ ‰, $\Delta^{17}O \approx -2.5$ ‰, and are defined by the ureilites with the more Mg-rich olivines (Mg# > 95, Fe/Mn < 10). Because ureilites are restites, abundances of most elements before extraction of the core and silicate partial melting cannot be directly deduced. However, the curvatures of the hyperbolas indicate that the second component (B) was by far the richer in C than the first (A). The exact nature of these two components is unclear, but they were most likely to have been primitive chondritic materials, both relatively rich in C. However, they were certainly unlike any known carbonaceous chondrites, as demonstrated by their stable Cr, Ti and Mo isotope systematics (Yamakawa et al., 2010; Qin et al., 2010; Warren, 2011; Budde et al., 2017), C and N isotope systematics (Downes et al., 2015) and by their slightly negative Tm anomalies, similar to non-carbonaceous chondrites and inner Solar System bodies (Barrat et al., 2016a).

Because redox reactions involving C were inhibited during the differentiation of UPB, this body was certainly much larger than generally thought (e.g., Goodrich et al., 2015 and references therein), and was at least 690 km in diameter, as calculated by Warren (2012). Moreover, the discovery of unusually "large" diamonds, displaying sector zoning, in the Almahata Sitta ureilite was interpreted as evidence for static growth inside the UPB (Miyahara et al., 2015). If correct, the UPB was at least ~1000 km in diameter, and could have been much larger. Additional constraints on the equilibrium conditions of these

229 diamonds, and on the size of the UPB, could be provided by the nature and compositions of
230 their inclusions.

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3.2. Implications for the compositions of the planetary building blocks and the origins of the volatile elements in the Inner Solar System.

235   Whatever the exact size of the UPB, our results have two important implications.
236 Firstly, they show that volatile-rich materials distinct from known carbonaceous chondrites
237 were present in some areas of the early inner Solar System, and were the main ingredients of
238 at least one large rocky protoplanet. Similar materials could have contributed to the growth of
239 other early embryos that were involved in the building of terrestrial planets. While a
240 contribution of such materials at the percent level would not be detected with O, Cr, Ti
241 isotope compositions usually used in discussions on the nature of planetary building blocks
242 (e.g., Fitoussi et al., 2016), even at such low levels, they would still have been important
243 carriers of volatile elements, especially C. Secondly, it is well accepted that less than 1 % of
244 the mass of the Earth was added after segregation of its core on the basis of platinum-group
245 element abundances (e.g., Chou, 1978). This late veneer is often thought to have essentially
246 been composed of CI and CM carbonaceous chondrite-like material, which in turn can
247 account for a large proportion of the terrestrial volatiles (e.g., Marty, 2012; Alexander et al.,
248 2012; Rubie et al., 2015). However, the volatile abundances of the bulk Earth remain poorly
249 constrained, notably because some of the phases involved are siderophile at high pressures,
250 and could have been partly sequestered by the core, as exemplified by C (Hirschmann, 2016).
251 Consequently, we don't know at present the proportion of terrestrial C in the mantle and core.
252 The average $\delta^{13}C$ value of the Earth's upper mantle ($\delta^{13}C \approx$ -5 ‰, Marty et al., 2013) is very
253 similar to average CM carbonaceous chondrites ($\delta^{13}C=$ -3.5 ‰), and if not modified by
254 mantle processes, is at first glance consistent with the view that the carbonaceous chondrites
255 were the main source of Earth's volatiles. However, it does not preclude the involvement of
256 other components (Wang et al., 2016; Li et al., 2016). Indeed, the destruction of the UPB
257 produced a multitude of debris, which on average display the same $\delta^{13}C$ value ($\delta^{13}C=$ -4.3 ‰,
258 n=32) as the Earth's mantle, and so potentially could have been an ingredient of the late
259 veneer. Interestingly, the distribution of volatiles in the bulk Earth displays a large negative
260 nitrogen anomaly (Fig. 5, e.g., Marty, 2012). Because nitrogen is siderophile at high
261 pressures, this element could have been partly sequestered by the core (Roskosz et al., 2013).

262   If correct, this would suggest a decoupling with C, which is not well understood at present.
263   Alternatively, the high C/N ratio of the bulk Earth could be partly inherited from some non-
264   chondritic components of the late veneer (Hirschmann, 2016). Significantly, ureilites are poor
265   in nitrogen and display very high C/N ratios (Fig. 5). The recent discovery in a chondrite of
266   graphite-bearing igneous clasts from a possible Moon-sized body (Hiyagon et al., 2016),
267   indicates that the UPB was not the sole C-rich differentiated body. Volatile-rich materials,
268   similar in composition to ureilites, may have been more important than has so far been
269   considered. Thus, the involvement of C-rich differentiated objects during the accretion of the
270   terrestrial planets should now be seriously re-evaluated.

271

272   ## 4. Conclusions

273   The data presented here demonstrates that the C isotopic composition of ureilites
274   correlates with the Fe/Mg ratios of the cores of their olivines. This observation has important
275   implications for the differentiation processes on their parent body, for its size, and for the
276   origin of the volatile elements in the inner Solar System.

277   Various models have been put forward to explain the origin of the wide range of
278   compositions of the ureilitic silicates. Carbon isotopic systematics are not consistent with the
279   recent model of low-temperature oxidation of metal by water derived from ice (Sanders et al.,
280   2017), nor with the more widely proposed smelting model, which assumes reduction of
281   silicates by C during melting (e.g., Singletary and Grove, 2003; Goodrich et al., 2007). The C
282   and O isotopic compositions indicate that the chemistry of the ureilitic mantle has recorded
283   the involvement of two C-rich reservoirs characterized by distinctive $\delta^{13}C$, $\delta^{18}O$, $\Delta^{17}O$ and
284   Fe/Mg ratios. The imperfect mixing of these two reservoirs during the accretion of the UPB
285   [merging of two planetesimals as suggested by Sanders et al. (2017)] can explain the $\delta^{13}C$
286   range and the mass independent variation in their O isotopic ratios that correlates with their
287   Fe/Mg ratios. The inhibition of the reactions of reduction of the silicates by C indicates that
288   the UPB was much larger than 690 km in diameter, in agreement with thermodynamic
289   modelling by Warren (2012), and the discovery of diamonds too large to be formed upon
290   impact (Miyahara et al., 2015), indicative of a body much larger than Ceres.

291   Although ureilites are in some ways unusual (same O isotopic compositions as
292   carbonaceous chondrites, but distinct Cr and Ti isotope systematics), the accretion of at least
293   one such large C-rich body was certainly not fortuitous. It indicates that C-rich primitive
294   matter, distinct from carbonaceous chondrites, was present in the early Solar System. The

direct involvement of ureilite-derived material, or material from other UPB-like bodies, may have played a significant role in the accretion histories of the terrestrial planets and contributed to their volatile element inventories.

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481   Table 1. Details of ureilite samples studied, olivine core compositions (Singletary and Grove, 2003;
482   Downes et al., 2008; Warren, 2012; Barrat et al., 2015 and references therein) and C isotopic
483   compositions (this work). Errors given here are calculated from the difference between the duplicates.

484

	source	split	Olivine cores Mg#	Fe/Mn (atomic)	$\delta^{13}C$ (‰)	Remarks
A 881931	NIPR	,71	78.7	48.1	-4.89 ± 0.02	n=2
ALH 77257	NIPR	,105	86.1	29.1	-7.30 ± 0.01	n=2
ALH 81101	MWG	,63	78.9	41.8	-0.84 ± 0.01	n=2
ALH 82130	MWG	,43	95.2	9.1	-7.73 ± 0.04	n=2
EET 83225	MWG	,37	88.3	22.1	-4.42 ± 0.06	n=2
EET 96042	MWG	,48	81.3	38.2	-6.43 ± 0.03	n=2
GRA 95205	MWG	,64	79.2	45.2	-1.74 ± 0.07	n=2
GRO 95575	MWG	,46	78.6	44.9	-1.87 ± 0.03	n=2
LAP 03587	MWG	,10	74.7	56.6	-0.28 ± 0.02	n=2
LAR 04315	MWG	,46	81.9	39.8	-7.80 ± 0.03	n=2
MET 78008	NIPR	,69	75.9	49.5	-1.46 ± 0.11	n=2
MET 01085	MWG	,23	88.8 (px)		-6.89 ± 0.01	n=2, no olivine
PCA 82506	MWG	,125	79.2	44.3	-6.40 ± 0.15	n=2
Y 74130	NIPR	,55	77.0	48.0	-1.71 ± 0.14	n=2
Y 790981	NIPR	,85	77.5	46.5	-1.77 ± 0.23	n=2
Y 791538	NIPR	,109	91.3	18.0	-7.49 ± 0.04	n=2
Y 981810	NIPR	,76	78.3	50.2	+0.11 ± 0.03	n=2
NWA 2234	NIPR		81.5	37.3	-7.76 ± 0.01	n=2
NWA 2236	NIPR		96.8	7.0	-7.54 ± 0.07	n=2
NWA 4471	J.A. Barrat		78.1	50.1	-3.32	n=1
NWA 4852	J.A. Barrat		87.5	25.2	-7.14 ± 0.23	n=2
NWA 5555	P. Marmet		90.8	19.5	-8.20 ± 0.02	n=2
NWA 5602	J.A. Barrat		79.0	46.3	-2.39 ± 0.03	n=2
NWA 5884	J.A. Barrat		78.6	47.4	-0.90 ± 0.02	n=2
NWA 6056	J.A. Barrat		84.8	31.8	-7.01 ± 0.05	n=2
NWA 7349	J.A. Barrat		76.5	51.3	-1.09	n=1
NWA 7630	J.A. Barrat		79.1	46.6	-2.91 ± 0.01	n=2
NWA 7686	J.A. Barrat		91.0	19.1	-8.41 ± 0.01	n=2
NWA 7880	J.A. Barrat		78.6	49.2	-1.17 ± 0.01	n=2
NWA 8049	J.A. Barrat		84.3	34.5	-8.48	n=1
NWA 8172	J.A. Barrat		76.9	53.6	-1.15 ± 0.03	n=2
NWA 10900	J.A. Barrat		77.3	52.4	-0.31 ± 0.10	n=2
Average					-4.27	32 samples
Standard						
LCgraphite	IPGP			this work	-18.41	2 σ = 0.19, n=6
				IPGP	-18.42	reference value

485   Source abbreviations are : IPGP= institut de Physique du Globe de Paris, MWG= NASA meteorite
486   working group, NIPR= National Institute of Polar Research, Tokyo, UBO= Université de Bretagne
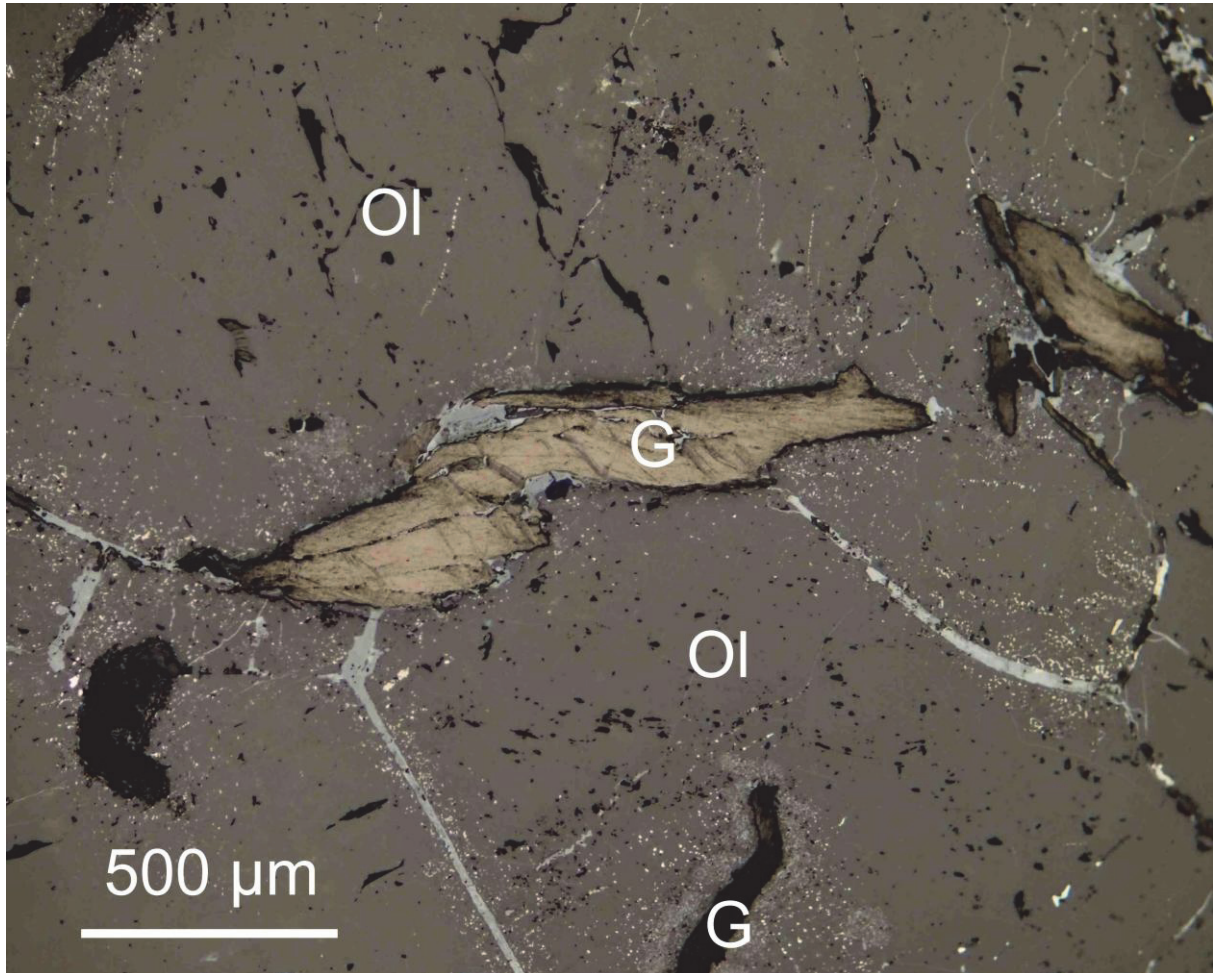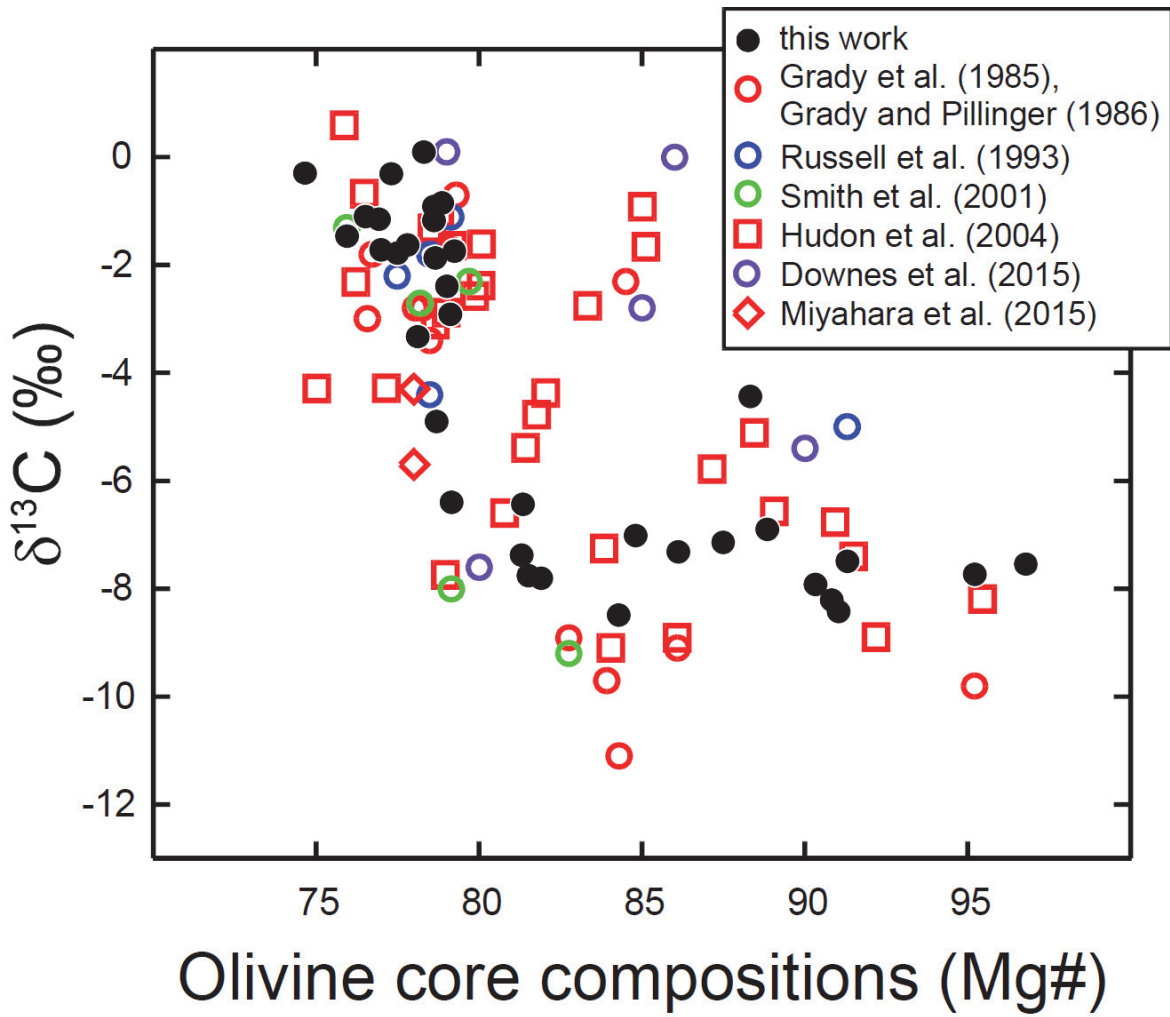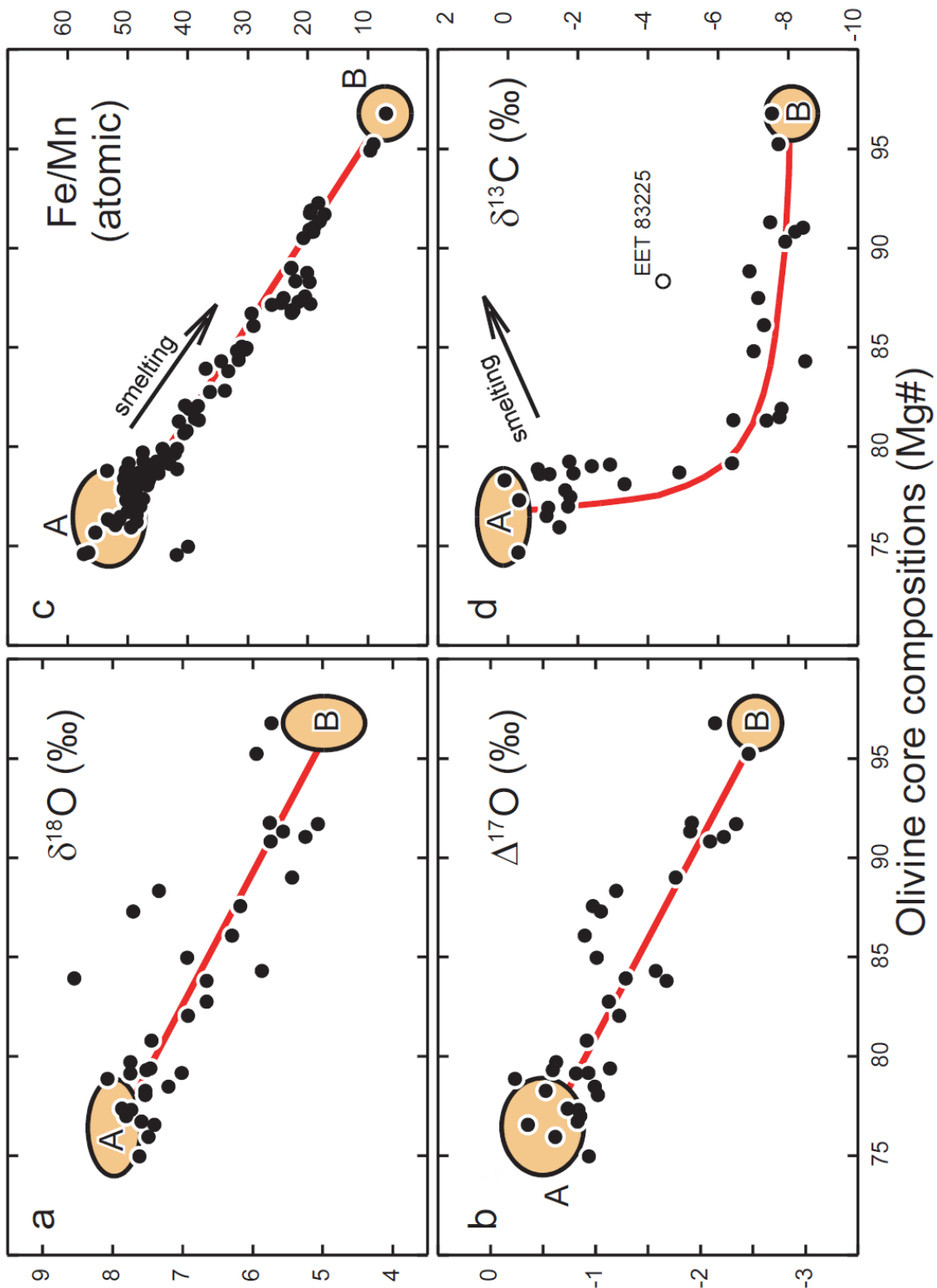487   Occidentale, Brest.

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Fig. 1. Reflected light view of C grains (here graphite) in NWA 8049, a typical unbrecciated ureilite (G: graphite; Ol: olivine).

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502   Figure 2. $\delta^{13}C$ vs. olivine core compositions (Mg#) from ureilites. Data from this study and
503   the literature.

504
505
506 Figure 3. $\delta^{18}O$, $\Delta^{17}O$, $\delta^{13}C$, Fe/Mn ratios in olivine cores vs. olivine core compositions (Mg#)
507 from unbrecciated ureilites. Oxygen isotopic compositions from Clayton and Mayeda (1996).
508 See Table 1 for the sources of other data. Mixing lines and curves between A and B, the two
509 endmembers, are drawn in red. The errors are equivalent to the size of the data points.
510
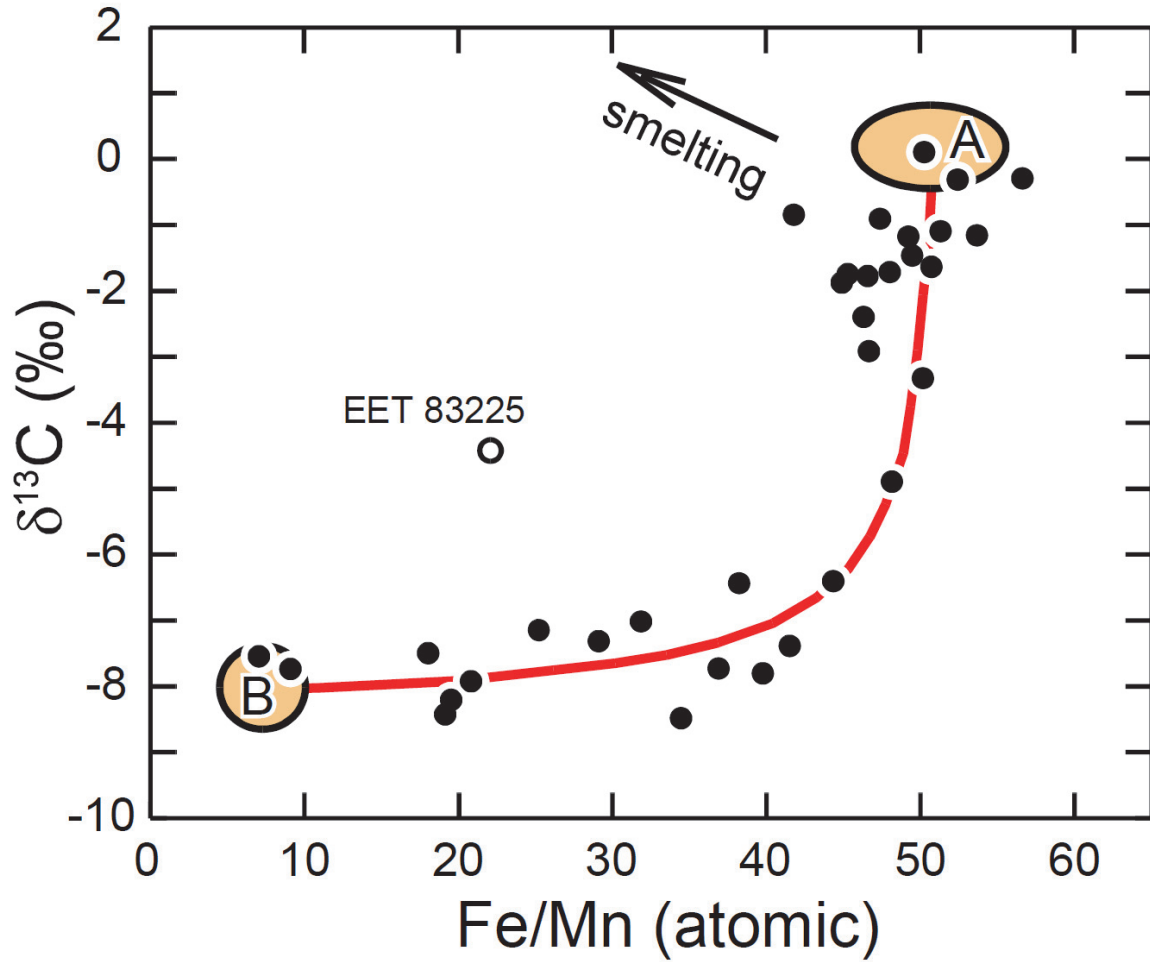
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513 Figure 4. Plot of $\delta^{13}C$ vs. Fe/Mn ratios in olivine cores from unbrecciated ureilites (see Table
514 1 for the source of the data). The errors are equivalent to the size of the data points.
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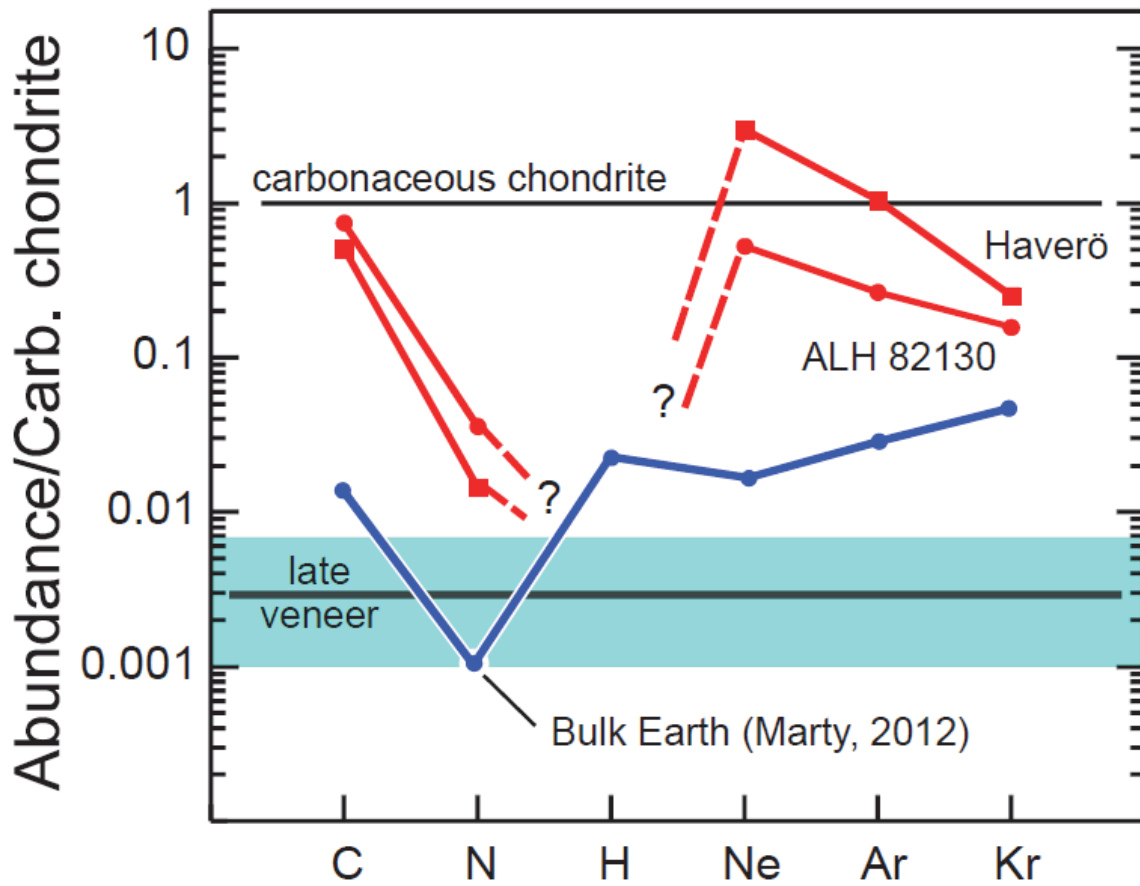
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518 Figure 5. Volatile abundances of Haverö and ALH 82130 (Grady et al., 1985; Grady and
519 Pillinger, 1986; Rai et al., 2003a and b), two representative ureilites, compared to the bulk
520 Earth composition, normalized to carbonaceous chondrite (Marty, 2012).
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