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

Jean-Alix Barrat[a,*], Pierre Sansjofre[a], Akira Yamaguchi[b,c], Richard C. Greenwood[d], Philippe Gillet[e]

[a] *Laboratoire Geosciences Océan (UMR CNRS 6538), Université de Bretagne Occidentale et Institut Universitaire Européen de la Mer, Place Nicolas Copernic, 29280 Plouzané, France*
[b] *National Institute of Polar Research, Tachikawa, Tokyo 190-8518, Japan*
[c] *Department of Polar Science, School of Multidisciplinary Science, Graduate University for Advanced Sciences, Tachikawa, Tokyo 190-8518, Japan*
[d] *Planetary and Space Sciences, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, United Kingdom*
[e] *Earth and Planetary Science Laboratory (EPSL), Ecole Polytechnique Fédérale de Lausanne, Institute of Condensed Matter Physics, Station 3, CH-1015 Lausanne, Switzerland*

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ABSTRACT

We analyzed the C isotopic compositions of 32 unbrecciated ureilites, which represent mantle debris from a now disrupted, C-rich, differentiated body. The δ^{13}C values of their C fractions range from −8.48 to +0.11‰. The correlations obtained between δ^{13}C, δ^{18}O and Δ^{17}O 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.

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., 2008) 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 re-

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[*] Corresponding author.
E-mail address: barrat@univ-brest.fr (J.-A. Barrat).

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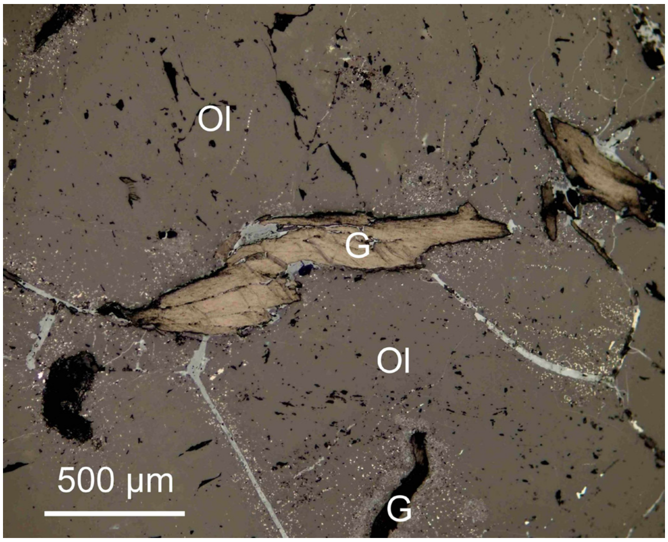

Fig. 1. Reflected light view of C grains (here graphite) in NWA 8049, a typical unbrecciated ureilite (G: graphite; Ol: olivine).

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

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

2. Samples and analytical procedure

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

Samples (0.25–1 g) were powdered using a boron-carbide mortar and pestle. About 250 mg of powder for each sample was digested on a hot plate heated to 125°C, using sequential mixtures of 10 N HF/14 N HNO_3, 14 N HNO_3 and 6 N HCl. This procedure ensures a perfect dissolution of all the phases, except graphite and diamond, which are not oxidized by these acids at this temperature. The resulting clear solution was carefully pipetted off, and the C residues rinsed twice using ultrapure water and then dried. Our procedure has the advantage of directly removing all terrestrial carbonates and all terrestrial C in the samples. Carbon isotopic compositions were determined at the Pôle Spectrométrie Océan (PSO), Institut Universitaire Européen de la Mer (IUEM, Plouzané, France). 0.1 to 0.2 mg of the C powder was introduced in tin capsules and δ^{13}C was determined following flash combustion using an EA-IRMS Flash-EA 2000 analyzer coupled to a Thermo Fisher Delta-V Plus mass spectrometer. The oxygen flux was optimized at 240 ml/min for a flash combustion of 15 s, to ensure a complete oxidation of the sample. Isotopic data are reported as parts per thousand deviation (‰) from the Peedee belemnite reference material (PDB): $\delta^{13}C = 1000\ [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1]$. Most measurements were determined in duplicate with an external reproducibility better than 0.2‰ (2σ). An in-house graphite standard (LCgraphite), kindly provided by Pierre Cartigny (IPG, Paris) has been repeatedly analysed during the course of this study in order to check the reproducibility and our calibration. These analyses are in excellent agreement with previous results obtained by the Institut de Physique du Globe, Paris (Table 1).

3. Results and discussion

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

Ureilitic C yielded δ^{13}C ranging from −8.48 to +0.11‰ (Table 1), in agreement with earlier results ranging from −11.1 to ≈+0.5‰ (Grady et al., 1985; Grady and Pillinger, 1986; Russell et al., 1993; Smith et al., 2001; Hudon et al., 2004; Downes et al., 2015; Miyahara et al., 2015). Many of our samples (e.g., the Antarctic ureilites found before 2000) were analysed previously, but a comparison with our results is unfortunately not straightforward. Most of the literature results are only available in conference abstracts, with few, if any, details of the analytical procedures used and data sometimes appearing only in figures (e.g., Hudon et al., 2004). In a δ^{13}C vs. olivine core composition plot, the previous results are scattered and no clear systematic behaviour is apparent (Fig. 2). However, results obtained by Hudon et al. (2004) show that C in ureilites with ferroan olivines have a tendency to be heavier than in those with the most forsteritic olivines. In contrast, our analyses, with the exception of one sample (Elephant Moraine (EET) 83225), fit hyperbolae in δ^{13}C versus olivine core composition plots (Figs. 2–4). The reasons for the spread in the literature data are unclear. Earlier results were mostly obtained by the stepped combustion technique on small whole-rock samples (e.g., Grady et al., 1985). Analytical biases are possible and could mask possible relationships. Alternatively, the spread could be indicative of strong intra-sample heterogeneities in δ^{13}C. However, the sole detailed in-situ study of a ureilitic clast failed to detect large C-isotopic variations (Miyahara et al., 2015), and weakens this possibility.

The hyperbolae in δ^{13}C versus olivine core composition plots obtained in this study (Figs. 3–4) provide strong constraints on the differentiation processes of the UPB. These results are pertinent to the three competing processes for the evolution of the UPB: (i) was the range in Mg#-values measured in ureilitic olivine cores the result of smelting; (ii) the pre-igneous oxidation of metal by H_2O from ice; or (iii) simply inherited from the accreted materials?

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):

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