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Hydrogen isotopic composition of water from fossil micrometeorites in howardites

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Abstract—We have measured the hydrogen isotopic composition (D/H ratios) of the water from 13 carbonaceous chondritic microclasts (CCMs, size <1 mm) trapped in two howardites (Kapoeta and Yamato-793497) early in the evolution of Solar System. The division into tochilinite-rich; magnetite-rich, olivine-poor; magnetite-rich, olivine-rich CCM types is corroborated by the hydrogen isotopic compositions. Both mineralogy and hydrogen isotopic compositions demonstrate that tochilinite-rich CCMs represent CM2 chondritic matter. In contrast, there is no good match between the isotopic and mineralogical properties of the magnetite-rich CCMs and the known groups of carbonaceous chondrites, suggesting that magnetite-rich CCMs represent a new kind of chondritic matter, not yet sampled in meteorite collections. This demonstrates that the view of the asteroid belt revealed by the collection of meteorites is incomplete. The study of (micro)clasts offers a unique opportunity to better decipher the nature and relative abundance of asteroids.

The average hydrogen isotopic composition of water belonging to CCMs, D/H = $(152.0 \pm 4.8) \times 10^{-6}$ ($1\sigma_m$), is similar to that of Antarctic micrometeorites (AMMs), D/H = $(161.2 \pm 3.8) \times 10^{-6}$ ($1\sigma_m$). The similarity, in terms of mineralogy and hydrogen isotopic composition, between CCMs and AMMs demonstrates that the composition of the micrometeorites has not been modified over the whole history of the Solar System. It indicates that the composition of the micrometeorite flux onto Earth has been, and is, dominated by a mixture of CM2-like; magnetite-rich, olivine-poor; magnetite-rich, olivine-rich carbonaceous chondritic matter exemplified by CCMs found in howardites. Because CCMs have not suffered atmospheric entry, they provide an abundant source of pristine micrometeorites.

The average D/H ratio of the whole population of CCMs is identical within errors to that of the Earth ($149 \pm 3 \times 10^{-6}$). The match between the CCMs D/H ratio and that of the Earth is especially remarkable because 1) three different populations of CCMs are needed to make the D/H ratio of the Earth; 2) there is no single carbonaceous chondrite group for which a similar match exists. This observation suggests that CCMs population might be representative of the late veneer agent(s) that delivered water to the Earth.

1. INTRODUCTION

Volatile-rich extraterrestrial materials provide a unique opportunity for deciphering the origin of Solar System, the early evolution of asteroids, and the formation of the planets. Until the Stardust sample return mission brings back dust from the Wild 2 Jupiter family comet in 2006, the only volatile-rich extraterrestrial samples we have at hand are carbonaceous chondrites (e.g., McSween, 1979), cm-sized carbonaceous chondritic clasts within meteorites (e.g., Nakashima et al., 2003; Zolensky et al., 1992), micrometeorites collected in the polar ice caps (e.g., Maurette et al., 1991; Engrand and Maurette, 1998; Taylor et al., 1998; Nakamura, 1999; Duprat et al., 2003) and interplanetary dust particles (IDPs) in the stratosphere (e.g., Zolensky et al., 1994; Rietmeijer, 1998). In addition to these already well-characterized samples, a new source of volatile-rich extraterrestrial dust has been recently identified.

Gounelle et al. (2003) have reported the finding of 71 submillimeter-sized carbonaceous chondritic microclasts (CCMs) in howardites. Howardites are achondritic meteorites members of the HED (howardites-eucrites-diogenites) clan, and believed to sample the regolith of a differentiated asteroid, possibly 4 Vesta (Binzel and Xu, 1993). Although mm- to cm-sized clasts in howardites have been known and studied for a long time (e.g., Wilkening, 1973; Zolensky et al., 1996b), submillimeter-sized clasts have been only recently identified and are very little studied.

A mineralogical study has shown that CCMs are made of C2-like chondritic matter (Gounelle et al., 2003). These samples are worth further study for a number of reasons. First, CCMs provide a new, abundant, source of carbonaceous, volatile-rich micrometeorites. Second, they might offer a view of the asteroid belt significantly different from that given by meteorites, and potentially less biased. Third, unlike polar micrometeorites, CCMs have not suffered alteration due to atmospheric entry (e.g., Toppani et al., 2001), so they are relatively pristine with regard to their bulk chemical composition, mineralogy and isotopic composition. Fourth, CCMs have been shown to be *fossil* micrometeorites that were present in the inner Solar System very early in its history (Gounelle et al., 2003). As such, they can help us to probe the nature of Earth-

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Table 1. Summary of the mineralogy of carbonaceous chondritic microclasts.[a]

		Tochilinite poor, magnetite rich	
	Tochilinite rich, magnetite poor	Olivine-rich	Olivine-poor
CCMs	Y35, Y46, K9, Y50, K54, Y37	K3, K18, K24	Y1, Y22, Y8, Y43
Olivine	++++	++++	+
Fo%	39–96	1–99	98–99
Pyroxene	++++	++++	+
En%	87–98	4–98	95–98
Wo%	0–3	1–51	1–3
Carbonate (calcite)	++	++	−
Phyllosilicate (saponite, serpentine)	++++	++++	++++
Magnetite	+	++++	++++
Chromite	+	−	−
Fe-Ni sulfide (pyrrhotite, pentlandite)	+++	+++	++++
Metal	+	−	++++
Tochilinite	++++	−	−
Previous classification[b]	CM2-like	CR2-like	CR2-like
Related CCs	CM2s	CR2s, Tagish Lake	CI1s

[a] ++++ = very abundant; +++ = abundant; ++ = common; + = occurrence; − = absent. Fo%, En%, Wo% = range of forsterite, enstatite and wollastonite contents respectively.
[b] Gounelle et al. (2003).

impacting material in the early Solar System. Specifically, because they are rich in water-bearing minerals such as phyllosilicates, CCMs in howardites can provide clues to the origin of water on Earth, thought to have been delivered as a late veneer by an unspecified agent (e.g., Wänke, 1981; Chyba, 1990; Morbidelli et al., 2000).

In this paper, we report measurements of the hydrogen isotopic composition of the water in phyllosilicates of the CCMs found in howardites. The adopted analytical technique (ion microprobe equipped with a O^- beam) can exclusively measure the isotopic composition of hydrogen *water* (Deloule et al., 1991; Deloule and Robert, 1995), and excludes contributions from organic molecules. Despite this limitation, our data can still help to address the problem of the origin of the Earth water for two reasons. (1) When water was delivered on Earth by a late veneer agent, the Earth's atmosphere was significantly more reducing than it is now, and it might be that hydrogen bound in refractory extraterrestrial organic matter has never been a significant part of Earth's hydrologic cycle. (2) Even if organic hydrogen has been oxidized, water accounts for ~80% of the hydrogen present in CCs (Robert, 2002) and therefore, although organic matter is usually enriched in D relative to water, the bulk D/H ratio of CCMs should not be very different from the water D/H ratio (see table 1 of Robert, 2002).

The primary goal of this study is to better characterize the light element geochemistry of this new population of primitive objects: carbonaceous chondritic microclasts in howardites. In addition, this study may help improve the classification of CCMs, tentatively built from mineralogical data (Gounelle et al., 2003). Finally, because of the unique fossil nature of CCMs in howardites, their hydrogen isotopic composition may provide some clues about the nature of the late veneer agent that delivered water onto Earth.

2. EXPERIMENTAL METHODS

The mineralogy of carbonaceous chondritic microclasts has been studied in detail by Gounelle et al. (2003). For the present project, we made additional measurements of the matrix composition with a CAMECA SX 50 electron microprobe operated at a voltage acceleration of 15 kV, beam current of 10 nA and with a 5 μm defocused beam. The hydrogen isotopic composition was measured with the CRPG CAMECA IMS 1270 ion microprobe in Nancy (France) following the procedures outlined in Deloule et al. (1991), and utilized for analyses of meteorites and micrometeorites (Deloule and Robert, 1995; Engrand et al., 1999). Beam size was ~10 μm; the use of an O^- primary ion beam for these analyses enhances the emission of H^+ ions from the H-bearing silicate phases over that of organic H^+ ions by a factor of >100 (Deloule and Robert, 1995). Our analyses therefore provide the hydrogen isotopic composition of the structural water and hydroxyl radicals contained in the phyllosilicates (serpentine and saponite) abundant in the matrix of CCMs. For simplicity, we will refer below to the hydrogen isotopic composition of phyllosilicate water, omitting the hydroxyl radicals. The analytical uncertainty for these analyses (taking into account reproducibility of standards, correction of the instrumental mass fractionation and internal reproducibility) is of the order of 40‰.

3. RESULTS

3.1. Mineralogy

Gounelle et al. (2003) have reported the discovery of seventy-one carbonaceous chondritic microclasts with sizes ranging from 25 μm to 800 μm in three howardites (Kapoeta, Jodzie, and Yamato-793497). Approximately half of them are tochilinite-rich and contain no or very little magnetite, while the other half are magnetite-rich and contain no or very little tochilinite. The tochilinite-rich and magnetite-rich microclasts were tagged CM2-like and CR2-like microclasts, respectively. However, because the elucidation of possible genetic links with carbonaceous chondrite groups is one of the aims of the present work, we will not adopt here this interpretative terminology. Furthermore, within the magnetite-rich microclasts, we will from now on distinguish between olivine-poor and olivine-rich CCMs. This distinction is a first step in trying to resolve the classification ambiguity noted by Gounelle et al. (2003) for CR2-like CCMs. Below, we briefly describe the mineralogy of 13 CCMs from Yamato-793497 and Kapoeta selected for the hydrogen isotopic study, with the aim of justifying the terminology adopted above. Table 1 summarizes the mineralogy, classifica-