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Hydrogen isotopic composition of water in CV-type carbonaceous chondrites

Laurette Piani*, Yves Marrocchi

CRPG, UMR 7358 CNRS, Université de Lorraine, 54500 Vandoeuvre-lès-Nancy, France

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ABSTRACT

Among the different groups of carbonaceous chondrites, variable concentrations of hydrous minerals and organic matter are observed that might be related to the time and/or place of formation of their asteroidal parent bodies. However, the precise distribution of these volatile-bearing components between chondrite groups and their chemical and isotopic compositions remain fairly unknown. In this study, we used a novel secondary ion mass spectrometry analytical protocol to determine the hydrogen isotopic composition of water-bearing minerals in CV-type carbonaceous chondrites. This protocol allows for the first time the D/H ratio of CV chondrite hydrous minerals to be determined without hindrance by hydrogen contributions from adjacent organic material. We found that water in the altered CV chondrites Kaba, Bali, and Grosnaja has an average D/H ratio of $D/H_{CV-water} = [144^{+8}_{-21}] \times 10^{-6}$ (or $\delta D_{CV-water} = -77^{+54}_{-131} \text{‰}$, 2σ), significantly higher than water in most CM-type carbonaceous chondrites ($D/H_{CM-water} = [101 \pm 6] \times 10^{-6}$ or $\delta D_{CM-water} = -350 \pm 40 \text{‰}$, 2σ). We show that because organic matter in CV chondrites is depleted in deuterium compared to that in CM chondrites, such differences could result from isotopic exchange between water and organics. Another possibility is that the CM and CV parent bodies sampled different reservoirs of water ice and organics characterized by variable isotopic compositions due to their different time and/or place of accretion.

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1. Introduction

The distribution of volatile elements and water in the Solar protoplanetary disk is a fundamental constraint on the conditions of water delivery to terrestrial planets (Marty, 2012), yet remains poorly known. The different types of carbonaceous chondrites accreted water in varying concentrations (Marrocchi et al., 2018) that make them suitable for constraining the dynamical processes that operated during asteroid accretion. Hydrogen isotopes (hereafter D/H) represent a powerful cosmochemical tracer that provides constraints on the origin and distribution of water within the different Solar System objects (Ceccarelli et al., 2014) but few precise estimations of the D/H compositions of water accreted by asteroids have been reported so far (Alexander et al., 2012; Piani et al., 2018). This is due to the complex sub-micrometer intergrowths of hydrated minerals and organic compounds (e.g., Le Guillou et al., 2014)—the two main H-bearing phases in primitive chondrites—that impede the estimation of water retained in hydrated minerals without any contribution from organic hydro-

gen (Bonal et al., 2013; Deloule and Robert, 1995; Remusat et al., 2010).

The abundances and D/H compositions of water in chondrites have long been approximated by their bulk D/H ratio or estimated by mass balance using bulk and isolated organic matter measurements (e.g., Alexander et al., 2010; Robert and Epstein, 1982). However, these estimates are affected by uncertainties on the organic content and its hydrogen abundance and isotopic composition (especially soluble and unknown organic compounds; Alexander et al., 2010, 2015). Based on bulk D/H and C/H measurements of CR- and CM-type carbonaceous chondrites, Alexander et al. (2012) showed that the D/H ratio of the mean C-free end-member can be estimated for chondrite types of which numerous samples exist, such as CR- and CM-type chondrites ($D/H_{\text{initial water}} = [171 \pm 17/10] \times 10^{-6}$ and $[87 \pm 4] \times 10^{-6}$ (1σ), respectively). For other types of carbonaceous chondrites (CV, CO, or CI) thought to represent different parent bodies, the limited number of hydrated samples available for bulk measurements precludes determination of the D/H composition of their water.

Recently, a new method has been developed to estimate the D/H ratio of water in chondrites from *in-situ* measurements of the C/H and D/H ratios by secondary ion mass spectrometry (SIMS; Piani et al., 2018). The novelty of the method was to measure the

* Corresponding author.

E-mail address: laurette.piani@univ-lorraine.fr (L. Piani).

D/H and C/H ratios in different areas of a given chondrite matrix containing varying proportions of hydrated minerals and organic matter and use the zero-intercept of the correlation between the two ratios to estimate the D/H ratio of hydrated minerals (with a C/H = 0) (see Piani et al., 2018 for more details). This method revealed that all hydrated CM chondrites accreted water with a similar D/H ratio of $[101 \pm 6] \times 10^{-6}$ ($\delta D_{\text{CM/SMOW}} = -350 \pm 40\%$, 2σ), consistent with the mean composition of CM chondrite water determined from bulk measurements. However, the least-altered lithologies of the least-altered CM chondrite Paris (Hewins et al., 2014; Marrocchi et al., 2014) show significantly higher D/H ratios ($D/H_{\text{Paris}} = [145 \pm 25] \times 10^{-6}$ or $\delta D_{\text{Paris/SMOW}} = -69 \pm 163\%$, 2σ) that could track the accretion of water ice grains that originated in the outer Solar System (Piani et al., 2018).

Vigarano-type carbonaceous (CV) chondrites have been affected by variable, but significant, secondary alteration processes (Doyle et al., 2015; Ganino and Libourel, 2017; Marrocchi et al., 2018), revealing that the CV chondrite parent bodies accreted water ice grains at an estimated water/rock ratio of 0.1–0.2 (Zolotov et al., 2006). CV chondrites are thought to have formed earlier during the evolution of the protoplanetary disk than hydrated CI and CM chondrites (Sugiura and Fujiya, 2014), and consequently could have accreted water ice grains characterized by unique hydrogen and oxygen isotopic compositions. Indeed, CV chondrite bulk, matrix, and secondary mineral oxygen isotopic compositions define a continuous trend resulting from isotopic exchange between ^{16}O -rich anhydrous silicates and $^{17,18}\text{O}$ -rich fluid (Marrocchi et al., 2018). Based on those results, it has been proposed that CV chondrites accreted water with $\delta^{18}\text{O} > 60\%$ (i.e., $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O} > 15\%$; Marrocchi et al., 2018), which could result from the contribution of $^{17,18}\text{O}$ -rich water ice from the outer Solar System (Sakamoto et al., 2007).

CV chondrites are subdivided into a reduced subgroup (CV_{red}) and two oxidized subgroups, Allende-like (CV_{oxA}) and Bali-like (CV_{oxB}), reflecting their complex alteration history (Ganino and Libourel, 2017; McSween, 1979). Bali-type CV3 chondrites (CV3_{oxB}; Weisberg et al., 1997) contain abundant H-bearing phyllosilicates (saponite, Na-rich phlogopite) in their fine-grained matrices (Howard et al., 2010), allowing the D/H composition of CV water to be determined. Here we report *in-situ* SIMS measurements of the D/H and C/H ratios of the matrices of the oxidized CV3 chondrites Kaba, Bali, and Grosnaja and discuss their consequences for the distribution of water isotopic compositions in the asteroid formation region.

2. Samples and methods

Samples of Kaba (NHMV_#ID_13236_[3a]), Bali (NHMV_#ID_524_[C]), and Grosnaja (NHMV_#ID_2745_[C]), were kindly provided by the Natural History Museum Vienna. Submillimeter-sized pieces of each chondrite were handpicked and pressed in indium foil. Scanning electron microscope mapping was performed to select flat areas of fine-grained matrix for SIMS analyses. For comparison, the CM2 chondrite Sayama (a highly altered CM chondrite; Yoneda et al., 2001) and the least altered lithologies of the CM2.7 chondrite Paris (Hewins et al., 2014) were analyzed during the same SIMS session (Piani et al., 2018, and references therein). SIMS measurements were performed with the IMS 1280HR at Centre de Recherches Pétrographiques et Géochimiques in Nancy, France. A 10 keV Cs⁺ primary beam was used for the measurements. Prior to analyses, 6 minutes of high-current (2.5 nA) pre-sputtering was applied to clean the sample surface and reach a steady state for cesium implantation and sputtering. The samples were then sputtered with a primary current of 2 nA and 250 pA for CV and CM chondrites, respectively, to obtain about 1.5×10^5 counts per second on H⁻ for all samples. The primary beam was

rastered over an area of $50 \times 50 \mu\text{m}^2$ on the sample surface. A normal incident electron gun was used to improve charge compensation. The analyzed area was restricted to $15 \times 15 \mu\text{m}^2$ in the center of the rastered area by using a 30% electronic gate. A high magnification mode (Max Area 40) and a small field aperture (FA 2000) were used to minimize H contamination from the border of the beam. H⁻, D⁻, $^{13}\text{C}^-$, and $^{29}\text{Si}^-$ ions were collected successively by changing the magnetic field and counted with the monocollection electron multiplier. The mass resolution power was set to $M/\Delta M = 3300$ to avoid interferences on $^{13}\text{C}^-$ ($^{12}\text{CH}^-$) and $^{29}\text{Si}^-$ ($^{28}\text{SiH}^-$). For each analysis, 40 cycles were collected with 2 s of counting time per cycle for H⁻, $^{13}\text{C}^-$, and $^{29}\text{Si}^-$ and 20 s for D⁻ for a total duration of 31 min.

A serpentine and four water-bearing glasses (in-house reference basaltic glasses with 0.85, 1.45, 3.64, and 4.29 wt.% H₂O) were chosen as references for hydrated minerals. Organic reference materials were a type III kerogen, insoluble organic matter (IOM) of the Antarctic Grosvenor Mountains 95502 (GRO 95502) ordinary chondrite, and IOM of the carbonaceous chondrite Orgueil (for details, see Piani et al., 2012, 2015). All samples and standards were pressed in indium and gold-coated before analyses. The statistical error on the D/H ratio for one analysis is $\leq 27\%$ (2σ) and the reproducibility is $\leq 68\%$ (2σ standard deviation) on the water-bearing glasses. The zero intercept of the D/H vs. C/H correlation in the fine-grained matrix is used to estimate the D/H ratios of inorganic phases (hydrated minerals) following the method described in Piani et al. (2018).

3. Results

Although the ^{29}Si and ^{13}C ionic emissions were similar for CV and CM chondrites, hydrogen ionic emissions of CV chondrite matrices were about one order of magnitude lower than those of the Paris and Sayama CM chondrites (Tables 1 and S1). Positive correlations between the measured D/H and C/H ratios were obtained for both CM and CV chondrites (Fig. 1). Kaba and Bali have C/H ratios ~ 7 –8 times higher than the CM chondrites, and their D/H and C/H ratios are positively correlated with Pearson correlation factors of 0.76 and 0.58, respectively (Fig. 1, Table 1). The co-variation of D/H and C/H ratios is not clear for Grosnaja, as its Pearson correlation factor is 0.04. Although the Si/H ratios of Grosnaja are of the same order as the other CV chondrites, its C/H ratios are about 3 times lower, indicating that Grosnaja contains less carbon than the other CV3 chondrites (Table 1, Fig. 1). In addition to linear fits for each CV chondrite, we calculated a linear fit for all the CV chondrite data combined (Pearson coefficient 0.81) (Fig. 1, Table 1). Linear fits and parameters were obtained using the Igor Pro software.

4. Discussion

4.1. H and C contents and D/H ratios of water in CV chondrites

The hydrogen signal measured in CV chondrite matrices is about one order of magnitude lower than that in CM chondrites Sayama and Paris (Table 1). Although it is difficult to quantitatively estimate the H content of chondrite matrices (i.e. Deloule and Robert, 1995), such results provide qualitative information on the low H content of CV chondrites. As shown by analyses of glass and serpentine standards (Fig. 2), H⁻/ $^{29}\text{Si}^-$ linearly correlates with H₂O/SiO₂. Assuming that the SiO₂ concentration is similar in CM and CV chondrite matrices, we thus estimate that the CV matrices contain about one order of magnitude less hydrogen than the CM matrices. This estimate is consistent with (i) bulk measurements reporting that the mass fraction of H is 830–2250 ppm in Kaba, 470 ppm in Bali, 1560 ppm in Grosnaja, and between 0.53 and 1.46 wt.% in CM chondrites (Alexander et al., 2012;

Table 1
Measured H^- (in counts per second per pA of primary current), $^{29}Si^-/H^-$, and $^{13}C^-/H^-$ ratios and hydrogen isotopic compositions of hydrated minerals different CV and CM chondrites. D/H ratios are corrected for instrumental mass fractionation using glass standard Tan25_0. N = number of analyses. SE = standard error.

	H^- (counts·s ⁻¹ ·pA ⁻¹)	$^{29}Si^-/H^-$ ($\times 10^{-2}$) \pm 2SE	$^{13}C^-/H^-$ ($\times 10^{-3}$) \pm 2SE	N	Pearson coeff.	D/H ($\times 10^{-6}$) \pm 2SE	δD (‰) \pm 2SE
Kaba (CV3 _{oxB})	60 \pm 42	59.9 \pm 3.5	67.5 \pm 4.4	42	0.76	139 \pm 14	-108 \pm 88
Bali (CV3 _{oxB})	56 \pm 31	80.9 \pm 9.2	62.0 \pm 4.9	28	0.58	153 \pm 13	-20 \pm 86
Grosnaja (CV3 _{oxB})	94 \pm 226	53.8 \pm 8.1	19.3 \pm 4.1	10	0.04	154 \pm 31	-11 \pm 199
All CVs	–	–	–	81	0.80	144 \pm 7	-77 \pm 44
Sayama (CM2)	427 \pm 89	6.6 \pm 0.3	7.9 \pm 1.7	16	0.81	105 \pm 9	-329 \pm 56
Paris (CM2.7/2.9)	443 \pm 213	6.9 \pm 1.9	9.1 \pm 3.9	7	0.94	127 \pm 12	-182 \pm 78

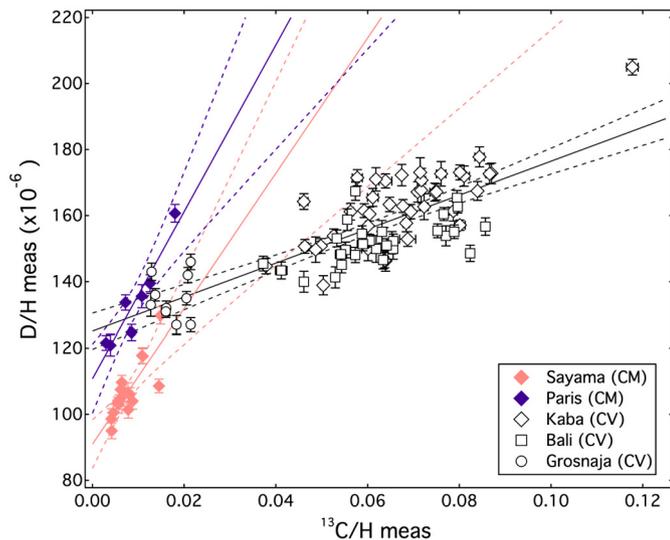


Fig. 1. Measured D/H vs. $^{13}C/H$ ratios in the matrices of CV chondrites Kaba, Bali, and Grosnaja and CM chondrites Sayama and Paris (measured during the same analytical session for reference). Linear fits (solid lines) and 95% confidence interval bands (dashed lines) were calculated for the combined CV dataset and the individual CM chondrites. Error bars represent internal error at 2σ .

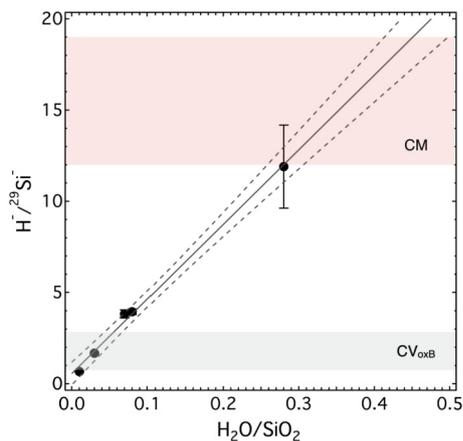


Fig. 2. Relationship between the secondary ion intensity ratio $H^-/^{29}Si^-$ and the known H_2O/SiO_2 contents of the serpentine standard Serp-12A ($H_2O = 12.2$ wt.%, $SiO_2 = 43$ wt.%) and four hydrous glass standards Tan25_0 and Tan25_4 ($H_2O = 0.85$ and 4.29 wt.%, respectively, $SiO_2 = 60.2$ wt.%), ETNA4 ($H_2O = 3.64$ wt.%, $SiO_2 = 46.8$ wt.%), and Glass 47963 ($H_2O = 1.45$ wt.%, $SiO_2 = 48.2$ wt.%). The ranges of $H^-/^{29}Si^-$ ratios obtained in this study for CM and CV_{oxB} chondrites are shown.

Kerridge, 1985), and (ii) the lower abundance of hydrated minerals in CV compared to CM chondrites (Howard et al., 2010, 2014; Krot et al., 1998).

Contrary to hydrogen, the ranges of carbon emission in CV and CM chondrites are of the same order (0.4–16.4 and 1.5–7.2 counts·s⁻¹·pA⁻¹, respectively; Table S1). The bulk C concentra-

tion in CV chondrites (1.07 wt.% in Kaba, 0.64 wt.% in Bali, and 1.1 wt.% in Grosnaja; Alexander et al., 2012; Kerridge, 1985) is about a factor of two lower than in most CM chondrites. However, because carbon is mainly present in the matrix, and the amount of matrix in CVs (~ 35 vol.%) is about half that in CMs (~ 60 vol.%), our results indicate that the carbon contents of CV and CM chondrite matrices are of the same order (Alexander et al., 2018; Zanda et al., 2009). We measured a lower carbon content in Grosnaja compared to the other CV chondrites (Table 1) that is not consistent with reported bulk measurements (Kerridge, 1985). It is thus possible that Grosnaja contains a heterogeneous distribution of organic particles and hydrated minerals, as reported for other CV chondrites such as Bali (Bonal et al., 2006; Keller et al., 1994).

The positive correlations between the C/H and D/H ratios of chondrite matrices can be interpreted as the result of mixing between two isotopically distinct H-bearing end-members: a D- and C-rich organic material and a C-free, D-poor inorganic material (Alexander et al., 2012; Piani et al., 2018). The zero intercepts of the C/H vs. D/H correlations can thus be used, after correction for instrumental mass fractionation, to estimate the D/H ratios of the inorganic phases (Piani et al., 2018). D/H ratios are corrected from the instrumental mass fractionation using glass standard Tan25_0 ($\alpha = 0.87 \pm 0.02$), which has the same H content and was measured with the same primary current conditions as the CV chondrite matrices. Because isotopic fractionation between water and hydrated minerals at the CM parent-body temperature is low compared to the precision of the measurements (Piani et al., 2018), the inferred D/H is a proxy of the hydrogen isotopic composition of the water accreted by the parent body. The D/H ratios of water in the Sayama and Paris CM chondrites are $D/H_{\text{Sayama-water}} = [105 \pm 9] \times 10^{-6}$ ($\delta D_{\text{Sayama-water}} = -329 \pm 56\text{‰}$, 2σ) and $D/H_{\text{Paris-water}} = [127 \pm 16] \times 10^{-6}$ ($\delta D_{\text{Paris-water}} = -182 \pm 78\text{‰}$, 2σ), respectively (Table 1, Fig. 3). These values are similar within error to previous estimates taking the Sayama D/H ratio as representative of the main water component in CM chondrites ($\delta D_{\text{CM-water}} \approx -350\text{‰}$; Alexander et al., 2012; Piani et al., 2018) and the least altered lithologies of Paris as preserving a deuterium-rich water signature present in the CM rock before alteration (Piani et al., 2018). In CV chondrites, the conditions (temperature and/or abundance of water) in which hydrated minerals formed are poorly constrained, resulting in (1) uncertainties on the possible water/hydrated mineral fractionation coefficients and (2) possibly no or very low fractionation as most of the water is probably consumed to form hydrated minerals. Smectite in Kaba was proposed to form in a temperature range of 0 to 100 °C by analogy to terrestrial occurrences (Keller and Buseck, 1990 and reference therein), but a recent mineralogical study by Ganino and Libourel (2017) proposed the hydrous phases in CV chondrites could witness the low temperature part (~ 200 °C) of the fluid assisted metamorphism trend possibly during parent body cooling. Given the full possible temperature range (0–200 °C), the isotopic fractionation factor between smectite and water can thus be contained between 87‰ at 0° and -10‰ at 200 °C (Méheut et al., 2010) or be closer to 0‰ if most of the water was consumed to form hydrated minerals. Taking our combined

Table 2Hydrogen content and isotopic composition in organic matter (OM) and hydrated minerals (Hydr. Min.) for CV_{oxB} chondrite Kaba and CM chondrites (mean value).

	Phase	Modal ab.	H content	Modal H (wt.%)	H _{OM} /H _{bulk}	H _{bulk} (wt.%)	D/H ($\times 10^{-6}$)	Bulk D/H _{calc} ($\times 10^{-6}$)	Bulk D/H _{meas.} ($\times 10^{-6}$)
CV (Kaba)	OM	0.68 wt.% C ^a	H/C (wt.) = 0.03 ^a	0.018	0.28	0.063	188 ^a	153	158 ^h
	Hydr. Min.	2.3 wt.% ^b	2.0 wt.% ^c	0.045			139 ± 14 ^f		
CM (average)	OM	0.9 wt.% C ^c	H/C (wt.) = 0.05 ^c	0.049	0.05	0.913	272 ± 9 ^c	110	175 ^h
	Hydr. Min.	Cronst. 31.0 wt.% ^d	1.0 wt.% ^d	0.864			101 ± 6 ^g		
		Serp. 38.3 wt.% ^d	1.4 wt.% ^d						

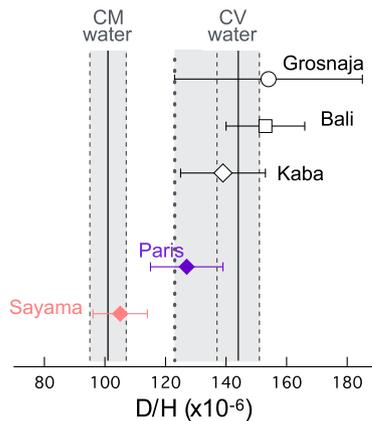
^a Total C content, H/C, and D/H ratios of insoluble OM in Kaba from Alexander et al. (2007).^b Modal abundances from Howard et al. (2010), calculated using densities from webmineral.com.^c Averaged values for all CM chondrites (except Bells) from Alexander et al. (2007).^d Modal abundances from Howard et al. (2014); average densities and H contents of CM2 chondrite cronstedtite (Cronst.) and Fe/Mg-serpentine (Serp.) from webmineral.com.^e H content in Kaba's phyllosilicates estimated from Keller and Buseck (1990).^f This study, cf. Table 1.^g Piani et al. (2018).^h Average values for all non-heated CM (except anormal Bells and Essebi chondrites) from Alexander et al. (2012).

Fig. 3. D/H ratios of water in the measured CV and CM chondrites after correction for instrumental mass fractionation (error bars at 2σ). The average compositions of CM chondrite water (Piani et al., 2018) and CV chondrite water (this study) are distinct (gray domains with 2σ standard error intervals for hydrated minerals delimited by the dashed lines). The dotted-line shows the minimum D/H value for CV water corresponding to the extreme case were CV hydrous minerals formed at 0°C (see details in Section 4.1). The less-altered lithology of Paris (purple diamond) is not representative of CM chondrite water but of a deuterium-rich water signature present in the CM rock before alteration. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

CV chondrite dataset, we obtained a D/H ratio for CV chondrite hydrated minerals of $D/H = [144 \pm 7] \times 10^{-6}$ ($\delta D = -77 \pm 44\%$, 2σ ; Table 1). We obtain similar estimates by considering each CV chondrite separately, although with higher uncertainties (Table 1). Given the whole range of possible formation temperature for hydrated minerals, this leads to a D/H ratio for CV chondrite water of $D/H_{\text{CV-water}} = [144^{+8}_{-21}] \times 10^{-6}$ (or $\delta D_{\text{CV-water}} = -77^{+54}_{-131}\%$, 2σ ; Fig. 3). Compared to the main water component of CM chondrites, water in CV chondrites is significantly enriched in deuterium with an enrichment factor of ~ 1.4 (Fig. 3).

4.2. Comparison of water and organics in CV and CM chondrites

Determining the D/H composition of the C-rich end-member (organics) would require assumptions on the $^{13}\text{C}/\text{H}$ ratios of the CM or CV organic components, inducing large uncertainties. Nevertheless, the clear divergence of the CM and CV mixing lines (Fig. 1) indicates that the C-rich end-member in CV chondrites is significantly depleted in deuterium compared to organics in CM chondrites. Indeed, IOM isolated from CV chondrites was found to have a lower D/H ratio than CM chondrite IOM (Alexander et al., 2007) and soluble organic compounds (Pizzarello et al., 2006). To further compare the D/H compositions of CM and CV chondrites,

we have estimated the respective contributions of organic matter and hydrated silicates to the bulk hydrogen budget based on their modal abundances and H concentrations in CM and CV chondrites (Table 2 and references therein). Among CV chondrites with well-characterized organic matter and hydrated silicates, the least-metamorphosed Kaba chondrite (Bonal et al., 2006) was taken as the most representative. The contribution of hydrogen in organic matter to the bulk H content is much higher in CV (29%) than in CM chondrites (5%). Using these estimates and assuming that the organic material corresponds to IOM that can be isolated by acid treatments, we estimate the CV bulk D/H to be 153×10^{-6} , in good agreement with the bulk D/H of 156×10^{-6} reported from gas-phase spectrometry (Alexander et al., 2012). This implies that the organic matter component in CV chondrites can be approximated from IOM. In contrast, the calculated CM bulk D/H ratio is 0.6 times the reported D/H ratio (Table 2). This discrepancy indicates that (i) IOM in CM chondrites is not representative of the entire organic matter component, and (ii) the total organic component currently present within CM chondrites is enriched in D compared to the organic materials known so far in CM chondrites.

4.3. Origin of the differences in the D/H ratios of water and organic matter in CM and CV chondrites

The water-derived H content of CV chondrites corresponds to about 5% of that of CM chondrites (Table 2). This difference can either be shaped by H loss during parent-body processes or inherited from different water ice contents in the CM and CV accretion zones. During aqueous alteration, water is believed to act as an oxidizing agent for metal, resulting in the reduction of water to H_2 (Alexander et al., 2010). The loss of volatile H_2 would be associated with Rayleigh-type distillation, enriching the remaining water in deuterium. Based on the iron valences estimated in CI, CM, CR, and OC chondrites, Sutton et al. (2017) proposed that all these chondrite types accreted water with a similar deuterium-depleted isotopic composition of $D/H \approx 60\text{--}180 \times 10^{-6}$ ($\delta D \approx -650$ to $+154\%$) depending on the reaction temperature ($0\text{--}200^\circ\text{C}$). Following their estimation, we fixed the initial D/H ratio of water in CV chondrites as that in CM chondrites, $D/H_{\text{CM}} = 101 \times 10^{-6}$ (Piani et al., 2018), and calculated the isotopic evolution of CV chondrite water during Rayleigh distillation at 0, 100, and 200°C using the equilibrium fractionation coefficients between H_2O and H_2 vapor defined by Lécluse and Robert (1994) (Fig. 4). The difference between the D/H ratios of CV and CM water can be related to the loss of about half of their initial water content (fraction of remaining water of 0.66 at 0°C , 0.58 at 100°C , and 0.51 at 200°C), but such a loss cannot explain the strong difference in water content between CM and CV chondrites (Table 2, Fig. 4).

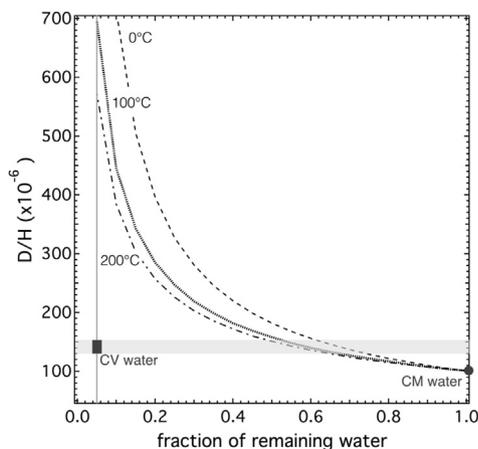


Fig. 4. Calculated D/H ratios of the remaining water fraction after Rayleigh fractionation at 0, 100 and 200°C for water with an initial D/H ratio equal to that of CM carbonaceous chondrite water, $D/H = 101 \times 10^{-6}$. Rayleigh fractionation cannot explain both the remaining fraction of water in CV chondrites relative to CM chondrite water and the D/H composition of CV water (gray lines).

Assuming that carbonaceous chondrites heterogeneously accreted water ice grains with similar D/H ratios would require to find a parent body process capable of enhancing the D/H ratio of water in CV chondrites but not in CM chondrites. Given the high proportions of C-bound (organic) to silicate-bound (water-derived) H in CV relative to CM chondrites (Table 2), H isotopic interactions between water and organic matter—if kinetically efficient—could have significantly affected the D/H ratios of both water and organics in CV chondrites. The efficiency of hydrogen isotopic exchange between aqueous fluids and extraterrestrial organic materials has long been discussed in literature (Alexander et al., 2007, 2010; Oba and Naraoka, 2009; Piani et al., 2015; Remusat et al., 2010; Sessions et al., 2004; Yabuta et al., 2007). The main challenges in constraining such hydrogen isotopic exchange lie in: (1) the multiple types of C–H bonds in organic materials, resulting in a large range of possible reaction constants and rates; (2) the complex nature of chondritic organic material for which no satisfactory terrestrial or synthetic analogues are available, precluding straightforward isotopic exchange experiments; (3) the presence of possible catalytic mineral surfaces that would modify the chemical reaction efficiency; and (4) the overlapping of several chemical mechanisms that cannot be unraveled without compound-specific D/H analyses of known organic materials, i.e., pure isotopic exchange, chemical

reactions that modify the molecular structure but not the chemical formula, and chemical reactions that modify the chemical formula (Sessions et al., 2004).

Considering only pure isotopic exchange between water and organic materials, the extent of isotopic exchange would depend on the duration and temperature of alteration. Theoretical calculations (Bottinga, 1969; Remusat et al., 2010) and experiment-based estimates (e.g., Sessions et al., 2004) indicate that, at equilibrium, organics should be depleted in deuterium relative to water. Given our calculated bulk D/H ratio and fractions of hydrogen in organic matter (H_{OM}/H_{bulk} ; Table 2) and water ($1 - H_{OM}/H_{bulk}$) in the CV chondrite Kaba, we calculated that the equilibrium D/H ratios of organics and water should be about $D/H_{OM} = 137 \times 10^{-6}$ and $D/H_{water} = 159 \times 10^{-6}$, respectively (time t_{Eq} in Fig. 5; see Appendix A for details). The presence of D-poor water relative to organics in both CM and CV chondrites indicates that, if isotopic exchange occurred between water and organics during aqueous alteration on asteroids, equilibrium was not reached (Fig. 1, Table 2). Hydrous pyrolysis experiments involving D-rich IOM isolated from CM chondrites and D-poor water have shown a strong decrease of the organic matter D/H ratios (δD decreasing by $\sim 800\%$) at $T = 270\text{--}330^\circ\text{C}$ in a few days (Oba and Naraoka, 2009; Yabuta et al., 2007), consistent with previous experiments involving terrestrial kerogens (Schimmelmann et al., 1999). For CM chondrites, such a rapid isotopic effect is difficult to reconcile with: (i) the lack of variation of IOM D/H ratios measured in these chondrites (Alexander et al., 2007); (ii) the absence of modification of the IOM aromatic moieties after aqueous alteration (Busemann et al., 2007; Cody and Alexander, 2005), contrary to pyrolysis experiments (Sephton et al., 2000); (iii) the absence of self-diffusion fronts in the D-poor hydrated minerals surrounding the D-rich organic particles (Remusat et al., 2010); and (iv) identical and well-defined matrix C/H vs. D/H correlations in different CM chondrites despite their drastically different degrees of alteration (Piani et al., 2018) and, assumedly, different extents of modification by pyrolysis.

In CV_{oxB} chondrites, the presence of scattering in the D/H vs. C/H trends (Fig. 1) and the range of D/H ratios measured for CV IOM (Alexander et al., 2007) could be the consequences of parent body alteration and/or metamorphism. The amount of water available to react with the organic materials is lower than that in CM chondrites and could have limited the efficiency of exchange reactions, explaining why equilibrium was not reached. Assuming the bulk D/H ratio of Kaba and that the amount of H in organic matter and water was preserved during the exchange reaction (i.e.,

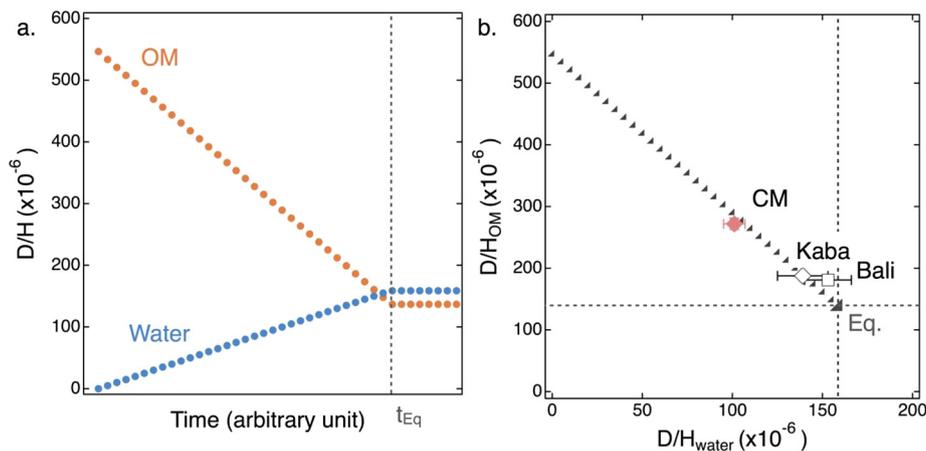


Fig. 5. Simplified model of isotopic exchange between water and organic matter during parent body alteration, assuming pure isotopic exchange in a closed-system. (a) The D/H ratios of water and organic matter (OM) evolved until reaching equilibrium at time t_{Eq} . (b) Coupled evolution of the D/H ratios of organic matter and water until reaching equilibrium (Eq.) from (a) compared to the D/H ratios of water and insoluble organic matter in CM chondrites (average) and CV chondrites Kaba and Bali (Table 2 and references therein; Appendix B).

since accretion), we calculated the interdependence of the D/H ratios of water and organic matter throughout the isotopic exchange reaction until equilibrium was reached (Fig. 5 and Appendix B). The starting compositions represent the unrealistic case where all available D atoms in CV chondrites are associated with organic material (Fig. 5a), corresponding to a maximum organic matter D/H ratio of 545×10^{-6} ($\delta D = 2500\%$). Interestingly, this value is below that reported for IOM in the CR and anomalous Bells chondrites ($\delta D \sim 3000\%$; Alexander et al., 2007), indicating that the D/H composition of CV organic matter before isotopic exchange with D-poor water on asteroids cannot be identical to that of CR chondrite IOM as proposed by Alexander et al. (2012). The coupled evolution of the water and organic matter D/H ratios is then compared to those of Kaba, Bali, and the average CM composition (Fig. 5b). The goal of this exercise is to see if CV chondrite water and organic matter could have a similar origin as or be derived from water and OM in CM chondrites. The averaged composition of CM chondrite water and organic matter falls on the CV evolution trend (Fig. 5b), indicating that pure isotopic exchange could explain the evolution of water and organic D/H ratios from CM to CV compositions.

We acknowledge that there are several issues with using this simple mechanism to understand the data. First, it is unclear why water and organics in CV chondrites would have experienced a greater degree of hydrogen isotopic exchange than in CM chondrites, which would have been a more favorable environment for isotopic exchange given their higher water/rock ratios compared to CV chondrites (e.g., Marrocchi et al., 2018). However, this could be linked to the higher alteration temperature experienced by CV chondrites (i.e., temperature range from 200 to 600 °C; Ganino and Libourel, 2017) relative to CM chondrites (i.e., 110 °C; Verdier-Paoletti et al., 2017). Consequently, the capability of C-bound hydrogen in extraterrestrial organic matter to exchange with water-bound hydrogen (exchangeability) could be limited at temperatures relevant to CM parent body hydrothermalism (Schimmelmann et al., 1999, and references therein).

It is also possible that the different D/H ratios of water and organics in CM and CV chondrites were inherited from the different place and/or time of accretion of their respective asteroidal parent bodies (Jacquet and Robert, 2013; Yang et al., 2013). This case could provide an explanation for the oxygen isotopic compositions of CV chondrite secondary phases that suggest that the aqueous fluid from which they formed was enriched in $^{17,18}\text{O}$ isotopes compared to CI-, CM-, and CR-type carbonaceous chondrites (Fujiya, 2018; Marrocchi et al., 2018). Water in CV chondrites would thus have been enriched in the heavy isotopes of both hydrogen and oxygen, suggesting a contribution of outer Solar System water to the CV chondrite parent body (Yurimoto and Kuramoto, 2004). The fact that CV chondrites sampled a higher contribution of outer Solar System water compared to most of the hydrated carbonaceous chondrites (CM, CR, CI), with the exception of Paris CM chondrites (Piani et al., 2018; Vacher et al., 2016), could be due to the slightly earlier accretion of the CV parent body (Sugiura and Fujiya, 2014).

5. Concluding remarks

Using a recently developed SIMS analytical method, we determined the D/H ratio of water present in CV_{oxB}-type carbonaceous chondrites Kaba, Bali, and Grosnaja. The D/H ratio of water in these CV chondrites ($D/H_{\text{CV-water}} = [144^{+8}_{-21}] \times 10^{-6}$ or $\delta D_{\text{CV-water}} = -77^{+54}_{-131}\%$, 2σ) is significantly higher than that of water in CM-type carbonaceous chondrites ($D/H_{\text{CM-water}} = [101 \pm 6] \times 10^{-6}$ or $\delta D_{\text{CM-water}} = -350 \pm 40\%$, 2σ ; Piani et al., 2018) and similar to that of the least altered lithologies of the CM chondrite Paris ($D/H_{\text{Paris}} = [145 \pm 25] \times 10^{-6}$ or $\delta D_{\text{Paris/SMOW}} = -69 \pm 163\%$, 2σ ; Piani et al., 2018). On the other hand, organic matter in CV

chondrites is depleted in deuterium relative to organic matter in CM chondrites. Assuming that (1) the differences between the D/H ratios of water and organics in CV and CM chondrite resulted from parent body processes and (2) both types of chondrites accreted water and organics with similar D/H ratios, the present D/H compositions can be explained by pure H isotopic exchange. However, the likelihood and efficiency of such an isotopic exchange has not been demonstrated, and may be linked to the higher metamorphism temperature of the CV relative to the CM parent body. It is also possible that the CV and CM parent bodies accreted water and organics with different isotopic compositions due to a difference in their time and/or location of formation.

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Appendix A. Isotopic fractionation at equilibrium

Using the fractionation factor estimated by Remusat et al. (2010) between ethyl benzene and water at 100 °C ($1000 \times \ln \alpha_{\text{OM-water}} = -150$ or $\alpha = 0.86$), we estimated the D/H composition of organic matter (OM) and water at equilibrium considering the fractions of H in OM and water to be $x_{\text{OM}} = 28\%$ (Table 2) and $1-x_{\text{OM}} = 72\%$, respectively, as:

$$\begin{cases} D/H_{\text{OM}} = \alpha D/H_{\text{water}} \\ D/H_{\text{bulk}} = x_{\text{OM}} \times D/H_{\text{OM}} + (1 - x_{\text{OM}}) \times D/H_{\text{water}} \end{cases}, \quad (\text{A.1})$$

$$\Rightarrow \begin{cases} D/H_{\text{OM}} = \alpha D/H_{\text{water}} \\ D/H_{\text{bulk}} = x_{\text{OM}} \times \alpha D/H_{\text{water}} + (1 - x_{\text{OM}}) \times D/H_{\text{water}} \end{cases}, \quad (\text{A.2})$$

$$\Rightarrow \begin{cases} D/H_{\text{OM}} = \alpha D/H_{\text{water}} \\ D/H_{\text{water}} = \frac{D/H_{\text{bulk}}}{x_{\text{OM}} \cdot (\alpha - 1) + 1} \end{cases}. \quad (\text{A.3})$$

Using our calculated bulk D/H ratios for Kaba and Equations (A.3), we calculated the equilibrium D/H ratios for organic matter and water to be $D/H_{\text{OM}} = 137 \times 10^{-6}$ and $D/H_{\text{water}} = 159 \times 10^{-6}$, respectively (time t_{Eq} in Fig. 5).

Appendix B. Kinetic isotopic exchange

Before reaching equilibrium, the D/H ratios of OM and water at a given time t are a function of the total amount of H and D, and should thus be linked by the linear relation:

$$D/H_{\text{bulk}} = x_{\text{OM}} \times D/H_{\text{OM}}^t + (1 - x_{\text{OM}}) \times D/H_{\text{water}}^t \quad (\text{B.1})$$

$$\Rightarrow D/H_{\text{OM}}^t = \frac{D/H_{\text{bulk}}}{x_{\text{OM}}} + \frac{(1 - x_{\text{OM}})}{x_{\text{OM}}} \times D/H_{\text{water}}^t. \quad (\text{B.2})$$

Using equation (B.2) and the x_{OM} and D/H_{bulk} values of CV chondrite Kaba, we calculated the coupled evolution of the D/H ratios of organic matter and water until reaching equilibrium at 100 °C (Fig. 5). On Fig. 5, we report the D/H isotopic compositions of Kaba and Bali, the two CV_{ox} chondrites for which the D/H ratios of water and organic matter are known (Tables 1 and 2). Interestingly, the average isotopic compositions of water and organic matter in CM chondrites also falls on the kinetic evolution line, indicating that the CM composition could have been the starting composition for CV chondrites, or an earlier stage of the same kinetically controlled isotopic exchange (Fig. 5).

Appendix C. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2018.09.031>.

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