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Bulk Hydrogen Isotopes in Ordinary Chondrites

by

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THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

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Bulk Hydrogen Isotopes in Ordinary Chondrites

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B.S., Geology, Western Carolina University, 2017

M.S., Earth and Planetary Sciences, The University of New Mexico, 2023

Abstract

Bulk hydrogen isotopes in nominally anhydrous meteorites are a key component in our understanding of the distribution of hydrogen in our solar system, including the provenance of water on the Earth. Here, we develop a step-heated continuous-flow method to measure the bulk hydrogen isotopes in nominally anhydrous rocks and use this method to significantly increase the dataset of bulk hydrogen isotopes in ordinary chondrites, nearly doubling the number of equilibrated members. We found that as thermal alteration increases from petrologic type 3.0 to 4, there is a correlated decrease in both hydrogen content and isotope ratio, followed by no significant change beyond 4. We associate this with the destruction of heavy insoluble organic matter as thermal metamorphism progresses. We suggest when considering ordinary chondrites as a component of mixing models, a δD of 12‰ be considered representative of the class.

Table of Contents

List of Figures	v
List of Tables	vi
Introduction	1
Methods	4
Samples	4
Continuous-flow mass spectrometry	4
Data Processing	5
Results	7
Discussion	10
Terrestrial contamination.....	10
Comparisons to historical measurements	12
What it all means for ordinary chondrites	16
Conclusions	17
References	18

List of Figures

Fig. 1: Continuous Flow Reaction Line	5
Fig. 2: Release Diagrams for the Step-Heating of Standard Biotites.....	7
Fig. 3: Average hydrogen Isotope Values in Each Step.....	8
Fig. 4: Release Diagrams for the Step-Heating of Ordinary Chondrites	13
Fig. 5: All Bulk Hydrogen Contents of Ordinary Chondrites.....	15
Fig. 6: All Bulk δD of Ordinary Chondrites	15

List of Tables

Table 1: Previously Reported Bulk Hydrogen Isotopic Compositions of Ordinary Chondrites	3
Table 2: Bulk Hydrogen Measurements of all Ordinary Chondrites in This Study	9
Table 3: Minerals Identified as Terrestrial Alteration Products	11
Table 4: Bulk Water Abundances and Hydrogen Isotopic Compositions of Chainpur	12

Introduction:

Hydrogen isotope characterization of bulk samples from a wide range of extraterrestrial materials is a necessary step to better our understanding of the origins and proliferation of water in our solar system. Rough determinations of hydrogen isotope ratios in planetary atmospheres have been conducted through remote sensing, but high-quality measurements of hydrogen held within the rocks of a body requires physical samples to be measured on instruments we have on the Earth. Historically, there has been a particular focus on volatile-rich chondrites and meteorites from known bodies (e.g. Kerridge 1985; Saal et al. 2013). The extensive measurements of hydrated meteorite groups can be attributed to the relative ease of hydrogen isotope measurements, CM chondrites' isotopic similarity to the Earth (Marty 2012), and the inherent scientific benefit of fully characterizing a suite of meteorites attributed to a specific class of asteroidal bodies. Despite all the work on hydrated chondrites, one class which has historically been underrepresented in literature due to its nominally anhydrous nature is the ordinary chondrites.

Ordinary chondrites make up the vast majority of meteorite finds on the Earth, accounting for more than 85% of all finds (Weisberg et al. 2006) and are a diverse group of meteorites with the potential to provide insights into the evolution of hydrogen in the solar system. To date, only 22 ordinary chondrites have had bulk hydrogen isotope measurements reported (see Table 1). Notably, there has been increased interest in hydrogen isotopes within ordinary chondrites over the past decade. However, the vast majority of studies have focused extensively on low petrologic types (Alexander et al. 2012) and specific components of the samples, using techniques like Secondary Ion Mass Spectrometry (Shimizu et al. 2021). *In situ* measurements within a sample are inherently flawed when considering the source of water to a body, as any water deposited will affect the entire volume of the meteorite, not only specific minerals. Since the early 1980s, bulk hydrogen isotope measurements of ordinary chondrites have almost only been conducted on Semarkona (Alexander et al. 2012), one of the least thermally altered of the class, with an anomalously high hydrogen isotope value [what is a "high isotope value"? D-rich?] compared to any other meteorite. This bias toward Semarkona has led to its hydrogen isotopic composition being used to represent the group (e.g. Desch and Robinson 2019; Lin and Van Westrenen 2019;

Wu et al. 2018), despite it being the most primitive ordinary chondrite found to date and the most anomalously heavy (see Table 1). In this study, we report the bulk hydrogen isotopic compositions of 13 ordinary chondrites, representing the range of classes and petrologic types, to obtain a more representative average hydrogen isotopic composition of ordinary chondrites.

The published δD values for ordinary chondrites are intriguing due to the fact that the meteorites identified as the least altered in the class have been found to have extraordinarily high D/H ratios. As seen in Table 1, the published bulk ordinary chondrite measurements show that Senarkona and Bishunpur have bulk δD of over 1000‰. The rest of the measured ordinary chondrites are almost exclusively positive, with the three exceptions being altered finds and higher petrologic types. Of the 22 meteorites which have been published, only 5 were above petrologic type 3. Due to the low numbers of samples which were measured, more samples are required to determine whether their relatively light values were a result of terrestrial contamination, and to look for any larger trends associated with petrologic type.

Bulk hydrogen isotope ratios in ordinary chondrites are primarily driven by the relative concentrations of different hydrogen reservoirs within the meteorite. Two of the most significant reservoirs of hydrogen in meteorites are hydrated minerals (water) and organics, in the form of insoluble organic matter (IOM). It has been found that, when plotting D/H against the ratio of carbon to hydrogen, bulk analyses of meteorites will fall on a mixing line between the water and organic values (Alexander et al. 2012; Kolodny et al. 1980). When plotting D/H against the C/H ratio of the meteorites, linear regression through the data can be used to calculate the D/H ratio of the pure phyllosilicate by extrapolating to the point where the C/H equals zero. Using this calculation, Alexander et al. (2012) found that the δD value of water is approximately -500‰ for CM, CI, and CO chondrites and +100‰ for CR chondrites. For ordinary chondrites, only the δD of Semarkona has been estimated using this method, resulting in an average of 1954‰ (Alexander et al. 2010); these authors note that this is likely an overestimation due to the calculation ignoring hydrogen in soluble organics.

Table 1: Previously reported bulk hydrogen isotopic compositions of ordinary chondrites.

Meteorite	Class	δD (‰)	Reported Values	Source
Semarkona	LL3.0	2904	1	McNaughton et al., 1981
Semarkona	LL3.0	1525	2	McNaughton et al., 1982
Semarkona	LL3.0	2901	3	Yang and Epstein, 1983
Semarkona	LL3.0	1615	1	Alexander, 2012
Bishunpur	LL3.1	2233	3	McNaughton et al., 1981
Bishunpur	LL3.1	622	5	McNaughton et al., 1982
Bishunpur	LL3.1	2049	1	Yang and Epstein, 1983
Krymka	LL3.2	100	2	McNaughton et al., 1982
Chainpur	LL3.4	163	14	Robert, 1978
Chainpur	LL3.4	560	2	McNaughton et al., 1982
Chainpur	LL3.4	71	2	Yang and Epstein, 1983
ALHA 77214	L3.4	190	1	McNaughton et al., 1982
ALHA 77278	LL3.6	325	2	McNaughton et al., 1982
Parnallee	LL3.6	-78	1	McNaughton et al., 1982
Kohar	L3.6	-85	1	Yang and Epstein, 1983
Tieschitz	L3.6	365	2	McNaughton et al., 1982
ALHA 77304	LL3.7	14	1	McNaughton et al., 1982
Mezo Madaras	L3.7	50	1	McNaughton et al., 1982
Hedjaz	L3.7	-93	7	Robert, 1978
Grady	H3.7	-82	1	McNaughton et al., 1982
ALHA 77299	H3.7	180	1	McNaughton et al., 1982
ALHA 77215	L3.8	51	2	McNaughton et al., 1982
Prairie Dog Ck	H3.8	-82	1	McNaughton et al., 1982
Carraweena	L3.9	85	1	McNaughton et al., 1982
Carraweena	L3.9	-128	1	Yang and Epstein, 1983
Bremervorde	H3.9	20	1	McNaughton et al., 1982
Goodland	L4	-78	1	Yang and Epstein, 1983
Weston	H4	-110	1	Robert, 1978
Weston	H4	16	1	McNaughton et al., 1981
Olivenza	LL5	-136	3	Robert, 1978
St Severin	LL6	-155	5	Robert, 1978
Bori	L6	-159	1	Robert, 1978
Bruderheim	L6	-138	1	Yang and Epstein, 1983
Guarena	H6	-190	3	Robert, 1978

*Included delta values are averages of all measurements presented in the given study.

What hydrogen is left outside of organics and hydrated minerals is found at low concentrations within nominally anhydrous minerals, primarily olivine, pyroxene, and

chondrule components not listed above. *In situ* measurements have been made of nominally anhydrous minerals in ordinary chondrites using Secondary Ion Mass Spectrometry (SIMS) and have shown the hydrogen isotope ratios to be range widely (Stephant et al. 2017).

Methods:

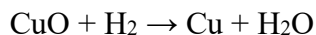
Samples:

A total of 13 ordinary chondrites (Table 2) were selected for bulk hydrogen isotope measurements. Samples were chosen to represent a range of petrologic types from all three classes of ordinary chondrites. Three of the 13 meteorites, Chainpur (McNaughton et al. 1982; Robert 1978; Yang and Epstein 1983), Parnalee (McNaughton et al. 1982), and Saint-Severin (Robert 1978), have been measured previously and serve as a comparison to historical methods. All meteorites chosen were identified falls to minimize the effects of terrestrial hydrogen contamination, as prolonged exposure to the copious amounts of water and organic hydrogen has been shown to have significant effects on nominally anhydrous meteorites (Stephant et al. 2018). Each sample was powdered to maximize volatile release during heating, and aliquots ranged from 7 to 30mg, depending on expected hydrogen content, with the majority being 20 ± 3 mg, separated for individual measurements.

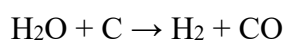
Continuous-flow mass-spectrometry:

For this study, a step-heated continuous-flow mass spectrometry method was used with a line constructed to extract hydrogen from nominally anhydrous minerals. Aliquots of each ground and homogenized sample, held in a silver foil capsule, was placed in a quartz-glass tube within a tube-furnace for heating. A continuous flow of dry helium, used as a carrier gas and passed through a liquid-nitrogen trap before entering the line, was run over each sample for a minimum of 8 hours before step heating commenced. Five steps, at 150, 300, 500, 700, and 900°C were conducted in a tube furnace (Fig. 1A), culminating in a final step where the sample was melted into a glass using an oxy-gas torch. Steps were chosen for their regularity and potential to suggest which minerals were the hydrogen carriers. The sample was held at each step for an hour, as that was found to be the time after which there

was no hydrogen left at that temperature range. All hydrogen released from the sample was converted to water through the reaction;



in a quartz glass tube filled with copper oxide at 600°C (Fig. 1B) to facilitate stoichiometric conversion. All resulting water was collected in a liquid nitrogen cryo-trap (Fig. 1C) for the duration of the heating step. After collection was complete, the trap was quickly heated, and all water released was passed over glassy carbon in a 1350°C furnace to convert back to measurable H₂ through the reaction (Fig. 1D):



The resulting gasses were run through a 5Å molecular sieve to separate the H₂ and CO, and the ratio of isotopes in the H₂ was measured in a Thermo Delta Plus XL mass spectrometer in the Center for Stable Isotopes at the University of New Mexico.

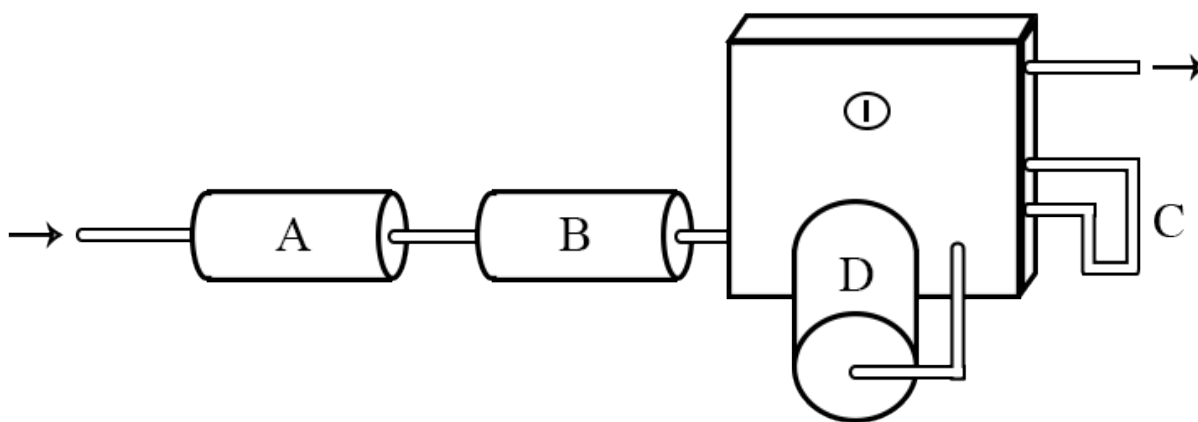


Figure 1: Continuous-flow reaction line. Arrows represent helium flow direction. A: sample reaction furnace, B: CuO furnace, C: liquid nitrogen trap, D: glassy C furnace. 5Å molecular sieve is located inside heated box.

Data processing:

Using our method, it was determined that accurate measurements were possible down to .05 mg of 2 wt% biotite, or 0.126 μmol of H₂. Measurements were standardized to a

known hydrogen gas, calibrated to USGS standards 57 and 58 (Qi et al. 2017), injected into the line before collected hydrogen from the sample was released to the mass spectrometer. Multiple injections of increasing volumes of H₂ gas were conducted to calculate an independent H₃ factor for each measurement. A correlation was determined between the water released by a sample, and thus the measured peak area, and error, so a standard regression was calculated for error. During sample collection for one hour, it is unavoidable for a negligible hydrogen blank to be collected, on the scale of ~50mV above background. Despite the blank hydrogen being negligible, one-hour blanks were collected before and after step-heating. The blank hydrogen for each step, based on measured blank values, was calculated out of the final water content of all samples using simple subtraction of peak areas, and the delta value using the equations:

$$d_{sample} = \frac{d_{Measured} * A_{Measured} - d_{Blank}A_{Blank}}{A_{Measured} - A_{Blank}}$$

$$A_{Sample} = A_{Measured} - A_{Pre-Blank} + (A_{Post-Blank} - A_{Pre-Blank}) * \frac{n_{step}}{7}$$

Suspecting significant contamination by terrestrial water, we present both water content and hydrogen isotope data all hydrogen released, everything released above 300°C, and everything released above 500°C.

Shortly prior to the period in 2019 in which all the meteorite measurements were taken, 14 standard biotites were step-heated, resulting in an error of ±13.36%. The error has been subsequently decreased as the method has been refined. Release diagrams for two biotite standards are shown in figure 2. In all biotites, zero hydrogen was released above background between 0 and 300°C. In both cases shown, hydrogen release between 300 and 500°C was less than 2.7% of the total hydrogen released by the samples and too small of a volume to produce accurate measurements. To determine the amount of hydrogen above background introduced by the process of step-heating, a terrestrial basalt was dehydrated in a 900°C furnace overnight and step-heated both the day after and one week later. In both cases, the only hydrogen measured above background was in the melting step, culminating in a total of 4.52x10⁻⁴ and 7.12x10⁻⁴ wt% H₂O, respectively.

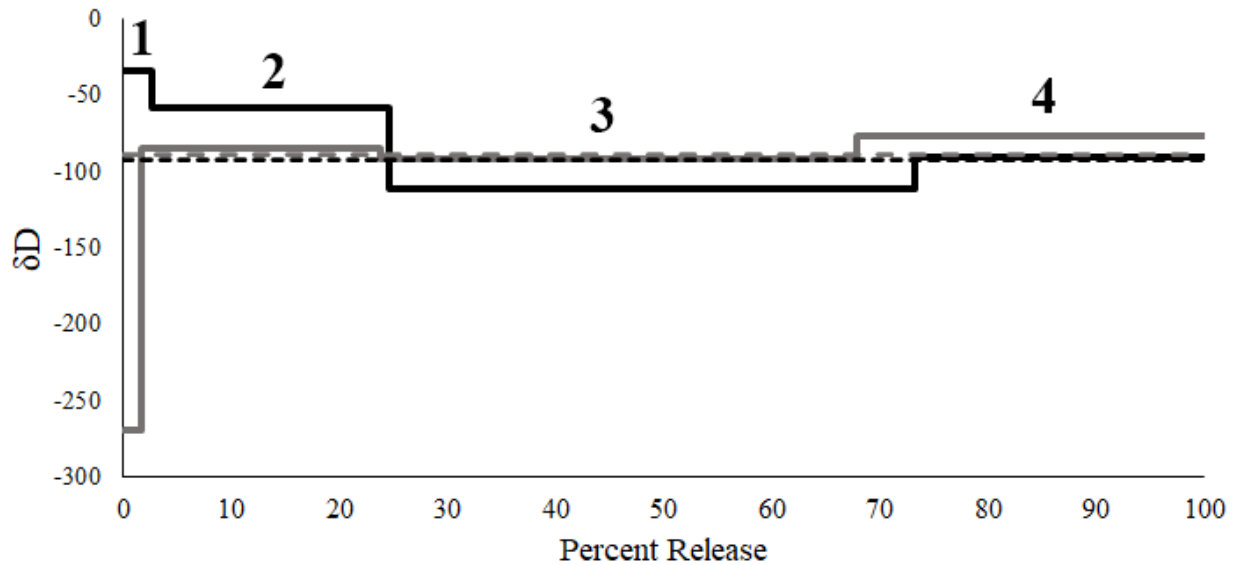


Figure 2: Release diagrams for the step-heating of standard biotites. The width of each step represents the percent of total hydrogen released and the height represents the isotope value of that release. No hydrogen was released. Numbers represent steps: 1; 300-500°C, 2; 500-700°C, 3; 700-900°C, 4; 900°C-melting. Horizontal dashed lines represent combined steps to create a bulk δD for the sample.

Results:

The majority of hydrogen release for every meteorite measured (57-88%, median 81%) occurred in the first 3 steps at temperatures up to 500°C (Fig. 3C, D). A significant increase in δD was observed in every meteorite above 500°C, where all meteorites fell between -126‰ and -40‰ with a median of -78‰ below 500°C, and all meteorites fell between -59‰ and 378‰ with a median of 19‰ above 500°C. Little correlation was observed between percent of total hydrogen release per step and meteorite class or petrologic type, with type 6 meteorites averaging a slightly higher percent release above 500°C. (Fig. 3C). More significant correlation was observed between δD and petrologic type, as type 3 meteorites tend to have a significantly higher δD than any other classes in the > 500°C steps. A relatively strong correlation was also observed for δD above 500°C based on meteorite type, with H meteorites (-10-60‰, median 26‰) significantly higher than L meteorites (-55-13‰, median -31‰), and LL meteorites spanning the range (-58-204‰, median 16‰). Below 500°C, no significant correlations were observed.

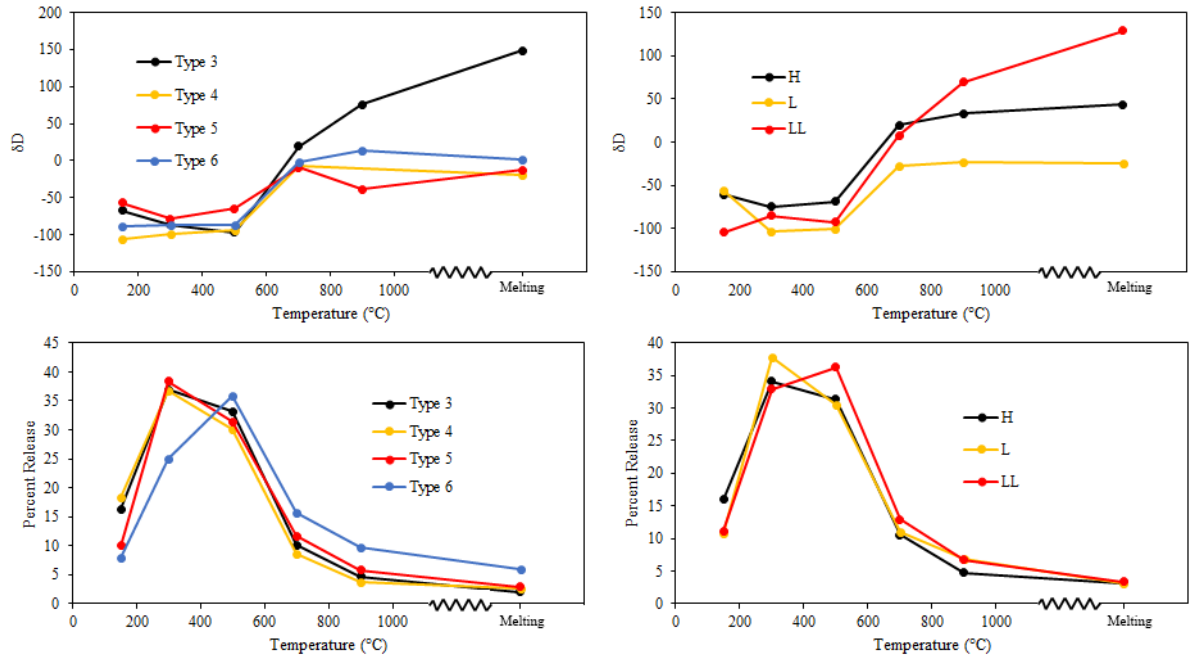


Figure 3: Average hydrogen isotope values in each step separated by (A) petrologic type and (B) meteorite group, and percent of total hydrogen release in each step by (C) petrologic type and (D) meteorite group.

Bulk δD values in this study are very consistent across the majority of meteorites measured, with the exception being Chainpur. As shown in Table 2, if all steps above 300°C are included in the bulk value, all meteorites have negative δD values, averaging -53‰ . When removing the 300-500°C step, including everything above 500°C in the bulk value, Chainpur's δD increases to $+204\text{‰}$ and the average for all samples becomes -3‰ . No significant correlation was observed between bulk δD and bulk hydrogen content in all meteorites measured.

Table 2: Bulk hydrogen measurements of all ordinary chondrites in this study.

Name	Class	H ₂ O Wt%	H ₂ O Wt% 300°C	H ₂ O Wt% 500°C	δD‰	δD‰ 300°C	δD‰ +500°C
Chainpur	LL3.4	3.00	1.54	0.43	-104	-84	196
		1.84	1.32	0.38	-35	-32	213
		2.55	1.43	0.48	-17	-7	170
Parnallee	LL3.6	0.61	0.25	0.07	-70	-43	30
		0.68	0.28	0.09	-65	-42	3
Chelyanbinsk	LL5	0.19	0.10	0.04	-64	-47	-33
		0.22	0.10	0.05	-90	-76	-83
Kheneg Ljouad	LL5/6	0.04	0.03	0.02	-39	-27	-16
		0.04	0.03	0.02	-55	-52	-48
St Severin	LL6	0.48	0.29	0.09	-81	-67	46
		0.46	0.29	0.09	-89	-77	30
Aba Panu	L3.6	0.16	0.08	0.03	-82	-62	-22
		0.13	0.06	0.02	-82	-64	-14
Bovedy	L3	0.98	0.46	0.16	-110	-106	-55
		0.94	0.40	0.11	-121	-121	-55
Daule	L5	0.34	0.17	0.07	-68	-50	-32
		0.33	0.16	0.06	-78	-78	-56
Vinales	L6	0.07	0.04	0.02	-64	-52	-13
		0.08	0.05	0.03	-42	-23	39
Dhajala	H3.8	0.25	0.15	0.05	-61	-52	23
		0.31	0.19	0.06	-38	-23	54
		0.26	0.14	0.05	-31	-14	67
Marilia	H4	0.68	0.32	0.13	-75	-60	-44
		0.59	0.27	0.08	-95	-73	2
		0.70	0.29	0.09	-82	-48	87
Nuevo Mercurio	H5	0.10	0.05	0.02	-9	20	75
		0.10	0.05	0.03	-42	-26	-3
Aiquile	H5	0.26	0.13	0.05	-68	-53	3
		0.30	0.15	0.06	-64	-49	-23

*Individual steps are combined to create bulk measurements.

*Columns for all steps, all steps above 300°C (0-150 & 150-300°C removed), and all steps above 500°C (0-150, 150-300, and 300-500°C removed) are included.

Discussion:

Terrestrial contamination:

As stated above, a ubiquitous problem with bulk element measurements in meteorites is terrestrial contamination. Contamination is a particularly significant issue with hydrogen, as it is so abundant on the Earth, readily adheres to surfaces, and is incorporated into alteration products. To minimize this effect, we chose meteorites with known fall dates and, using step-heating, removed the lower-temperature hydrogen which was likely mostly terrestrial. In Table 2, we present bulk data with all steps included, the 0-300°C steps removed, and with the 0-500°C steps removed. One of the most significant decisions to be made in the interpretation of the data in this study is to determine at what step the terrestrial contamination was removed. In the vast majority of step-heated hydrogen studies of chondrites (e.g. Robert et al. 1979, Kolodny et al. 1980, and McNaughton et al. 1982) only the hydrogen released below 200°C was removed, based on the work of Boato (1954). Boato determined, using carbonaceous chondrites, that all the hydrogen released below 180°C was terrestrial, due to the fact that the hydrogen he observed was always in the range of terrestrial variations. In steps above 180°C, he observed more variation in hydrogen, with some measurements being outside the terrestrial range. Thus, that is the step at which the majority of terrestrial contamination is removed. Using the same logic, and with a significantly expanded knowledge of terrestrial hydrogen isotope values since 1954, we do not see significant variations outside the terrestrial range in our measurements until steps above 500°C, thus the majority of terrestrial contamination in our ordinary chondrites was not removed until that point.

In their review of terrestrial weathering of chondrites, Bland et al. (2006) highlighted a range of minerals that will form as a result of a meteorite's interaction with both Earth's atmosphere and any liquid water that it comes into contact with. Many of the identified phases have been shown to dehydrate at relatively low temperatures, and a selection of some low-temperature hydrated phases which have been identified specifically in ordinary chondrites are listed in Table 3. Despite the fact all the given minerals are considered to dehydrate at low temperatures, gypsum is the only mineral identified here that does not have a dehydration temperature range going above 200°C. Thus, if any of the common terrestrial

contamination products are present, heating steps above the 180°C limit proposed by Boato (1954) and the 200°C limit commonly used by step-heating studies are likely contaminated by terrestrial hydrogen. Terrestrial contamination is exacerbated when examining nominally anhydrous meteorites, such as ordinary chondrites, as minute amounts of contamination can quickly overprint an extraterrestrial signal.

Table 3: Minerals identified as terrestrial alteration products by Gooding (1986)¹, Marvin (1980)¹, and Buchwald and Clarke (1989)², and their measured dehydration temperature ranges.

Terrestrial Contamination Mineral	Dehydration Temperature (°C)	Dehydration Study
Nesquehonite ¹	55-254	Jauffret et al. 2015
Hydromagnesite ¹	210-395	Hollingbery and Hull 2010
Starkeyite ¹	310-330*	Paulik et al. 1981
Epsomite ¹	310-330*	Paulik, J. et al., 1981
Gypsum ¹	100-140	Strydom et al. 1995
Goethite ²	226-426; 225-370	Prasad et al. 2006 Song and Boily. 2016
Akaganeite ²	176-345	Song and Boily, 2016
Lepidocrite ²	250-289	Song and Boily, 2016

*The dehydration of magnesium sulphate hydrates occurs in steps as hydrogen molecules are lost.

Included dehydration temperature range is that of MgSO₄·1H₂O.

The conventional approach to minimize the effect of terrestrial contamination, which we have used in this study, is to exclusively measure meteorite falls (those observed to fall, as opposed to “finds”, which typically have much longer terrestrial ages), so fall date can be controlled for. Hallis et al. (2012) examined a range of Martian meteorites, including the fall Nakhla, to ascertain the degree of terrestrial contamination in alteration veins. It was found that, while falls were so contaminated that the alteration phases could be shown to be definitively of terrestrial origin, the finds contained both alteration veins which were purely terrestrial and others which still contained an extraterrestrial signal. Hallis et al. (2012) note that these minerals can equilibrate with terrestrial hydrogen quickly, as a Nakhla thin section which was exposed to the atmosphere since its creation 13 years before the study contained only terrestrial hydrogen in its alteration veins. As we only see variation beyond terrestrial values in steps above 500°C, multiple common terrestrial minerals having dehydration temperatures in the 300-500°C range, and the observation of relatively significant terrestrial contamination in meteorite falls, we conclude that removing all hydrogen released below

500°C from the bulk value is necessary to obtain the most accurate composition of extraterrestrial hydrogen in the ordinary chondrite we measured.

Table 4: Bulk water abundances (weight percent) and hydrogen isotopic compositions of Chainpur (Robert, 1978).

Robert (1978) Chainpur +200°C					
Number ^a	H ₂ O Wt%	δD‰	Number	H ₂ O Wt%	δD‰
2	0.362	201	10	0.147	168
3	0.077	233	11	0.378	271
4	0.358	188	13	0.234	30
6	0.175	419	14	0.146	54
7	1.3	-133	15	1.63	-5
8	0.247	393	16	0.149	117
9	0.203	98	17	0.197	246

*The measurements were separated into hydrogen released above and below 200°C; only those measurements above 200°C are included here.

^aNumber corresponds to the analysis numbers of Robert.

Comparisons to historical measurements:

The bulk measurements of hydrogen in ordinary chondrites which have been made have a large variation, even for the same meteorite. The variation is seen both within single publications and between different labs. When examining the Chainpur meteorite alone, the average isotope value within individual publications ranges from a δD of 71‰ (Yang and Epstein 1983) to 560‰ (McNaughton et al. 1982). Within a single publication, Francois Robert presented 14 measurements of Chainpur (Table 4), with a δD range of 552‰ and an H₂O Wt% range of 1.573%. Assuming the samples with extremely high water contents are outliers, the range decreases to 389‰ in δD and 0.301% in H₂O Wt%. Our measurements follow this trend of variation larger than that of the error in the method, but the variation we see is smaller, overall. In our Chainpur measurements, we had a range in δD of 77‰ above 300°C and 43‰ above 500°C, and in H₂O Wt% of 0.22% and 0.10%, respectively. Our widest range in δD was for Marilia above 500°C at 131‰, while the greatest H₂O range was Chainpur with all steps included, at 1.16%. Our hydrogen content measurements were particularly precise, with the largest range outside of Chainpur being all the steps of Marilia

combined at 0.11 Wt% H₂O. As the majority of the ranges in hydrogen content and isotope ratios in the same meteorite are well outside analytical uncertainty and every study ultimately standardized to SMOW, the only reasonable explanation for the observed variations is heterogeneity within the meteorites themselves. Heterogeneity in the meteorites would also explain the reduced degree of variation that we observed, as the powdering step that we conducted homogenizes the samples in a way previous studies did not.

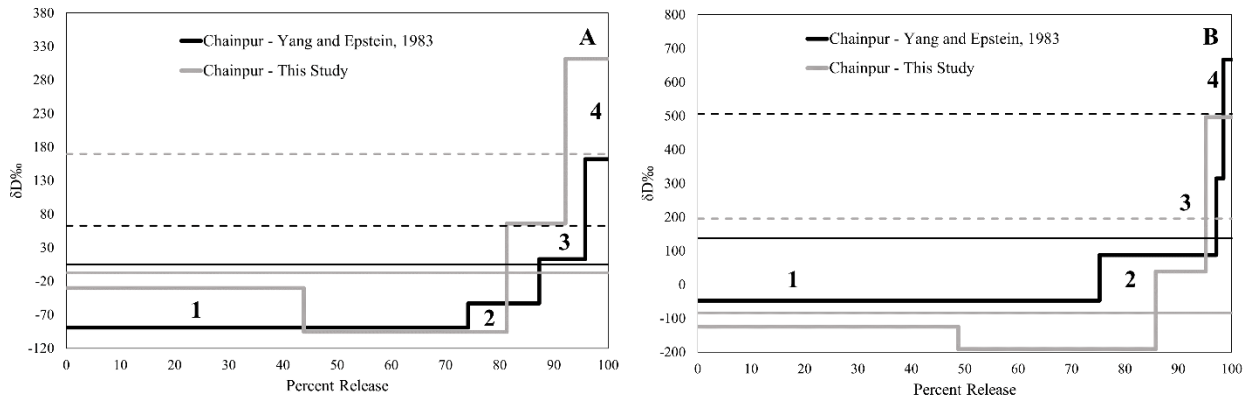


Figure 4: Release diagrams for the step-heating of ordinary chondrites. The width of each step represents the percent of total hydrogen released and the height represents the isotope value of that release. Numbers represent steps: 1; 0-300°C, 2; 300-500°C, 3; 500-700°C, 4; 700-1300°C (melting). Horizontal lines represent combined steps to create a bulk δD for the sample. Solid horizontal lines include everything above 300°C and dashed lines include everything above 500°C.

The majority of measurements of ordinary chondrites have not been step heated beyond a low-temperature degassing, and those which were step heated have not been heated to externally consistent steps. As a result, the only direct comparison that can be made to the work in our study is the step-heating of Chainpur in Yang and Epstein (1983). Figure 4 compares the two step-heated Chainpur samples reported by Yang and Epstein with two of the Chainpur samples from the present study. Overall, the steps show the same trend, with an increasing δD and decreasing volume of hydrogen released as temperatures increase, the exception being 0-300°C. In both cases, Yang and Epstein had a significantly larger release in the 0-300°C step followed by a much smaller, but heavier 300-500°C step. The explanation for this difference may be incomplete release in our first step, but McNaughton et al. (1981) shows a much more similar ratio of hydrogen release to ours in their first two steps, 0-200°C and 200-450°C, when step-heating both Chainpur matrix and chondrules.

The variation between samples both within a single study and between multiple is apparent here. With their step heating data, we are able to compare bulk measurements of Chainpur both at their published cutoff of 300°C and our preferred 500°C. With the first pair of measurements which are compared (Fig. 4A), bulk values at 300°C are very similar, but due to our heavier later steps, our bulk value is significantly higher at 500°C. This trend is the opposite when comparing our measurements with the heaviest bulk value to theirs (Fig. 4B), where their heavier later steps along with our lighter initial steps keep their bulk values higher.

The effect of the removal of the 300-500°C step compared to historical measurements justifies more discussion. Figures 5 and 6 show all the published hydrogen content data for ordinary chondrites along with our bulk measurements both above 300 and 500°C. Only two of the meteorites we measured, Chainpur (LL3.4) and Saint-Severin (LL6) have bulk hydrogen contents above 300°C significantly higher than the rest of their petrologic type. Luckily, both meteorites have published hydrogen contents in the studies we have discussed *ad nauseam*. In both cases, removal of the 300-500°C decreased the total water content of the sample to the level seen in previous studies and other meteorite of the same type measured here. In the case of Chainpur, the δD also increased to be in line with previous measurements, as we believe the hydrogen driven off was terrestrial.

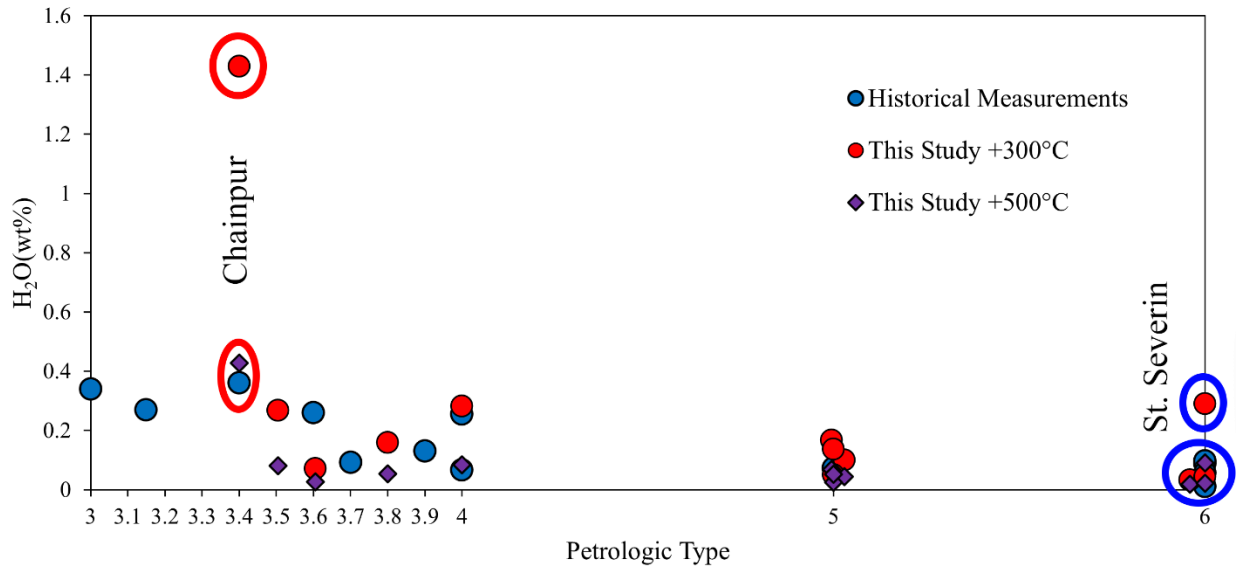


Figure 5: All published hydrogen contents of ordinary chondrites (Robert, 1978; McNaughton et al., 1981; McNaughton et al., 1982; and Yang and Epstein, 1983) with the hydrogen contents measured in this study above 300 and 500°C. Each point represents an average of all measurements of a single meteorite in a given category. Red ellipses indicate Chainpur measurements and blue ellipses indicate Saint-Severin.

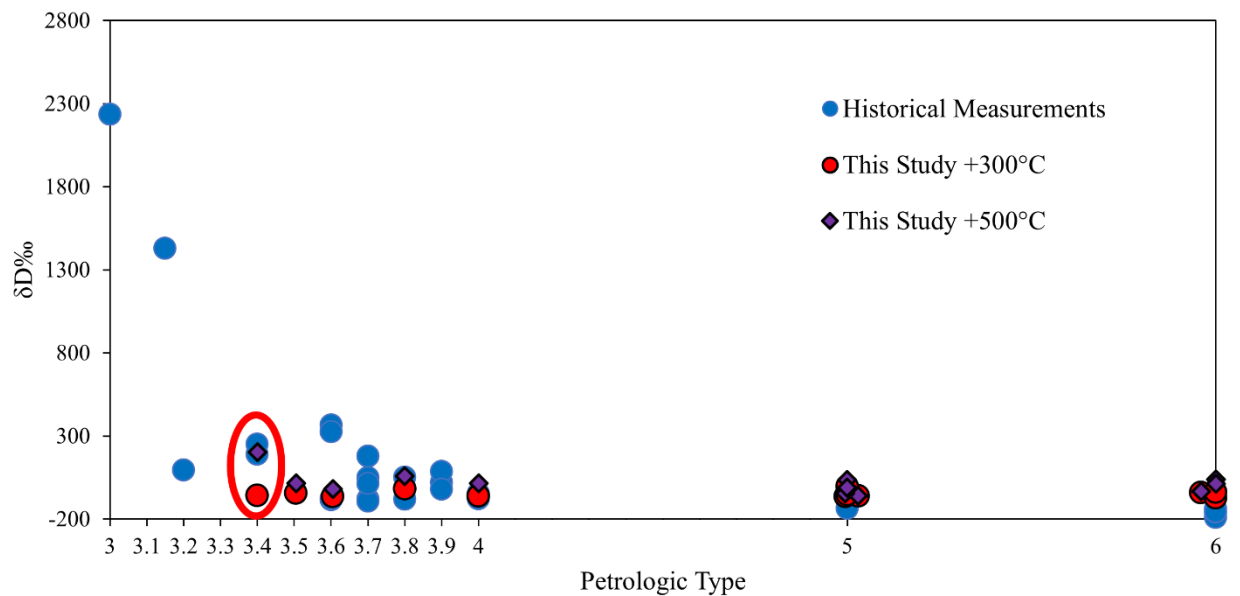


Figure 6: Bulk δD of all published ordinary chondrites as shown in Tables 1 and 2. Each point represents an average of all measurements of a single meteorite in a given category. Red ellipse indicates Chainpur measurements.

What it all means for ordinary chondrites:

Now that our measurements are in the context of previous studies, we can use all bulk measurements to better understand the broad evolution of hydrogen in ordinary chondrites. As shown in Figure 6, a broad trend of decreasing bulk hydrogen content and δD exists as petrologic type increases from 3.0 to 4 followed by no significant change between petrologic types 4 and 6. The trend we observe shows that, in the process of thermal metamorphism between petrologic type 3.0 and type 4 ordinary chondrites, a heavy hydrogen reservoir is being lost. As discussed previously, the primary heavy reservoir in ordinary chondrites is their heavy organics. The near complete disappearance of insoluble organic matter above petrologic type 3.7 due primarily to oxidation during thermal metamorphism has been characterized (Alexander et al., 1989; Grady et al., 1989; Yang and Epstein, 1983) and is comprehensive to the point that meteorite with petrologic types above 3.7 are excluded from studies examining organic matter in meteorites (i.e. Alexander et al. 2007). With the conclusion that the decrease in δD within ordinary chondrites is primarily a result of the processing of organic matter, it is important to note that intra-type variations do exist in both the organic matter and δD , which have been attributed to the dramatic effects of parent body processes (Alexander et al. 2007).

The area where a strong understanding of the hydrogen isotope ratios in ordinary chondrites is the most consequential is examinations into the volatile sources of different bodies. While some recent mixing models acknowledge the relatively light δD of the majority of ordinary chondrites (e.g. Barnes et al. 2016; Sharp 2017) many others use the very heavy values of Semarkona and Bishunpur to represent the ordinary chondrite contribution as a whole (e.g. Desch and Robinson 2019; Lin and Van Westrenen 2019; Wu et al. 2018). We have shown, with modern methods, that the hydrogen isotope ratios of the most primitive ordinary chondrites are not representative of the class as a whole and should not be used as such. The time in which accretion should be considered, however, and can be used to justify the use of only primitive hydrogen if the mixing being examined is likely to have occurred prior to the alteration on the ordinary chondrite parent body which destroyed the heavy reservoir. Thus, due to the fact that the most primitive ordinary chondrites are so incredibly rare in the sample collection, we consider Semarkona and Bishunpur to be outliers

and that a δD of 12‰, the result of averaging all other bulk ordinary chondrites, to be the most accurate composition of extraterrestrial H for the group.

Conclusions:

Here, we developed a new method to measure the bulk isotopes of nominally anhydrous minerals and use it to significantly increase the dataset of bulk hydrogen isotopes in ordinary chondrites, nearly doubling the number of equilibrated ordinary chondrites measured.

1. Step-heated continuous-flow mass spectrometry is a viable method for measuring the bulk hydrogen isotopes in nominally anhydrous meteorites and other extraterrestrial samples. For this study, where most measurements were conducted in 2019, a minimum of 0.126 μmol of H_2 was required for a measurement, and further refinement since has decreased that number.
2. Terrestrial contamination is a significant factor when measuring the bulk hydrogen isotopes in any meteorite, especially nominally anhydrous ones. In our measurements, terrestrial hydrogen was seen all the way up to 500°C, accounting for up to 88% (57-88%, median 81%) of all hydrogen released. This can be problematic, as the decision of where to put the low-temperature cutoff for bulk measurements can significantly change the resulting bulk value. Our bulk hydrogen contents and sample δD s best matched with correlated meteorites from previous studies with a higher temperature cutoff than was used historically, so the correct temperature range to remove may be method dependent.
3. When all bulk hydrogen measurements in ordinary chondrites are combined, a trend of decreasing δD between petrologic types 3 and 4 followed by uniform values from 4 to 6 is observed. We believe this is a result of the destruction of the heavy hydrogen reservoir, the organic matter, during thermal metamorphism.
4. As a result of their anomalously high concentrations of heavy hydrogen, we believe that the most primitive ordinary chondrites which have been measured, Semarkona and Bishunpur should be excluded from any mixing models using ordinary chondrites as whole. Thus, a δD of 12‰ should be used as a representative value for the class. The only exception to this rule being mixing which likely occurred before thermal metamorphism on the ordinary chondrite parent body.

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