



# Hydrogen in acapulcoites and lodranites: A unique source of water for planetesimals in the inner Solar System

A. Stephant<sup>a,b,\*</sup>, X. Zhao<sup>b</sup>, M. Anand<sup>b</sup>, J. Davidson<sup>c</sup>, C. Carli<sup>a</sup>, T. Cuppone<sup>d</sup>, G. Pratesi<sup>d,a</sup>, I.A. Franchi<sup>b</sup>

<sup>a</sup> Istituto di Astrofisica e Planetologia Spaziali - INAF, Roma, Italy

<sup>b</sup> School of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK

<sup>c</sup> Buseck Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA

<sup>d</sup> Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Firenze, Italy

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## ABSTRACT

Acapulcoites and lodranites are primitive achondrites, sampling a common planetesimal formed a few million years after calcium-aluminium rich inclusions in the inner Solar System, that provides information into melting and differentiation processes in the early inner Solar System. The chemistry and mineralogy of their chondritic parent body lies in between enstatite and ordinary chondrites. As they record a range in planetary differentiation degree, from 1% up to 20% partial melting, with lodranites experiencing the most melt extraction, we investigate (i) the behaviour of hydrogen in terms of abundance and isotopic composition during the early stages of planetary differentiation and (ii) the source(s) of hydrogen for the acapulcoite-lodranite parent body in order to place it in our current understanding of the source(s) of water in the inner Solar System. In this study, we analysed water content and hydrogen isotopic composition of phosphates and nominally anhydrous minerals in a range of acapulcoite and lodranite meteorite samples. While apatites seemed to have recorded a degassing signature, no such variations were observed in the H<sub>2</sub>O- $\delta$ D systematics of the nominally anhydrous minerals suggesting that subsequent to their crystallisation, acapulcoites and lodranites experienced minimal modifications to their volatile composition during thermal metamorphism and partial melting. The low abundance of water in acapulcoite and lodranite nominally anhydrous minerals (i.e., average  $5.2 \pm 1.6$   $\mu\text{g/g}$  H<sub>2</sub>O) suggests that their parent body was much drier than what has been estimated for enstatite and ordinary chondrite parent bodies. We estimated a bulk water content for the acapulcoite-lodranite parent body of 3 to 19  $\mu\text{g/g}$  H<sub>2</sub>O, similar to the ureilite parent body. The hydrogen isotopic composition of nominally anhydrous minerals in acapulcoites and lodranites ( $-211 \pm 145\text{‰}$ ), and in particular for the two falls Acapulco and Lodran ( $-239 \pm 149\text{‰}$ ), matches with the hydrogen isotopic composition recorded by nominally anhydrous minerals in ordinary chondrite falls, eucrites, S-type asteroid Itokawa, consistent with a common source of water for the inner Solar System planetesimals, isotopically distinctive to bulk carbonaceous chondrites.

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## 1. Introduction

Understanding the source of water (a term referring to H/OH/H<sub>2</sub>O) in the inner part of the Solar System, and in particular on Earth, is one of the important scientific questions that motivates cosmochemistry research (e.g., Broadley et al., 2022; Hallis, 2017; McCubbin and Barnes, 2019). In this regard, a plethora of recent

studies have investigated the water content and hydrogen isotopic ratio of meteorites deriving from inner Solar System planetesimals, previously thought to be dry, in order to gain information on the water source(s) in the early Solar System. Achondrites derived from the earliest generation of planetesimals, formed  $\sim 4.56$  Ga ago (e.g., Kleine and Wadhwa, 2017), are key targets to constrain the timing and the source of volatiles in the inner Solar System. In that context, angrites (Deligny et al., 2021; Sarafian et al., 2017), eucrites sampling the asteroid 4-Vesta (Barrett et al., 2019; Sarafian et al., 2019; Stephant et al., 2021) and ungrouped achondrites (Tartèse et al., 2019), have recently been investigated. Additionally, chondritic materials deriving from the inner part of the main asteroid belt,

\* Corresponding author at: Istituto di Astrofisica e Planetologia Spaziali - INAF, Roma, Italy.

E-mail address: [alice.stephant@inaf.it](mailto:alice.stephant@inaf.it) (A. Stephant).

i.e., originating from E- and S-type asteroids, are also strategic targets. Enstatite chondrites (Piani et al., 2020), ordinary chondrites (Alexander, 2019; Jin et al., 2021) and the near-Earth S-type asteroid Itokawa (Chan et al., 2021; Jin and Bose, 2019) seem to have retained a substantial amount of hydrogen. Moreover, some of these recent studies measured isotopically lighter  $\delta D$  values in *in-situ* phase analyses of these inner Solar System materials compared to that of the Earth and average bulk carbonaceous chondrite (Lécuyer et al., 1998; Piani et al., 2021). Indeed, nominally anhydrous minerals of eucrites, ordinary chondrites, and grains collected from the asteroid Itokawa record  $\delta D$  values lower than  $-300\%$  (Chan et al., 2021; Jin et al., 2021; Stephant et al., 2021). Additionally, low  $\delta D$  values were also measured in angrite melt inclusions (i.e.,  $-348 \pm 53\%$  Deligny et al., 2021). These results have led to the reconsideration of the potentiality of nebular H contribution as one of the sources of water in inner Solar System bodies, that could have occurred through various mechanisms such as nebular ingassing (Sharp, 2017; Wu et al., 2018) or H chemisorption on forsterite grains (e.g., Asaduzzaman et al., 2015).

In order to resolve the timing and source(s) of water in the inner Solar System, it is imperative to examine samples from other planetesimals from which we already have meteorites in our sample collections but have not yet fully explored their inventory of volatiles. Moreover, an important but scarcely studied parameter is the effect of melting and differentiation processes on hydrogen concentration and isotopic composition of a planetesimal. These processes have been mostly investigated in terrestrial samples where redox state and volatile composition are distinct from most early-formed planetesimals (e.g., Richter et al., 2016). For instance, Bindeman et al. (2012) demonstrated through the modelling of melting processes on terrestrial basalts that no significant hydrogen isotopic fractionation is expected during mantle partial melting. Thermal metamorphism on eucrites and enstatite chondrites appears to induce opposite effects (Piani et al., 2020; Stephant et al., 2021), potentially linked to the presence of insoluble organic material in the latter, while it did not affect the  $\delta D$  values of OCs and CKs (Vacher et al., 2020). Moreover, two recent angrite hydrogen studies are contradicting each other regarding the potentiality of angrite parent body degassing (Deligny et al., 2021; Sarafian et al., 2017). Primitive achondrites are suitable samples for addressing this issue, being among the oldest achondrites formed only a few Ma after calcium-aluminium rich inclusions (CAIs) (Schulz et al., 2010), and remnants of the precursors of the planets recording some of the earliest stage of planetary differentiation (Keil and McCoy, 2018 and references therein). To that extent, Peterson et al. (2023) analysed water content in nominally anhydrous minerals (NAMs) of the ureilites, a group of primitive achondrites, and interpreted their relatively low water content as a result of secondary and magmatic processes inducing degassing, such as impact or partial melting on the parent body.

The primitive achondrite groups, acapulcoites and lodranites, defined by the fall of Acapulco and Lodran, are the best-studied examples of a partially melted parent body. We refer the reader to the comprehensive review of Keil and McCoy (2018) on acapulcoites and lodranites. They are defined by a crystalline igneous, hence achondritic, texture, but with near-chondritic bulk compositions (e.g., Floss, 2000; McCoy et al., 1997a, 1997b, 1996; Mittlefehldt et al., 1996; Palme et al., 1981; Patzer et al., 2004). Acapulcoites and lodranites represent residues of different degrees of partial melting (from  $<1$  up to 20 vol. %) of a single chondritic precursor (Clayton and Mayeda, 1996; Floss, 2000; Greenwood et al., 2012; McCoy et al., 1997b, 1996; Mittlefehldt et al., 1996), that occurred in a moderately reducing environment  $\sim 4.557$  Ga ago (McCoy et al., 1996; Neumann et al., 2018; Palme et al., 1981). Acapulcoites are highly metamorphosed nebular materials (Palme et al., 1981). As such, these fine-grained achondrites (i.e., average

grain size of 150–230  $\mu\text{m}$ ) were heated to relatively low temperatures (i.e., 980–1170  $^{\circ}\text{C}$ ), producing up to 4% of Fe,Ni-FeS cotectic partial melting, with melt migration forming  $\mu\text{m}$  to cm scale Fe,Ni-FeS and phosphate veins (McCoy et al., 1996). Silicates in acapulcoites experienced recrystallisation but no melting. In contrast, lodranites are residues of igneous processes occurring on their parent body (Mittlefehldt et al., 1996). These primitive achondrites were heated to higher temperatures than acapulcoites (i.e., 1150–1250  $^{\circ}\text{C}$ ), resulting in a coarse-grained texture (i.e., average grain size 540–700  $\mu\text{m}$ ) and in 5 to 20% of Fe,Ni-FeS cotectic and basaltic partial melting (McCoy et al., 1997a). Removal of low temperature silicate melts has been observed through the depletion of troilite and plagioclase in some lodranites relative to acapulcoites (McCoy et al., 1997b). As such, acapulcoites and lodranites represent different layers of their partial melted parent body (Li et al., 2018), with burial depths estimated to have been from 7 to 13 km on a  $\sim 260$  km radius body (Neumann et al., 2018). From mineralogy, geochemistry and isotopy of acapulcoites and lodranites, it has been inferred that their chondritic precursor had an intermediate composition between enstatite and H ordinary chondrites (e.g., Floss, 2000; McCoy et al., 1996).

Hydrogen (H) abundance and isotopic composition have not been previously reported in acapulcoites and lodranites. However, Palme et al. (1981) demonstrated that moderately volatile and volatile elements (e.g., Mn, Ga, Ge, Zn) were preserved in Acapulco in spite of high temperature recrystallisation (i.e., 1170  $^{\circ}\text{C}$ ). Abundant concentrations of other volatiles (i.e., CO, CO<sub>2</sub>, S, Cl, Na) were also measured in Acapulco and Lodran (McCoy et al., 1997b). Utilising recent advancements in *in situ* secondary ion mass spectrometry (SIMS) analyses of H, we have investigated the water content and isotopic composition of NAMs and apatites in a suite of acapulcoite and lodranite samples. The main objectives are (i) to investigate the variations of H<sub>2</sub>O and  $\delta D$  in samples that experienced various degrees of partial melting, (ii) to estimate the amount of hydrogen in the acapulcoite-lodranite parent body (ALPB) and (iii) to determine the potential water source of this ALPB and other planetesimals in the inner Solar System.

## 2. Samples and Methodology

### 2.1. Samples and preparation for H analyses in nominally anhydrous minerals

Thin sections and chips of acapulcoites Acapulco, NWA 10074 and Dhofar 125, as well as lodranites Lodran, NWA 11970 and Gibson were provided by the Buseck Center for Meteorite Studies (BCMS). A description of each sample is available in supplementary information, together with a summary of these meteorite characteristics in Table 1. Because low H abundance was anticipated from the samples, they were mounted in indium to minimise background signal during NanoSIMS measurements (cf. Fig. S1), following well established SIMS protocols (e.g., Aubaud et al., 2007; Mane et al., 2016). Since Acapulco was available as two chips and large enough that they were not embedded in acrylic for polishing, we decided to test on the effect of isopropanol for polishing. Hence Acapulco #1 was polished with isopropanol while Acapulco #2 was dry polished. Nominally anhydrous minerals (NAMs) were analysed in the indium mount while apatites were analysed in thin sections. An exception was made for Lodran, which has been only studied in thin section as a chip was not available for preparing an indium mount. This methodology allows us to ensure that the H isotopic composition and water content of NAMs experience negligible to minimum terrestrial contamination during sample preparation.

**Table 1**

Main characteristics of acapulcoites and lodranites studied here. Cosmic ray exposure (CRE) ages are the average of values retrieved from Keil and McCoy (2018). \*For NWA 10074 and NWA 11970 which do not have any measured CRE age, we took the average of all acapulcoite-lodranite, since the range is restricted between 4 to 7 Ma.

Sample	Group	Find/Fall	Shock	Weathering	Type	CRE age (Ma)
Acapulco	Acapulcoite	Fall	S1	W0	Monomict	6.5±1.1
NWA 10074	Acapulcoite	Find	S1	W1	Monomict	5.8±1.8*
Dhofar 125	Acapulcoite	Find	S1	W1/W2	Monomict	5.2±1.1
Lodran	Lodranite	Fall	S1	W0	Monomict	6.9±1.6
NWA 11970	Lodranite	Find	S1	W1	Breccia	5.8±1.8*
Gibson	Lodranite	Find	S1	W4 (19.4%)	Monomict	5.6±0.5

## 2.2. Methodology

### 2.2.1. Mineralogical and petrological analyses

Elemental X-ray maps of Ca, Fe, Mg, P and Si were collected on the Cameca SX-100 electron probe microanalyser (EPMA) at University of Arizona to identify phosphates in thin sections of Acapulco, NWA 10074, Dhofar 125 (supplementary Fig. S2). Chemical characterization of olivine and pyroxene in the Lodran thin section was also performed. Chemical characterization of pyroxenes in the indium mount and phosphates in thin sections was carried out with a JEOL Superprobe JXA-8230 EPMA (Department of Earth Sciences, University of Firenze). Quantitative analyses were performed in wavelength dispersive mode, with an accelerating potential of 15 kV. A focused beam of 20 nA with a 1 µm and 3 µm spot size were used to analyse Lodran silicates and indium pyroxenes and phosphates, respectively. ZAF correction was applied to all measurements. Typical detection limits were 0.02–0.05% for major element oxide abundances. Cl and F concentrations were corrected and the OH component was estimated using the method of Ketcham (2015). The chemical composition of phosphates, pyroxenes and olivines are presented in supplementary Table S1, S2 and S3, respectively.

### 2.2.2. Hydrogen abundances and isotopic compositions

Secondary ion mass spectrometry (SIMS) measurements of D/H ratios and H<sub>2</sub>O concentrations in 58 ortho- and clino-pyroxene grains, 16 olivines, as well as 10 phosphates from acapulcoites and lodranites were performed with the Cameca NanoSIMS 50 L at The Open University. For nominally anhydrous minerals, H<sup>-</sup>, D<sup>-</sup>, <sup>13</sup>C<sup>-</sup> and <sup>16</sup>O<sup>-</sup> secondary ions were measured using electron multipliers (<sup>16</sup>O<sup>-</sup> on Faraday) using a Cs<sup>+</sup> primary beam of ~2 nA rastered over a 10 µm × 10 µm surface area (supplementary Fig. S3). For apatites, H<sup>-</sup>, D<sup>-</sup>, <sup>13</sup>C<sup>-</sup> and <sup>18</sup>O<sup>-</sup> secondary ions were measured using a Cs<sup>+</sup> primary beam of ~1.4 nA rastered over a 8 µm × 8 µm surface area (supplementary Fig. S2). The electron gun was tuned to an electron current of approximately 5000 nA. <sup>13</sup>C<sup>-</sup> was used to monitor any potential terrestrial contamination. Blanking was performed, and only the 4 µm × 4 µm (25%) interior of the surface area was analysed, with each measurement consisting of 2000 cycles of ~0.54 seconds each, providing a total analysis time of ~20 minutes. Prior to the analysis, an area of 12 µm × 12 µm was pre-sputtered for ~10 minutes using the same primary beam current. The vacuum in the analytical chamber was around 2.0 to 2.2 × 10<sup>-10</sup> Torr. The H<sub>2</sub>O contents in nominally anhydrous minerals and apatites were determined using a H<sup>-</sup>/<sup>16</sup>O<sup>-</sup> and H<sup>-</sup>/<sup>18</sup>O<sup>-</sup>, respectively, vs. H<sub>2</sub>O calibration (supplementary Fig. S4) based on terrestrial standards (supplementary Table S4) and the nominally anhydrous San Carlos olivine, all mounted in indium. Analyses on San Carlos olivine were performed before and after sample analyses to monitor the instrumental background for both H<sub>2</sub>O (Fig. S5) and D/H ratio (Fig. S6). The H<sub>2</sub>O background during NAMs session corresponds to a

water content ranging from 1.3±0.1 to 1.8±0.3 µg/g (2SD) (Table S5). The background for H<sub>2</sub>O concentrations in apatites corresponds to a water content of 5.5 ± 1.4 µg/g (2SD). The measured D/H ratios are expressed in terms of δD values, defined as follows:  $\delta D = [(D/H_{\text{sample}})/(D/H_{\text{VSMOW}}) - 1] \times 1000$ , where  $D/H_{\text{VSMOW}} = 155.76 \times 10^{-6}$ , corrected from instrumental mass fractionation (IMF – Fig. S7), background contamination (Fig. S6) and spallation production using cosmic exposure age of samples. Reproducibility of blank D/H monitoring on San Carlos is <13% for NAMs (Fig. S6) and 30% for apatites. Blank H<sub>2</sub>O and D/H values and associated errors, as well as IMF values, used for correction of both H<sub>2</sub>O and D/H ratio of acapulcoite-lodranite NAMs and apatites can be found in supplementary Table S5. Details on the analyses protocol can be found in supplementary information (cf., Stephant et al., 2021).

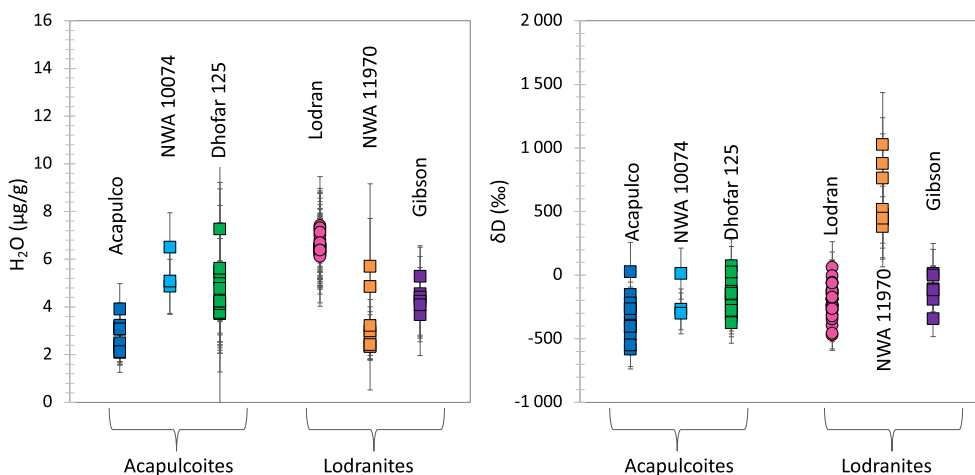
## 3. Results

### 3.1. Chemistry

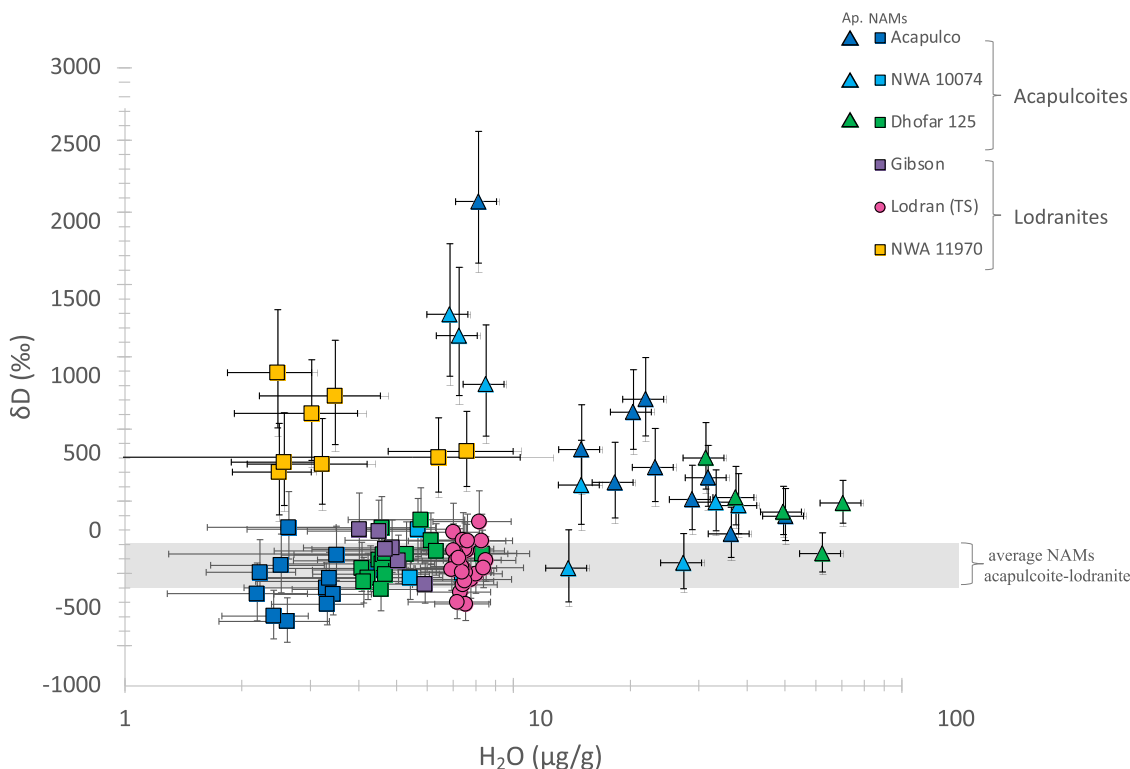
We report the modal abundances for NWA 10074 and NWA 11970 using XMapTools (Lanari et al., 2014). Acapulcoite NWA 10074 is composed of: 28.4 vol.% olivine, 40.5 vol.% orthopyroxene, 4.5 vol.% clinopyroxene, 14 vol.% feldspar, 0.5 vol.% phosphate and 12 vol.% opaque phases. These abundances are very similar to Dhofar 125, which is consistent with that of most other acapulcoites. Dhofar 125 and NWA 10074 also show similar textures (see supplementary Fig. S2). The brecciated lodranite NWA 11970 is composed of: 48.7 vol.% olivine, 26.1 vol.% orthopyroxene, 18.3 vol.% clinopyroxene, 0.1 vol.% phosphate and 6.9 vol.% opaque phases. Phosphates are principally ranging from fluorapatites to chlorapatites, with F content ranging from 2.5 to 4.3 wt.% and Cl content ranging from 0.5 to 2.9 wt.%. Chemical compositions of phosphates are available in supplementary Table S1. These Ca-rich apatites are either found as interstitial grains or associated with FeNi metal grains (cf. supplementary Fig. S2). With few exceptions pyroxenes are all orthopyroxenes with chemical composition consistent with acapulcoites-lodranites (Keil and McCoy, 2018 and ref. therein). Chemical compositions of pyroxenes and olivines are available in Tables S2 and S3, respectively.

### 3.2. Hydrogen content and isotopic composition in NAMs

The range of water contents and hydrogen isotopic composition in NAMs are presented in Fig. 1 and Fig. 2 (data are available in Supplementary Table S5). Pyroxene water contents in acapulcoites and lodranites vary from 2.1±0.5 to 7.3±2.6 µg/g H<sub>2</sub>O and from 2.3±0.6 to 7.8±1.3 µg/g H<sub>2</sub>O, respectively. Olivine water contents in Lodran range from 6.1±1.6 to 7.3±2.2 µg/g H<sub>2</sub>O. Overall, all acapulcoites and lodranites retain a similar and restricted range of water content in their olivines and pyroxenes (Fig. 1A). Consequently, the average of H<sub>2</sub>O content in NAMs is considered as representative of each sample (Fig. 3). The H<sub>2</sub>O content average and 1SD are: 2.8±0.6 µg/g H<sub>2</sub>O for Acapulco, 5.5±0.9 µg/g H<sub>2</sub>O for



**Fig. 1.** (A) Nominally anhydrous mineral hydrogen content in acapulcoites and lodranites, reported in µg/g H<sub>2</sub>O. (B) Nominally anhydrous mineral hydrogen isotopic ratio in acapulcoites and lodranites, expressed as an offset from standard mean ocean water (δD value in permil).



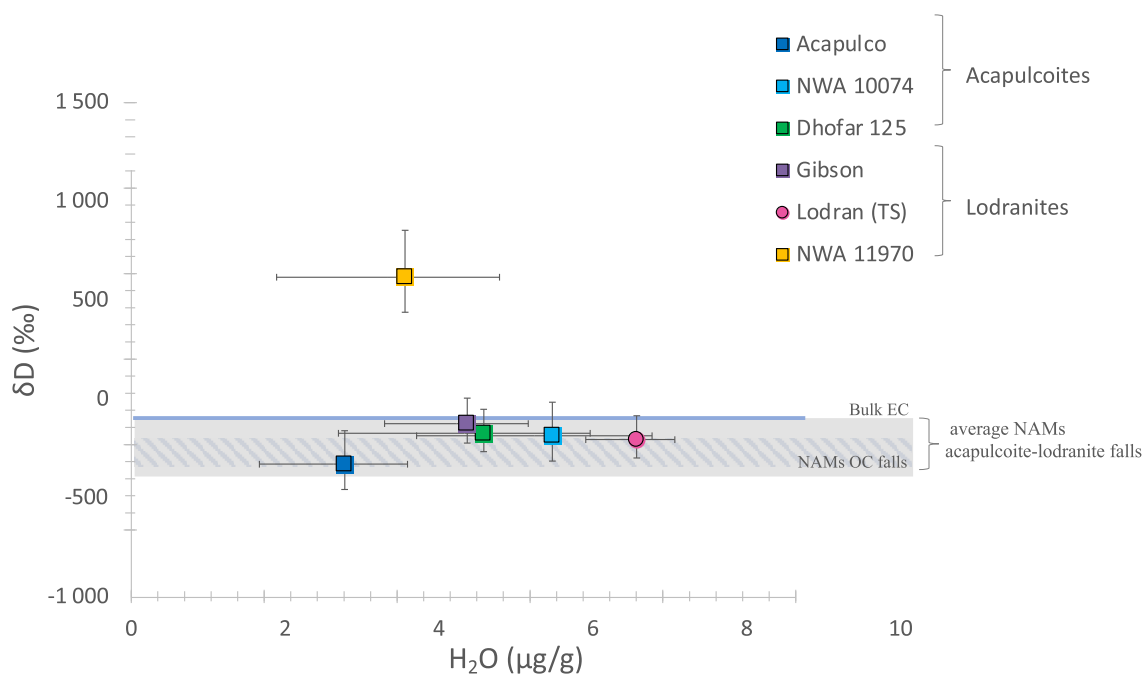
**Fig. 2.** Water contents (µg/g H<sub>2</sub>O) and δD values of nominally anhydrous minerals (square and circle symbols) and apatites (triangle symbols) in acapulcoites and lodranites. Apatites with the lowest δD in the three acapulcoites fall within the range defined by NAMs (−211±145‰, 1SD). The rest of the apatites follow a hydrogen degassing trend. The lodranite breccia NWA 11970 presents significantly higher δD than the rest of the acapulcoite-lodranite samples.

NWA 10074; 4.6±0.9 µg/g H<sub>2</sub>O for Dhofar 125; 6.6±0.7 µg/g H<sub>2</sub>O for Lodran, 3.3±1.3 µg/g H<sub>2</sub>O for NWA 11970 and 4.4±0.5 µg/g H<sub>2</sub>O for Gibson (cf. Table 2). As such no systematic variations are observed between acapulcoites and lodranites.

In terms of δD values in NAMs, no systematic intra-sample variations are observed (Fig. 1B; Supplementary Table S5), including H<sub>2</sub>O–δD trends (Fig. 2), removing the potentiality for acapulcoite and lodranite δD values in NAMs to have recorded magmatic or secondary processes. As such, we consider the average of δD values (spallation corrected; ±1SD) as representative of the samples (Fig. 3). The two falls exhibit the lowest δD values with −329±172‰ for Acapulco and −203±124‰ for Lodran (Table 2). Northwest Africa 10074, Dhofar 125 and Gibson ex-

**Table 2**  
Average H<sub>2</sub>O (µg/g H<sub>2</sub>O) and δD (‰) values measured in acapulcoite and lodranite nominally anhydrous minerals. TS stands for thin section, as the other samples have been analysed in an indium mount.

All NAMs	H <sub>2</sub> O (µg/g)	1SD	δD (‰)	1SD
Acapulco	2.8	0.6	−329	172
NWA 10074	5.5	0.9	−186	172
Dhofar 125	4.6	0.9	−173	124
NWA 11970	3.3	1.3	615	240
Gibson	4.4	0.5	−124	131
Lodran (TS)	6.6	0.7	−203	124



**Fig. 3.** Average water contents ( $\mu\text{g/g H}_2\text{O}$ ) and  $\delta\text{D}$  values (‰) recorded by NAMs for each acapulcoite and lodranite. The grey line defined the average of Acapulco and Lodran, the two clan falls (average =  $-239 \pm 149\text{‰}$ , 1SD). Interestingly, NWA 11970 does not fit within the range defined by the others. Either this sample has suffered significant isotopic fractionation due to some H degassing, or the CRE age is significantly older than 7 Ma, questioning the affiliation of this sample to the lodranite group.

hibit extremely similar  $\delta\text{D}$  values, respectively at  $-186 \pm 172\text{‰}$ ,  $-173 \pm 124\text{‰}$  and  $-124 \pm 131\text{‰}$ , within errors of what has been observed for Acapulco and Lodran (Table 2). The lodranite NWA 11970 exhibits a substantial difference in terms of  $\delta\text{D}$ , with an average of  $+615 \pm 240\text{‰}$ . This lodranite being a breccia, several explanations could be advanced to explain this discrepancy: degassing induced by impact, distinct exposure age, or diverse material present in the sample. As such, this sample is not representative of the acapulcoite-lodranite parent body. Consequently, it will not be discussed further.

### 3.3. Hydrogen content and isotopic composition in phosphates

The range of water contents and hydrogen isotopic composition in phosphates are presented in Fig. 2 (Supplementary Table S5). Interestingly, phosphates from Acapulco, NWA 10074 and Dhofar 125 are H-poor, i.e., from  $6.1 \pm 0.7$  to  $53.5 \pm 6.5 \mu\text{g/g H}_2\text{O}$ , and display negative trends in their  $\text{H}_2\text{O}-\delta\text{D}$  systematics, with  $\delta\text{D}$  values ranging from  $-239 \pm 249\text{‰}$  to  $+2133 \pm 456\text{‰}$  (Fig. 2). These negative  $\text{H}_2\text{O}-\delta\text{D}$  trends can be ascribed to H degassing. Moreover, the lowest  $\delta\text{D}$  value recorded by phosphates of NWA 10074 and Dhofar 125 fit in the average  $\delta\text{D}$  value of NAMs (Fig. 2). As a result, we consider the average  $\delta\text{D}$  of NAMs for all acapulcoites-lodranites as representative of their parental body, i.e.  $-211 \pm 145\text{‰}$ ; which is in fact similar within errors to the average estimated based on the two falls Acapulco and Lodran, i.e.  $-239 \pm 149\text{‰}$ .

## 4. Discussion

### 4.1. Water contents in acapulcoites-lodranites

#### 4.1.1. Reliability of analyses – Potential terrestrial contamination

The biggest challenge of measuring such low water contents and their associated  $\delta\text{D}$  values is to make sure that the terrestrial contamination is negligible. Terrestrial contamination can be acquired during sample preparation and/or terrestrial residence (Davidson et al., 2020; Mane et al., 2016; Stephant et al., 2018; Vacher et al., 2020). The indium mount was carefully prepared

following well established protocols, and discussion on sample preparation contamination is available in supplementary information. Lodran exhibits a slightly higher water content ( $6.6 \pm 0.7 \mu\text{g/g H}_2\text{O}$ ) that could be assigned to Lodran being prepared as a thin section. However, Lodran  $\delta\text{D}$  average (i.e.,  $-203 \pm 124\text{‰}$ ) is lower than the acapulcoite and lodranite finds, which suggests the epoxy contamination to have negligible impact on the  $\delta\text{D}$ , hence on the  $\text{H}_2\text{O}$  contents. Moreover, the  $3 \mu\text{g/g H}_2\text{O}$  variation between Lodran and Acapulco argues against significant terrestrial contamination of Lodran. As such, we consider here that although Lodran was mounted in a thin section it does not preclude having good quality, contamination-free analyses.

Terrestrial contamination is also related to the period of terrestrial residence of the sample, as well as the location of the find. Jin et al. (2021) have shown that Antarctic thin sections of ordinary chondrite (OC) finds have water content on average 300 ppm higher compared to OC falls, together with terrestrial-like D/H ratios, suggesting that water ice has likely altered the original hydrogen signatures of these OC finds. The three acapulcoite-lodranite finds of our study are from the hot deserts of Northwest Africa (NWA 10074, Dhofar 125 and Gibson). They exhibit similar  $\delta\text{D}$  and  $\text{H}_2\text{O}$  values. Interestingly, Gibson has been highly terrestrially altered (19.4 wt.% of alteration products), likely corresponding to a W4 weathering grade on the Wlotzka's scale (Wlotzka, 1993). Unexpectedly, the water content of Gibson is within the range of the other acapulcoites-lodranites, whose weathering grade are from W0 to W1 (cf., Table 1). Similarly, ureilites ranging from weathering grade W1 to W4 do not show a correlation between their water contents in their NAMs and their degree of weathering (Peterson et al., 2023). This is in contradiction to the study on the terrestrial alteration of a Martian meteorite, Tissint, in the desert of Arizona (Stephant et al., 2018), which showed that the alteration reaches up to 2 mm in olivine grains after 3 years of terrestrial residence. Tissint is severely shocked (Mane et al., 2016), resulting in highly fractured phases, that could be easily infiltrated and contaminated by terrestrial water. As such, the lack of fractured NAMs and the possibility that the chip sampled the interior of the meteorite stone could explain the lack of terrestrial contamination.

**Table 3**

Estimated bulk water content ( $\mu\text{g/g H}_2\text{O}$ ) for the acapulcoite-lodranite parent body (ALPB) using a single-step batch melting and various pyroxene-melt  $\text{H}_2\text{O}$  partition coefficient.

	Acapulco	NWA 10074	Dhofar 125	Gibson	Lodran
$\text{H}_2\text{O}$ average NAMs	$2.8\pm 0.6$	$5.5\pm 0.9$	$4.6\pm 0.9$	$4.4\pm 0.5$	$6.6\pm 0.7$
% PM	1%	1%	1%	5%	20%
<i>Using <math>D=0.1</math> at 0.1 Mpa (Sarafian et al., 2019)</i>					
$\text{H}_2\text{O}$ bulk ALPB	<b>3</b>	6	5	6	<b>19</b>
<i>Using <math>D=0.1</math> at 0.1 Mpa for acapulcoites and <math>D=0.0085</math> for lodranites (Sarafian et al., 2019)</i>					
$\text{H}_2\text{O}$ bulk ALPB	<b>3</b>	6	5	30	<b>161</b>
<i>Estimation from O'Leary et al. (2010)</i>					
D cpx-melt	0.02		0.02		
$\text{H}_2\text{O}$ bulk ALPB	<b>4</b>		<b>7</b>		
<i>Estimation from O'Leary et al. (2010)</i>					
D opx-melt	0.004	0.004	0.005	0.010	0.051
$\text{H}_2\text{O}$ bulk ALPB	<b>9</b>	18	14	26	<b>31</b>

tion for weathered W4 Gibson sample. Moreover, pyroxene might be less prone to terrestrial alteration than olivine. Interestingly, the two falls, Acapulco and Lodran, have slightly lower  $\delta\text{D}$  values, although within errors (i.e.,  $-329\pm 175\text{‰}$  and  $-203\pm 124\text{‰}$ ), compared to the three finds (i.e., Dhofar 125  $-173\pm 124\text{‰}$ , NWA 10074  $-186\pm 172\text{‰}$  and Gibson  $-124\pm 131\text{‰}$ ) consistent with a lower exposure to terrestrial alteration. As such, the two falls Acapulco and Lodran might be the best proxies for the acapulcoite-lodranite parent body and their average  $\delta\text{D}$  value represents the upper limit for the ALPB ( $\delta\text{D} = -239\pm 149\text{‰}$ , 1SD).

#### 4.1.2. Comparison of olivine and pyroxene water contents

The partition coefficient of  $\text{H}_2\text{O}$  between olivine and orthopyroxene in Lodran is close to 1, in agreement with that measured and discussed in Peterson et al. (2023) for ureilite pigeonite and olivine. It has been shown that H incorporation in terrestrial NAMs is strongly dependent on the pressure, water activity, mineral mode and  $\text{Al}_2\text{O}_3$  content (Demouchy and Bolfan-Casanova, 2016; and references therein). This can result in a transfer of H from pyroxene to olivine with depth, increasing the Ol/Px partition coefficient. However, for terrestrial settings, the partition coefficients between olivine and orthopyroxene do not exceed 0.5 (Demouchy and Bolfan-Casanova, 2016; and references therein). As such, we agree with Peterson et al. (2023) that most likely the similarity of  $\text{H}_2\text{O}$  contents in olivine and pyroxene results from an uncharacterized partitioning behaviour, since only clinopyroxene-melt  $\text{H}_2\text{O}$  partition coefficient has been characterized at low pressures (0.1–200 MPa) (Sarafian et al., 2019), which is appropriate for asteroidal settings such as primitive achondrite parent bodies. Indeed, acapulcoites would have formed at low pressure of 10 MPa while most lodranites would require 100 to 300 MPa (McCoy et al., 1997a). Ureilites could have formed at pressures between 10 MPa to 180 MPa, based on the latest estimation (e.g., Peterson et al., 2023). As such, the partitioning coefficient of water between NAMs and melt estimated for terrestrial conditions (e.g., 0.5 to 6 GPa) are unlikely to be adequate.

#### 4.1.3. Estimation of bulk ALPB water content

By modelling the ordinary chondrite parent body, Jin et al. (2021) estimated that thermal metamorphism of type 6 on an OC would not induce more than 12% water loss. Considering the range of water contents estimated for NAMs in acapulcoite-lodranite (average:  $5.2\pm 1.6$ ; Table 3), 12% corresponds to  $\sim 0.6 \mu\text{g/g H}_2\text{O}$ , hence negligible here, considering the error bars. As our results and those of Peterson et al. (2023) reveal that terrestrial olivine-pyroxene  $\text{H}_2\text{O}$  partition coefficients are not consistent with the water abundances in NAMs of ureilites and acapulcoites-lodranites, we used partition coefficients determined by Sarafian et al. (2019), who

conducted phase equilibria experiments at low pressures of 0.1 MPa (i.e.,  $0.1\pm 0.05$ ) to 200 MPa (i.e.,  $0.0085\pm 0.0005$ ), and T of  $1160^\circ\text{C}$  and  $1020^\circ\text{C}$ , respectively, and with pyroxene water contents of  $\sim 20$  and  $\sim 300 \mu\text{g/g H}_2\text{O}$ , respectively.

McCoy et al. (1997b) defined four groups of acapulcoites-lodranites as a function of their degree of partial melting (PM):  $<1$  vol.%, 2–3 vol.%, 5 vol.%,  $>10$  vol.%. The absence of silicate partial melting in Acapulco places it in the  $<1$  vol. % partial melting group. The larger grain size of Gibson ( $540 \mu\text{m}$ ) compared to acapulcoites led to an estimation of 5 vol.% PM, since silicate partial melt must have been available for grain growth. Finally, Lodran would have reached more than 20 vol.% of PM with the loss of these melts. Dhofar 125 has been grouped in the typical acapulcoites by Patzer et al. (2004) that did not suffer from silicate partial-melt loss. Northwest Africa 10074 closely resembles Dhofar 125 and would also fit this low degree of partial melting.

Using a simple single-stage batch melting model similar to Peterson et al. (2023), we estimated the parent body of the acapulcoites-lodranites to have contained between 3 to  $161 \mu\text{g/g H}_2\text{O}$  using the 0.1 MPa and 200 MPa mineral-melt  $\text{H}_2\text{O}$  partition coefficient for acapulcoites and lodranites, respectively (cf. Table 3). This range is restricted to 3 to  $19 \mu\text{g/g H}_2\text{O}$  if we used the 0.1 MPa mineral-melt  $\text{H}_2\text{O}$  partition coefficient for both acapulcoites and lodranites. Interestingly, analytical data on pyroxene and MIs from ureilites agreed with the  $0.1\pm 0.05$  partition coefficient value calculated for a pressure of 0.1 MPa (Peterson et al., 2023), although the same authors estimated a pressure of 180 MPa on the ureilite parent body (UPB). As ureilite and acapulcoite-lodranite parent bodies are similar in terms of redox conditions (oxygen fugacities varying from IW–3.25 to IW–1.5 (Righter et al., 2016 and ref. therein)) and pressure, we consider this partition coefficient as the best proxy for asteroidal conditions. In fact, using the O'Leary et al. (2010) equation to estimate clino- and ortho-pyroxene-melt  $\text{H}_2\text{O}$  partition coefficients, the bulk water content for the acapulcoite-lodranite parent body is similar, ranging from 4 to  $31 \mu\text{g/g H}_2\text{O}$ . Hence, our preferred range of estimation for the ALPB is 3 to  $19 \mu\text{g/g H}_2\text{O}$ . This value is extremely similar to the ureilite parent body estimation, i.e., 2 to  $20 \mu\text{g/g H}_2\text{O}$  (Peterson et al., 2023), as well as in the range of Vesta bulk water content, i.e., 12 to  $23 \mu\text{g/g H}_2\text{O}$  (Stephant et al., 2021) (cf. Table 4).

#### 4.2. Behaviour of H through various degrees of partial melting

The effect of melting and differentiation processes on hydrogen concentration and isotopic composition of basaltic rocks is an indeterminate parameter for asteroidal settings. Bindeman et al. (2012) demonstrated that from 1 to 15% of partial melting, water in terrestrial MORB glasses is un-degassed, and no variations

**Table 4**  
Summary of hydrogen isotopic compositions of S-type objects (determined by SIMS).

Samples	Instrument	Bulk/ Phase analyzed	$\delta D$ (‰)	H <sub>2</sub> O measured (ppm)	Bulk H <sub>2</sub> O PB (ppm)	References
<b>Enstatite chondrites</b>						
Average	SIMS 1280	Bulk	−146.5 to −97.8	800 – 5400	800 – 5400	Piani et al. (2020)
Sahara 97116 (Least altered EC)	SIMS 1280	Bulk	−103±3	4000 – 5400		Piani et al. (2020)
<b>Ordinary chondrites</b>						
OC falls average	NanoSIMS	Px	−263±63	558±116	254 – 518	Jin et al. (2021)
OC finds average	NanoSIMS	Px	−129±24	844±173		Jin et al. (2021)
OC chondrules	NanoSIMS	Px & Ol	−164±137 to +52±163	76±38 to 674±337		Stephant et al. (2017)
<b>Itokawa</b>						
	NanoSIMS	Px	−68±70 −42±69	680±65 970±93	160 – 510	Jin and Bose (2019)
	NanoSIMS	Px	+328±328	278±14		Chan et al. (2021)
	NanoSIMS	Ol	−305±104	235±60		Chan et al. (2021)
	NanoSIMS	Al	−177±128	993±252		Chan et al. (2021)
<b>Ureilites</b>						
	NanoSIMS	NAMs		2–6	2 – 20	Peterson et al. (2023)
<b>Acapulcoites - lodranites</b>						
Average	NanoSIMS	Px & Ol	−211±145	5.2±1.6	3 – 19	This study
Falls	NanoSIMS	Px	−239±149	2.8±0.6 to 6.8±1.0		This study
<b>Angrites</b>						
d'Orbigny and Sahara 99555	1280	Px, Ol and MI	−348 to −118	600 – 17600	150 – 2755	Deligny et al. (2021)
d'Orbigny and Sahara 99556	NanoSIMS	Olivine Ol average	−146 to +127 −31±39	8 – 19	230	Sarafian et al. (2017)
d'Orbigny and Sahara 99557	NanoSIMS	Silicophosphates	−262 to +1034	36 – 1701		Sarafian et al. (2017)
<b>Eucrites</b>						
Average	NanoSIMS	Px	−263±70	5 – 18	12 – 23	Stephant et al. (2021)
Average	NanoSIMS	Px	−228±49	4.0±0.2	10 – 70	Sarafian et al. (2019)
<b>Earth</b>						
VSMOW			0			
Bulk			−62 to −24		1000 – 3900	Lécuyer et al. (1998); Marty (2012); Palme and O'Neill (2014); Peslier et al. (2017)
Deep mantle	SIMS 1280	Ol-hosted melt inclusions	< −218			Hallis et al. (2015)

are observed in  $\delta D$  values, meaning that the measured H<sub>2</sub>O– $\delta D$  systematics in MORB glasses should reflect that of the mantle. As such, they argued that large ranges of  $\delta D$  values in some mantle-derived magmas cannot be explained by small degrees of partial melting but need to be explained by other processes like degassing or contamination with other water reservoirs. However, the Bindeman et al. (2012) study investigated terrestrial MORB glasses with water concentrations ranging from 0.25 to 1.49 wt.%, far from the average of 5.2±1.6  $\mu\text{g/g}$  H<sub>2</sub>O measured in NAMs of acapulcoites-lodranites. Moreover, the redox state is also distinct between the Earth and most of the early-formed planetesimals (e.g., Righter et al., 2016).

Regarding asteroidal and planetesimal conditions, some studies have investigated the effect of thermal metamorphism and partial melting on the H abundances and isotopic composition of meteorite minerals. Overall, meteorite parent bodies that suffered from thermal metamorphism or partial melting still preserve some hydrogen in their minerals and phases (e.g., Deligny et al., 2021; Jin et al., 2021; Piani et al., 2020; Sarafian et al., 2019, 2017; Stephant et al., 2021; Vacher et al., 2020). Jin et al. (2021) modelled that ordinary chondrites should not have lost more than 1 ppm and that  $\delta D$  should not have shifted for more than 1‰ over 5000 years of thermal metamorphism. This is because the cooling rates of OCs are relatively high (200–400 K/ky) (Ganguly et al., 2016), prohibiting high post-shock temperatures to drive hydrogen out and modify the minerals'  $\delta D$  values. Another study observes no  $\delta D$  variations among OCs of various petrologic types (Vacher et al., 2020). Recently, Newcombe et al. (2023) argued for efficient water loss of

achondritic parent bodies following internal heating and melting of planetesimals. This statement is based on the very low water contents (<2  $\mu\text{g/g}$  H<sub>2</sub>O) measured in achondritic NAMs from the outer region of the Solar System, with the assumption that their chondritic precursors had contained at least 1 wt.% of H<sub>2</sub>O. However, no isotopic data can corroborate this statement.

ALPB cooling rates have been estimated recently to be as high as  $\sim 10^1$  to  $\sim 10^{-1}$  °C/yr from peak to near-peak magmatic (down to 750 °C) and from  $10^{-1}$  to  $10^{-3}$  °C/yr below 750 °C (Lucas et al., 2022). These cooling rates are in the range or higher than what has been estimated for ordinary chondrites. As such, following Jin et al. (2021) model, acapulcoites-lodranites should not have any variations, introduced by thermal metamorphism, in their original  $\delta D$ –H<sub>2</sub>O systematics. Thermal metamorphism on eucrites and enstatite chondrites appears to have induced opposite effects (Piani et al., 2020; Stephant et al., 2021). Indeed, the thermal metamorphism of EC was linked to a decrease in  $\delta D$  values, potentially through the loss of D-enriched H-bearing organic matter (Piani et al., 2020). Conversely, thermal metamorphism of eucrites seems to favour an increase of  $\delta D$ , due to simple loss of H<sub>2</sub> or H, which is consistent with a reduced environment (e.g., Grewal et al., 2020). Finally, it is still under debate whether angrites have lost H following magmatic degassing (Deligny et al., 2021; Sarafian et al., 2017). Indeed, Sarafian et al. (2017) argued that d'Orbigny whole rock experienced some significant degassing of H<sub>2</sub>, while Deligny et al. (2021) showed that similar hydrogen isotopic compositions were carried by the most primitive and most evolved melt in d'Orbigny, hence discarding the hypothesis of any H<sub>2</sub> degassing.

Regarding acapulcoites and lodranites, no correlation is observed between their degree of partial melting and the H<sub>2</sub>O- $\delta$ D systematics of their NAMs (Fig. 3). The intra-sample homogeneity of water content and  $\delta$ D value in NAMs suggests that initial  $\delta$ D-H<sub>2</sub>O systematics are preserved (Fig. 2). In fact, Lodran which shows evidence of at least 20% PM still has a lower  $\delta$ D value than acapulcoite-lodranite finds with 1 to 5% PM (Fig. 3). While water concentrations in nominally anhydrous minerals of acapulcoites and lodranites are much lower than the H<sub>2</sub>O content in MORB from the Bindeman et al. (2012) study, partial melting from 1% to 20% does not generate H isotopic fractionation. Nonetheless,  $\delta$ D-H<sub>2</sub>O negative trends are observed for phosphates (Fig. 3), characteristic of degassing trends. Such a  $\delta$ D-H<sub>2</sub>O signature of phosphates in acapulcoites-lodranites, distinct from the NAMs, must result from their formation process. Partial melting leads to oxidation of P dissolved in FeNi metal. During crystallisation of the partial melt, P<sub>2</sub>O<sub>5</sub> will be enriched in the residual liquid, leading to the crystallisation of phosphates (Zipfel et al., 1995). As such, newly crystallised phosphates potentially recorded a more degassed H signature than the NAMs.

McCoy et al. (1997b) measured the volatile contents of Acapulco and Lodran to test the effect of volatiles on the removal of partial melt for the latter, and the pyroclastic volcanism model of the acapulcoite-lodranite parent body. They show that Acapulco contains abundant amounts of CO (600 ppm) and CO<sub>2</sub> (1940 ppm) compared to Lodran (CO: 0 ppm; CO<sub>2</sub>: 300 ppm). In fact, this is consistent with the C concentration of Acapulco and Lodran, i.e., 400 ppm and 100 ppm, respectively, measured by Grady et al. (1993). As such, it is more likely that these gases, released at silicate partial melting temperatures reached by Lodran, played a role in the removal of the partial melts. Conversely, the very low amount of water in all acapulcoites-lodranites, hence in the bulk ALPB, would rather suggest that H did not play a role in the thermal metamorphism, partial melting and/or melt removal of acapulcoites-lodranites, and that both water contents and  $\delta$ D values of NAMs remain unchanged after thermal metamorphism and partial melting of the ALPB. Moreover, Lodran contains more nitrogen than Acapulco (17 ppm vs. 2.8 ppm) (Grady et al., 1993). As such, high thermal metamorphism and low degree of partial melting did not affect all volatiles and their isotopic composition. In particular H, N and noble gases appear to be un-degassed, while C components (i.e., C, CO, CO<sub>2</sub>) could have been lost during thermal events on the ALPB. As a result,  $\delta$ D average of the falls Acapulco and Lodran ( $-239 \pm 149\%$ ) as well as the bulk water content estimated from NAMs (3 to 19  $\mu$ g/g H<sub>2</sub>O) can be considered representative of the ALPB hydrogen composition.

### 4.3. Comparison with inner Solar System parent bodies – A unique source of hydrogen

The source and delivery of water in the inner Solar System is an active area of current cosmochemistry research, as studies have shown that inner Solar System bodies are not as dry as first thought (e.g., McCubbin and Barnes, 2019). Recently, nucleosynthetic isotope signature of meteorites (e.g., O, Cr, Ti) has revealed the existence of spatio-temporally resolved reservoirs of planetesimal materials (Warren, 2011). The rapid ingrowth of Jupiter in the early Solar System appears to have spatially and temporally separated the inner (non-carbonaceous – NC) and outer (carbonaceous – CC) regions of the Solar System during the first 1 to ~4 Ma after CAIs formation (e.g., Kleine et al., 2020; Kruijjer et al., 2019). The O, Cr and Ti isotopic signatures of ordinary chondrites, enstatite chondrites and most primitive and differentiated achondrites place these meteorite parent bodies in the NC reservoir (Kruijjer et al., 2019; Sanborn et al., 2019). Moreover, spectral properties of OCs, ECs, angrites, ureilites, howardites-eucrites-diogenites (HEDs),

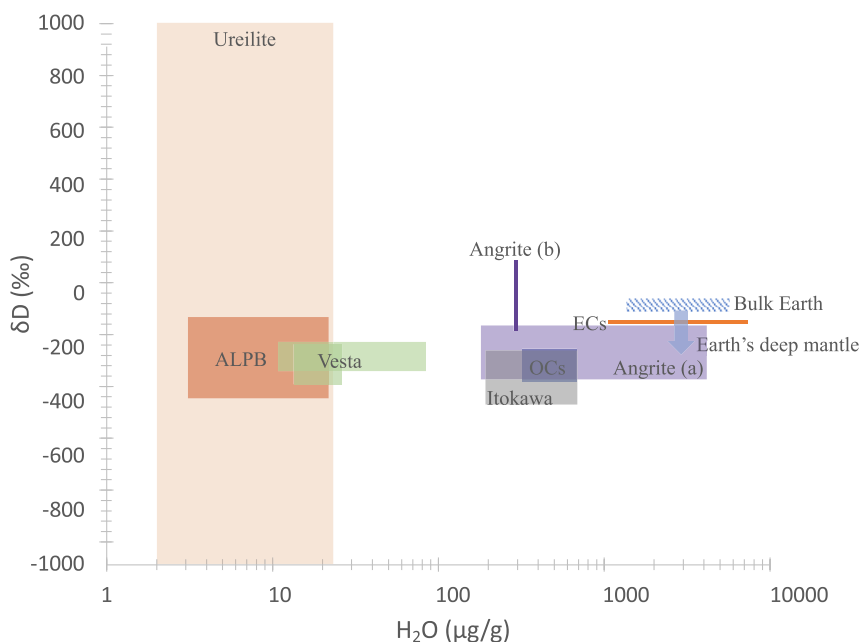
acapulcoites-lodranites suggest that their potential parent bodies resided in the inner portions of the main asteroid belt (e.g., Binzel and Xu, 1993; Burbine et al., 2006; Lucas et al., 2022), i.e. deriving from S-type, V-type, E-type, and F-type asteroids in the inner and middle main asteroid belt (e.g., DeMeo and Carry, 2013), where the inner asteroid belt is delimited between the  $\nu$ 6 (2 AU) and 3:1 (2.5 AU) secular and Jupiter mean resonances and the middle asteroid belt is further delimited up to the 5:2 mean resonance (2.8 AU). As such, comparing the  $\delta$ D-H<sub>2</sub>O signature of planetesimals from the NC and the inner part of the Solar System would give insight into the source and time of delivery of water in this region of the Solar System.

From mineralogy, geochemistry, and isotopy of acapulcoites and lodranites, it has been inferred that their chondritic precursor had an intermediate composition between enstatite and H ordinary chondrites, although their precursor material has yet not been sampled, possibly because it has not been preserved (Floss, 2000; McCoy et al., 1997a, 1996; Mittlefehldt et al., 1996; Palme et al., 1981). As for OCs, ALPB is associated with an S-type asteroid (Lucas et al., 2022), the most common object in the inner asteroid belt (DeMeo and Carry, 2013). Jin et al. (2021) showed that the  $\delta$ D average in NAMs of OC falls is lower than the chondritic value, as well as lower than OC chondrule and matrix  $\delta$ D value (e.g., Deloule and Robert, 1995; Piani et al., 2015; Stephant et al., 2017), with an average  $\delta$ D of  $-263 \pm 63\%$  (cf. Fig. 3). This value is concordant with the  $\delta$ D inferred for the ALPB ( $-239\% \pm 149\%$ ), consistent with a similar precursor for ordinary chondrites and ALPB. These H isotopic signatures are also similar to the lowest  $\delta$ D measured in an olivine grain of Itokawa ( $-305 \pm 104\%$ ) (Chan et al., 2021), implying a similar source of water for S-type objects. Moreover, the  $\delta$ D value inferred for the ALPB from acapulcoite and lodranite NAMs match the  $\delta$ D values of other planetesimal samples originating from the NC reservoir from which the hydrogen isotopic signature has been inferred: Vesta (Stephant et al., 2021), as well as the lowest  $\delta$ D measured in angrites (Deligny et al., 2021; Sarafian et al., 2017) (Fig. 4 – Table 4). However, the  $\delta$ D value of ECs is slightly higher than the others (i.e.,  $-103 \pm 3\%$ ) (Piani et al., 2020). This slight discrepancy could be due to the presence of D-rich H-bearing organic matter in the ECs, as this argument was evoked to explain the  $\delta$ D evolution with thermal metamorphism.

Interestingly, ALPB hydrogen abundance is similar to the estimation for the UPB (2–6  $\mu$ g/g H<sub>2</sub>O) (Peterson et al., 2023) and for Vesta (12–23  $\mu$ g/g H<sub>2</sub>O) (Stephant et al., 2021), but much lower than what has been inferred for bulk OCs (Jin et al., 2021), ECs (Piani et al., 2020), Itokawa (Chan et al., 2021; Jin and Bose, 2019), and the angrite parent body (APB) (Deligny et al., 2021; Sarafian et al., 2017) (cf. Fig. 4 and Table 4). Peterson et al. (2023) argue that the lower bulk water content inferred for the ureilite parent body compared to OCs and ECs invokes volatile degassing. We disagree with this statement concerning the ALPB, as the similarity of its  $\delta$ D value with that of other inner Solar System planetesimals suggests that ALPB incorporated the same source of hydrogen as other NC planetesimals, and in particular S-type asteroids, but in lesser quantity. This result reveals a distinctive and homogeneous hydrogen source for the NC reservoir in the early stages of the Solar System, which was incorporated in different quantities among the parental bodies. In fact, it has been already proposed that different chondritic parent bodies (e.g., CIs, CMs, CKs, OCs) have accreted variable amounts of water-ice grains (Vacher et al., 2020). Moreover, while the H content of acapulcoites and lodranites is lower than ordinary chondrites, their primordial noble gas concentrations of primordial gases are much higher than those of more evolved achondrites, highlighting that volatile contents in planetesimals with similar precursor material can vary.

Acapulcoites-lodranites, as well as OCs, ureilites, angrites and HEDs are proxies to unravel the primordial source(s) of water in





**Fig. 4.** Water content ( $\mu\text{g/g H}_2\text{O}$ ) and  $\delta\text{D}$  ( $\text{‰}$ ) values estimated for bulk parent bodies in the inner Solar System. Data are represented in Table 4: ureilites are from Peterson et al. (2023) (no  $\delta\text{D}$  values are available), Vesta from Sarafian et al. (2019) and Stephant et al. (2021), OCs from Jin et al. (2021), Itokawa from Jin and Bose (2019) and Chan et al. (2021), angrites (a) from Deligny et al. (2021), angrites (b) from Sarafian et al. (2017), ECs from Piani et al. (2020), bulk Earth is defined after  $\delta\text{D}$  values from Lécuyer et al. (1998) and bulk water content estimation from Marty (2012), Palme and O'Neill (2014) and Peslier et al. (2017). Earth's deep mantle has been estimated to be  $< -218\text{‰}$  and representative of Earth's original  $\delta\text{D}$  signature (Hallis et al., 2015). Inner Solar System bodies share a common  $\delta\text{D}$  reservoir, depleted in deuterium compared to the Earth. S-type objects are more depleted than E-type asteroids. Parent bodies might have incorporated various amounts of hydrogen from this common reservoir.

the inner Solar System. Indeed, these meteorites' parent bodies all started their accretion or fully accreted within the first 2 Ma after CAIs condensation (Budde et al., 2015; Monnereau et al., 2013; Neumann et al., 2018, 2014; Schiller et al., 2015). As such, the contemporaneity of the ALPB, APB, UPB, Vesta, as well as the OC parent body strengthen the possibility of a unique source of water in the inner NC reservoir of our Solar System, with an upper limit for the hydrogen isotopic composition of approximately  $-250\text{‰}$ , but which could be even originally lower than  $-300\text{‰}$  considering some of  $\delta\text{D}$  values inferred (cf., Fig. 4 – Table 4). Indeed, this  $\delta\text{D}$  value estimated for the inner Solar System is lower than the average  $\delta\text{D}$  value measured in bulk CM chondrites (i.e.,  $-74 \pm 21\text{‰}$ , 2SE) (Piani et al., 2021, and reference therein). While the exact mechanism by which the NC and the inner Solar System planetesimals could have acquired D-poor hydrogen is unclear, several possibilities could account for this depleted water source. Interestingly, CM chondritic water-ice grains have been estimated to be  $\sim -350\text{‰}$  (Marrocchi et al., 2023; Piani et al., 2021; Vacher et al., 2020). Piani et al. (2021) modelled that D-rich water-ice from the molecular cloud would episodically feed the protoplanetary disk. With a combination of isotopic exchange between molecular cloud D-rich water-ices with the D-poor protosolar  $\text{H}_2$  (Jacquet and Robert, 2013), sublimation of these water-ice, high-temperature isotopic equilibration and/or recondensation, these initially D-rich water ices could reach the estimated  $\delta\text{D}$  of CM chondritic water. As such, one possibility would be that such water-ice grains were also incorporated into inner Solar System parent bodies.

Another possibility regarding the origin of this D-poor water is a contribution of nebular hydrogen to the water budget of the inner Solar System parent bodies. Jin et al. (2021) argue that the lower  $\delta\text{D}$  value of OCs compared to terrestrial and chondritic  $\delta\text{D}$  values reflects a mix of 45 to 95% of D-poor nebula-sourced water with D-rich water from chondritic components. The most  $\delta\text{D}$ -poor values recorded by angrite glasses as well as eucrite NAMs also hint at the presence of a nebular hydrogen component both in the APB and Vesta, respectively (Deligny et al., 2021;

Stephant et al., 2021). Incorporation of nebular H by diverse mechanisms, at mineral (Asaduzzaman et al., 2015) or parent body scale (e.g., Sharp, 2017), could account for this D-poor water reservoir. Acapulcoite-lodranite hydrogen isotopic composition thus may indicate a unique source of water in the early and inner NC Solar System that appears to have had an isotopically light hydrogen composition, that might be a signature of chondritic CM water-ice grains incorporation or nebular hydrogen contribution.

## 5. Conclusion

The  $\text{H}_2\text{O}$ - $\delta\text{D}$  systematics of NAMs in acapulcoites-lodranites suggest that thermal metamorphism and partial melting (up to 20%) did not induce any significant hydrogen isotopic fractionation. This demonstrates that NAMs are recording primordial signatures of the  $\delta\text{D}$  and  $\text{H}_2\text{O}$  contents of their bodies. However, the  $\text{H}_2\text{O}$ - $\delta\text{D}$  systematics of apatites possibly record the isotopic signature of a late-stage degassed melt from which they subsequently crystallised. The hydrogen isotopic composition of the ALPB, best inferred using the NAM data on the two falls Acapulco and Lodran, i.e.,  $-239 \pm 149\text{‰}$  (1SD) is similar to OC falls, and other planetesimals formed in the NC reservoir within 2 Ma after CAIs condensation. The water content of the ALPB, i.e.,  $3\text{--}19 \mu\text{g/g H}_2\text{O}$ , is similar to the estimates for some other NC planetesimals such as the UPB or 4 Vesta. However, they are much drier than other bodies, like OCs, the APB or Itokawa. This result suggests a unique source of hydrogen in the NC reservoir, the composition of which indicates either contributions from some protosolar nebula hydrogen or from D-poor CM water-ice grains, which were incorporated in various amounts within the different precursor materials.

## CRediT authorship contribution statement

**A. Stephant:** Conceptualization, Investigation, Visualization, Writing – original draft. **X. Zhao:** Investigation. **M. Anand:** Conceptualization, Supervision, Writing – review & editing. **J. Davidson:**

Investigation, Resources, Writing – review & editing. **C. Carli:** Conceptualization, Supervision. **T. Cuppone:** Investigation. **G. Pratesi:** Resources, Writing – review & editing. **I.A. Franchi:** Validation, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data are available in the supplementary material

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### Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2023.118202>.

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