

THE ISOTOPIC D/H RATIO OF IRON METEORITES. C. Defouilloy¹, R. Duhamel¹, F. Robert¹, M. Clog²,
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Introduction: Iron Meteorites are interpreted as samples from the core of differentiated planetesimals. This interpretation could be better documented via the determination of the hydrogen isotopic compositions (D/H ratio) in Iron Meteorites.

To this aim, two parameters need to be known: (i) the D/H of the water that was (possibly) reduced in the form of H₂ dissolved in the silicate melt (ii) the isotopic fractionation associated with the reduction of this water.

The parameter (i) is now well documented. The *chondritic water* D/H ratio peaks at 150×10^{-6} with a distribution lying between 120 and 300×10^{-6} (as recorded in carbonaceous chondrites)[1] while the so called Protosolar H – hosted by the primordial H₂ – has a much lower ratio with a $(D/H)_{H_2} = 20 \pm 5 \times 10^{-6}$.

The parameter (ii) needs to be experimentally determined. Since the D/H ratio from protosolar hydrogen is markedly different from the hydrogen resulting from water reduction during the planetesimal differentiation, the D/H ratio in Iron Meteorites could be an indicator of the origin of H. Therefore, an analytical technique for measuring the D/H ratio of Iron meteorites using an ion microprobe has been developed.

Method: Hydrogen isotopic composition is determined with the CAMECA IMS 3f at the National Museum of Natural History in Paris, France. Samples are mounted either in epoxy and Au-coated or as polished thin sections and sputtered with a primary positive Cs⁺ beam. Because of the highly conductive nature of these metallic samples, the use of an electron gun is unnecessary. Entrance and Exit slits as well as the Energy slit are kept wide open. Under these conditions, the mass resolution is <400 (with the Cs⁺ primary beam the possible mass interference between H₂⁺ is D⁺ is negligible). Moisture from evaporation of absorbed water in the ion probe was kept as low as possible by using a liquid nitrogen trap.

Experiments showed that with a primary beam intensity ranging from 5 to 10 nA with a 30 µm diameter beam, it is impossible to eliminate efficiently all the contribution of absorbed surface water. Therefore, we used a larger ion spot (500 µm) combined with a 150 µm aperture field, so that the ions from the center of the “crater” are selectively collected. The intensity had to be increased up to 40 nA in order to reach 10^4 cps for H. Data were collected in peak jumping mode, with counting time of 5 and 15 s for H⁺ and D⁺ respectively.

Results: In order to assess the possible terrestrial contamination a sample from the Coahuila IIA Iron meteorite has been saw and polished with deuterated alcohol. Alcohol D/H ratio is 1%. Results are compared with its non-deuterated counterpart (figure 1).

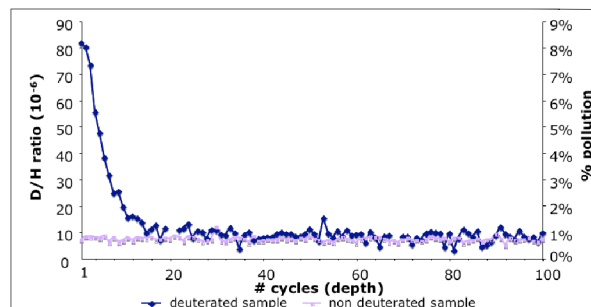


Fig. 1. Depth profiles of the D/H ratio in samples from the Coahuila meteorite. Blue spots show the profile of the deuterated sample.

The comparison of the depth profiles between deuterated and non-deuterated sample shows a contamination restricted at the surface of the sample (equivalent of 20 minutes of sputtering). Further inside, no evidence of contamination is detectable i.e. the D/H ratio of the deuterated sample reaches a plateau with depth that is indistinguishable from the non-deuterated sample. The absolute values for H concentration and D/H ratio are within $\pm 0.5\%$ and $\pm 20\%$, respectively (2 sigma) [2].

To determine the instrumental fractionation, we measured the D/H ratio of Copiapo, a IAB Iron meteorite, by degassing all its hydrogen through a traditional vacuum pyrolysis extraction line. A CT scan of a 4,85g sample has been performed previously to insure the absence of silicate inclusions inside the metallic fragment. This sample was heated for 2 hours at melting temperature (1400-1500°C).

The D/H ratio of the extracted hydrogen was then measured in a mass-spectrometer at $133.8 \pm 0.5 \times 10^{-6}$.

On the IMS 3f, the D/H ratio for Copiapo was about $66 \pm 4.5 \times 10^{-6}$. The instrumental fractionation was thus of 0.49 ± 0.03 .

The background being negligible and assuming there is no other effect to be corrected, we can then use this Copiapo “Standard” to calculate the D/H ratio of other Iron meteorites analysed with the IMS 3f. Three others meteorites have been studied so far: Ballinoo from the IIC group, Coahuila from the IIA group and

Toluca from the IA. The calibration (Table 1) shows that their D/H ratio is 142×10^{-6} , 154×10^{-6} for Ballinoo and Coahuila respectively. The Toluca meteorite contains 2 phases, kamacite and plessite, whose D/H ratio are somewhat different: 131×10^{-6} for kamacite and 157×10^{-6} for plessite. Table 1 shows the measured (*read*) and absolute (*true*) D/H values for our 4 samples.

Meteorite	D/H read (10^{-6})	D/H true (10^{-6})	mean	error (2 sigma)
Copiapo (Standard)	63	128	134	9
	65	132		
	64	130		
	68	138		
	67	136		
	70	142		
Ballinoo	65	132	142	43
	63	128		
	58	118		
	63	128		
	71	144		
	68	138		
	66	134		
	65	132		
	65	132		
	96	195		
Coahuila	87	176	155	16
	75	152		
	65	132		
	71	144		
	73	148		
	76	154		
	75	152		
	75	152		
	72	146		
	76	154		
	76	154		
	81	164		
	77	156		
	75	152		
Toluca kamacite 1	82	166	158	30
	75	152		
	74	150		
	83	168		
	75	152		
	67	136		
	77	156		
	80	162		
	73	148		
Toluca kamacite 2	73	148	154	14
	73	148		
Toluca plessite 1	65	132	142	6
	70	142		
	73	148		
	65	132		
Toluca plessite 2	64	130	130	6
	67	136		
	63	128		
	63	128		

Table 1. Table of the D/H ratio read and true, corrected thanks to the Copiapo standard.

The concentration of Hydrogen in the Copiapo meteorite has also been measured: 50 ± 2.5 ppm. This concentration was used to calibrate the H concentration in Iron meteorites (the secondary current is linearly related to the primary current in the domain where the meteorites are measured; cf. Figure 2).

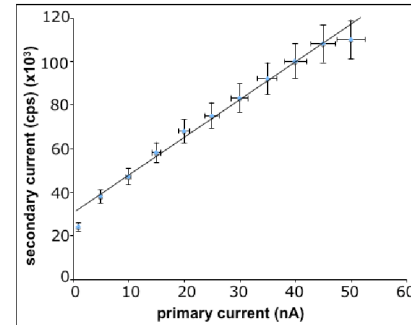


Fig. 2. Secondary current (in count per second) versus primary current (in nA) measured for the Coahuila meteorite. It can be seen that between 5 and 35 nA primary current is linearly related to secondary current.

Discussion: The D/H ratio measured in Copiapo is 133×10^{-6} , so this Hydrogen does not come from the Nebula (at 20×10^{-6}). Consequently, this Hydrogen must be coming from the reduction of water by the Iron.

A Rayleigh distillation of water on Iron was performed at the LGIS IPG-Paris, France. Slugs of Iron were heated at 1000°C in an extraction line. Water was injected and reduced on Iron in several steps, each one not exceeding few % of the total amount of water. The H_2 produced was collected and the successive D/H ratios were measured. Several corrections were applied to calculate α - the isotopic fractionation factor between water and hydrogen; namely, (i) the D/H ratio of the remaining water was recalculated at each step and (ii) the possible Rayleigh distillation was taken into account in the calculation of α . These corrections turn out to be negligible. We obtained $\alpha = 1.49 \pm 0.16$.

We now use this value of α in the *academic* situation where the reduction of water takes place by contact between the water vapor phase of the Nebula and the hot iron body of Copiapo. The water reservoir being infinite, the original D/H ratio of water vapor was: $133 \times 10^{-6} \times 1.49 = 200 \times 10^{-6}$. Since in Chondrites, the D/H ranges from 130×10^{-6} to 160×10^{-6} such a scenario in the Nebula seems highly unlikely.

Consequently, the reaction of reduction of water on Iron must have taken place inside the parent body where most of the reduced water was trapped as H_2 in the metallic melt. A step-by-step calculation in a Rayleigh model shows that, for an initial D/H ratio of 150×10^{-6} (a possible Chondritic value) 90% of the initial water is dissolved in this Iron meteorite and exhibits the measured D/H ratio in Copiapo (133×10^{-6}).

These experiments confirm the idea that Iron meteorites originate from the differentiation of a chondritic parent body.

References: [1] Deloule E. and Robert F. (1995) *Geochim. Cosmochim. Acta*, 59, 4695-4706. [2] Defouilloy et al. (2009), *Meteoritics & Planet. Sci. Supplement*, 5145.