

Using the D/H ratio to estimate the terrestrial water contamination in chondrites. F.Robert¹ E. Deloule²,
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Introduction: Several studies have reported the distribution of D/H ratios in extraterrestrial samples (SNC, Chondrites, IDPs; [Ref]). All these studies are subject to controversies because the effect of the terrestrial contamination on the D/H ratio has never been precisely quantified. Judging from literature discussions, two issues can be distinguished: (1) When an extraterrestrial sample exhibits a D/H ratio clearly out of the terrestrial range, what is the exact contribution of the terrestrial contamination on this ratio? (2) When in the terrestrial range, can we firmly assert that the initial indigenous water (or -OH) has a terrestrial-like D/H ratio? Here we report a detailed study of these problems (more than 650 individual determinations of D/H ratios were performed). The Semarkona meteorite has been analyzed with the 3f ion-microprobe. Samples were prepared using terrestrial and deuterium-rich water. All possible sources of contamination were considered and quantified.

Experimental: An experimental protocol for preparing and analyzing the samples was rigorously applied. Two water tanks were used: W#1: D/H=939 ±20 ×10⁻⁶ and W#2: D/H=146.4±0.1 ×10⁻⁶. For W#1, the D/H ratio has been determined by weighting and checked by mass spectrometry on diluted aliquots; the D/H value was adjusted to be closed to the highest values measured in this meteorite.

100 mg of Semarkona #1 saw from 2 gr. of whole rock in presence of liquid W#1, mounted in epoxy and gently polished using W#1. In order to reproduce the cleaning procedure of all our samples analyzed with the ion microprobes, the section was submitted to ultrasonication during 10 minutes using W#1. The section - about 2 mm thick - was then kept at room temperature during 1 month under the water vapor pressure of W#1. Therefore, during its preparation, the sample has never been in contact with natural water. After analysis with the ion-microprobe, about 4 μm thick was removed from the surface of the section by polishing in presence of W#2 (Semarkona #2) and the section was then submitted to ultrasonication using W#2. The sample was kept about one month under the water vapor pressure of W#2. The determination of the D/H ratio was made on the very same ion-spot for Semarkona#1 and #2; the results are thus directly comparable.

Another sample, Semarkona#3 was prepared as follows: the previous whole rock sample (≈ 2 g) was embedded in a metallic alloy (Wood), saw and polished

using W#2. The sample is 5 mm thick and can be used for other purposes. Mineral phases at the ion spot were determined by electron microprobe and microscopy.

Results In measuring the water concentration with the ion-probe, one should distinguish the precision of the individual determination and the systematic error (the accuracy) linked to the fact that the secondary H⁺ are not filtered in energy. The relative precision on [H₂O] wt.% is between ±1 and ±8% for [H₂O] between 1 and 0.2%, respectively. The accuracy on [H₂O] is ± a factor of 2 i.e. the water concentration in the same mineral, run within two different calibration sessions, can differ by a maximum of a factor of 2. No background was subtracted from the H⁺ sample signal.

No systematic error is detectable on the D/H ratio. In most cases, the relative precision on D/H varies linearly with [H₂O] and lies between ±2% and ±20% for water concentration equal to 1% and to 0.2%, respectively.

The experimental protocol has allowed us to quantify (1) The very surface contamination (likely from the gold coating) (2) The absorption of terrestrial water by the meteorite sample. Note that isotopic exchanges between "extraterrestrial" indigenous hydrogen and terrestrial water cannot be distinguished from the absorption process. (3) The contamination by epoxy (4) The sensitivity to terrestrial contamination among the different mineralogical assemblages of the meteorite. To discuss these points, Figures 1 to 3 were chosen as examples.

Discussion *Surface contamination:* In Figure 1 are reported the D/H and H⁺ profiles versus the duration of the experiment and thus the depth of the ion spot. The surface contamination does not correspond to the D/H ratio of the W#1 and thus is caused by the emission of H⁺ standing at (or just bellow) the surface of the gold. In all cases, a plateau in D/H is reached in <1000 sec. In Figure 1, the water contamination is the most pronounced example of all our samples and reaches 20%.

Absorption - Isotopic exchange In Figure 2, the water contamination on all the analyzed minerals having [H₂O]<0.8% (Ol. Pyrox., Mesostasis) is clearly detectable. Assuming that the contamination is the same for all these minerals, that they all have the same indigenous D/H ratio and that the shift in D/H is only caused by water contamination, we can calculate the corresponding overall contamination. The relative variations in the mean D/H value for the two populations #1 and #2 stands for this overall contamination; that is

6.4±5.0%. Note that a terrestrial water free (60 ppm) olivine has given a background value for water corresponding to 0.05 wt. %. The average concentrations reported in Figure 2 ($0.15\% < [H_2O] < 0.6\%$) are therefore only a factor of 4 above the background. In all samples having $[H_2O] > 0.8$ wt.%, (cf. Fig.2) the water contamination is invisible (results not shown here).

Epoxy Epoxy exhibits low D/H ratio (90×10^{-6} ; cf. Figure 2) and in principle, could be at the origin of some hydrogen contamination of thin sections. However, as reported in Figure 3, for thick sections - and provided that no resin can reach the surface of the polished sample - the contribution of the Epoxy is undetectable. Note the clear hyperbolic distribution of the data in Semarkona, which demonstrates that a low indigenous D/H ratio ($\approx 100 \times 10^{-6}$ after contamination correction) associated with a water concentration up to 0.8 wt.%, exists in Semarkona. The contamination corresponds to the vertical branch of the D/H ratio at $[H_2O] \approx 0.2\%$. The data which are not on the hyperbolic function and pointing to high D/H ratios ($[H_2O] = 0.6\% - 0.8\%$) are caused by the mixing of the deuterium-rich phases (D/H up to 600×10^{-6} ; not shown here).

Mineral sensitivity The water contamination is virtually undetectable in all deuterium-rich phases exhibiting $[H_2O] > 1\%$

Conclusions In light of the large D/H variations observed in Semarkona, the problem of the terrestrial contamination can be ignored. To be more precise, a possible correction of - at maximum - 15% can be propagated on the measured D/H ratios. Another contamination scenario can nevertheless be considered : some clay minerals, whose isotopic composition cannot be changed after their formation, have growth inside the rock during its stay in Museum. Such a type of contamination cannot not be detected by our experiments... but is rather ad-hoc.

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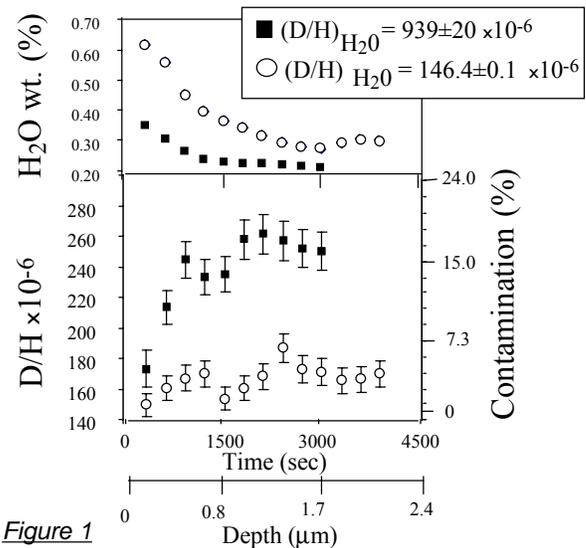


Figure 1

Mesostasis in a Pyroxene

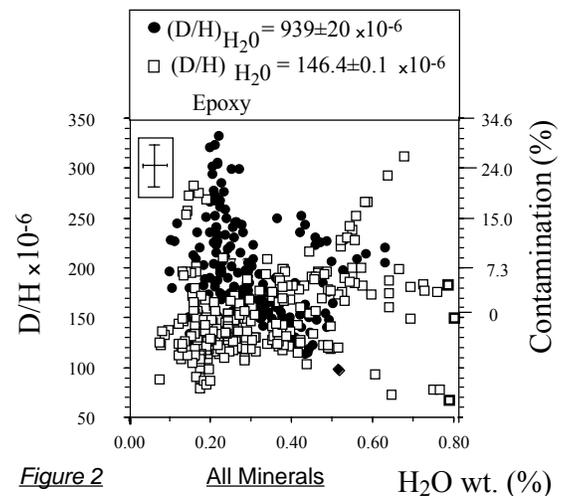


Figure 2

All Minerals

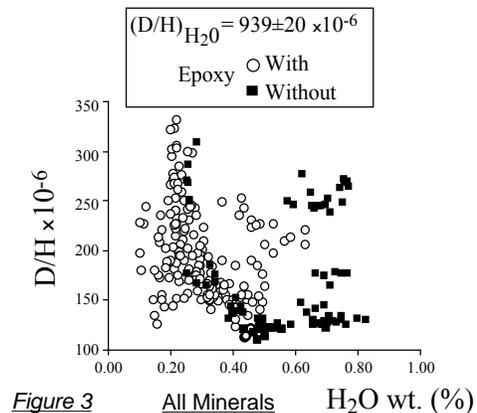
H₂O wt. (%)

Figure 3

All Minerals

H₂O wt. (%)