Hydrogen isotopic fractionation in secondary ion mass spectrometry using polyatomic ions

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ABSTRACT

Isotopic measurements at the micron scale using secondary ion mass spectrometry (SIMS) require an accurate control on the instrumental mass fractionation (IMF). The IMF correction is challenging since substantial mass fractionation can occur during both emission and detection processes. In this work, we report hydrogen isotopic measurements on a series of organic standards using polyatomic ions (CH^-, CD^-, C_2H^-, C_2D^-) with the NanoSIMS-50 instrument. We show that the D/H ratios resulting from the measurement of CD^-/CH^- and C_2D^-/C_2H^- ratios are close to the true D/H ratios of the samples over more than 3 decades and allow accurate hydrogen isotopic measurements to be performed in solid samples. Large secondary emission yields are usually associated with high electron affinities and correlate presently with low IMF effects. Moreover, we show that even when large variations in secondary ionic current are observed, an accurate isotopic ratio can still be inferred.

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1. Introduction

Secondary ion mass spectrometry (SIMS) is a powerful tool to constrain the isotopic composition of solid samples at the micron or submicron scale. However, isotopic ratios measured by SIMS are different from their true values because of instrumental mass fractionation (IMF). There are several sources of IMF: (i) isotopes may be produced with slightly different ion emission yields; (ii) isotopes may be emitted with different angular and energy distributions so that their collection efficiencies are slightly different; (iii) isotopes are not detected with exactly the same efficiency by electron multipliers.

Since most of the time it is not possible to single out these effects and perform appropriate corrections in isotopic measurements, one is led to use reference standards with known isotopic compositions and compare the measured isotopic ratios R_{MS} on the standard with the standard true isotopic ratios R_{TS}. The α parameter currently used to characterize the global isotopic effect is defined as,

$$\alpha(2/1) = \frac{R_{MS}}{R_{TS}}$$

It is often interesting to retrieve D/H ratios in hydrocarbon samples that are heterogeneous at a fine scale (μm), and to correlate these D/H ratios with isotopic ratios from other elements. Moreover, D/H ratios can be measured using polyatomic species as indicated by [1] using SiH^- and SiD^- ions. They checked the possibility to measure D/H ratios on silicon samples implanted with HD^+ ions, but they were confronted to unresolved mass interferences in their instrument. The NanoSIMS-50 (CAMECA) is an instrument suited for that type of work owing to its capability of detecting simultaneously different ionic species and to the possibility of tuning the instrument for high mass resolution (HMR) analysis, which allows to select H-containing polyatomic secondary ions free of mass interference [2].

In the work presented here, we use $^{12}CH^-$ and $^{12}C_2H^-$ ions because their high electron affinities (EA) result in high yields when samples are bombarded with Cs^+ ions. The production of secondary ions is a complex phenomenon for which there is no unified theory. Indeed, the cascade of atomic collisions triggered inside the solid

target by a single primary impact lasts less than a picosecond and generates the ejection of five or more target atoms distributed over a great variety of species, neutral and charged, monatomic particles and various polyatomic clusters.

Accumulation of primary impacts leads to a sputtering process that removes sample atoms and continuously renews the sample surface while Cs particles are implanted. Radiation defects and atomic mixing are likely to produce a thin superficial buffer layer made of previously implanted Cs atoms and atoms originating from the bulk. When a stationary state is reached it is assumed that previously implanted Cs atoms are sputtered away with an outgoing flux equal to the flux of incoming Cs primary ions. That buffer layer is constantly renewed and its composition, which differs from the bulk composition because of the large contribution of implanted Cs among others, is still a function of the underlying bulk composition and plays an important role in controlling sputtering and ionization yields.

When dealing with atomic secondary ions emitted as a stationary state is reached, the number of counted secondary ions is assumed to be proportional to both the atomic concentration of this element in the sample and to the number F_{Cs} of primary ions. In the case of polyatomic ions, one can generalize this rule and state that $N_I(^{12}CH)$, the number of emitted $^{12}CH^-$ ions, is proportional to the product $[^{12}C]\cdot[H]$ of atomic concentrations, where $[^{12}C]$ or $[H]$ refers hereafter to atomic concentrations in the bulk sample. Thus we have,

$$N_I(^{12}CH) = k_{CH}[^{12}C] \cdot [H] \cdot F_{Cs} \quad \text{and} \quad N_I(^{12}CD)$$
$$= k_{CD}[^{12}C] \cdot [D] \cdot F_{Cs}$$

$$\rightarrow \quad R_{MS} = \frac{N_I(^{12}CD)}{N_I(^{12}CH)} \quad \text{and} \quad R_{MS} = \frac{k_{CD}}{k_{CH}} \cdot \frac{[D]}{[H]}$$

Those equations do not assume any given process for cluster formation and/or ionization. Their purpose is to single out the isotopic [D]/[H] ratio of the sample bulk to allow a direct comparison between measured and true ratios. The coefficients k_{CH} and k_{CD} depend on the composition of the buffer layer and they average all pathways over many independent primary impact events leading to the production of $^{12}CH^-$ and $^{12}CD^-$ ions. Samples with different atomic compositions or chemical formula may have different k_{CH} and k_{CD} values and the same sample under different experimental conditions producing a different buffer layer may also exhibit different values for those coefficients.

Similar conclusions can be drawn for C_2H^- ions with similar relations leading to,

$$R_{MS} = \frac{N_I(^{12}C_2D)}{N_I(^{12}C_2H)} \quad \text{and} \quad R_{MS} = \frac{k_{C_2D}}{k_{C_2H}} \cdot \frac{[D]}{[H]}$$

Thus, measuring CH^-, CD^-, C_2H^- and C_2D^- ions lead to two α parameters for IMF characterization:

$$\alpha' = \frac{k_{CD}}{k_{CH}} \quad \text{and} \quad \alpha'' = \frac{k_{C_2D}}{k_{C_2H}}$$

In the present work, we address the situation where standards are made of the same polymer, a polystyrene (PS) film, in which only the D/H ratios have been changed in a controlled manner. We study the evolution of both α' and α'' in a series of standards with different [D]/[H] ratios.

2. Samples and methods

In order to study the IMF in hydrocarbons samples over a large range of D/H ratios, we produced a set of four polystyrene (PS) film samples with D/H ratios of about 1, 4, 8 and 2000 times the standard mean ocean water (SMOW) value $[(D/H)_{SMOW} = 1.5576 \times 10^{-4}]$ [3], hereafter referred as PS-1, PS-4, PS-8 and PS-D (see Table 1). To prepare these standard samples, varying proportions of polymer powders of non-deuterated polystyrene $(CH_2-CH(Ph))_n$ and deuterated polystyrene $(CD_2-CH(Ph))_n$, purchased from Polymer Source with a purity of 99%, were dissolved in toluene (see Table 1). Toluene has a high polystyrene dissolving capacity (the solubility of PS with a number average molar mass Mn $\sim$ 54,000 g/mol in toluene is 0.60 g/mL [4]) and a high volatility. Each sample was prepared by using 10 mL of toluene to ensure a complete dissolution of the powders and a rapid homogenisation of each solution. Then, from each solution, we prepared thin films by depositing a drop of solution on a clean substrate and letting toluene evaporate. The PS films were subsequently ultra-microtomed (with a thickness of $\sim$200 nm) using a Leica Ultracut UCT, and deposited on a silicon wafer. Additional details on the sample preparation are provided in Supplementary section A.

We controlled the D/H ratio of the PS-D sample by independent infrared measurements performed at the synchrotron SOLEIL (Saint-Aubin) on the SMIS beam line (Spectroscopy and Microscopy in the Infrared using Synchrotron – see Supplementary section B). The D/H ratio of the PS-1 sample was measured at the Institute for Geological and Geochemical Research in the Hungarian Academy of Sciences, from H_2 produced from H_2O separated by vacuum distillation, after oxidizing the sample with CuO at $\sim$500 °C.

The true D/H ratios of the PS-4 and PS-8 films were calculated from the mixing ratios of the two end members, PS-1 and PS-D (see Supplementary section C and Table 1 for details).

The uncertainties on the true D/H ratios of the PS-4 and PS-8 films are resulting from both the uncertainty on the measurement of the D/H ratio of the PS-1 and from the uncertainty on the D/H ratio of the PS-D determined by infrared measurements. Their relative error (Rel-err) is about 3% (see Table 1).

We also performed measurements on a terrestrial anthracite sample (a charcoal called DonH8) crushed into a gold foil. The D/H ratio of DonH8 was independently measured by mass spectrometry gas source and it is equal to $(1.40 \pm 0.01) \times 10^{-4}$ [5].

The isotopic measurements were performed by scanning ion imaging with the NanoSIMS-50 at Institut Curie in Orsay. The NanoSIMS isotopic images were acquired with a 16 keV Cs$^+$ primary ion beam (setting the sample potential at -8 kV) with a probe dwell time of 0.5 ms per pixel. Multi-frame scanned images were acquired over 25 μm $\times$ 25 μm areas with 256 $\times$ 256 pixels per frame on PS samples and 50 μm $\times$ 50 μm (512 $\times$ 512 pixels per frame) on DonH8. A primary Cs$^+$ beam of $\sim$12 pA was obtained by

Table 1

Composition of the four polystyrene (PS) films prepared and their associated (D/H)$_{true}$ ratios with uncertainties ($\sigma_{(D/H)}$ at 1σ level) deduced from the values on PS-1 and PS-D samples (see text for details). Rel-err is the relative error of the true D/H ratio. $m(C_8H_8)$ and $m(C_8H_6D_2)$ are the respective masses of powders of non-deuterated and deuterated polystyrene used for the mixing dissolution. f is the ratio of the true D/H ratio of the sample compared with that of the SMOW value (1.5576 $\times 10^{-4}$) [3].

PS films	$m(C_8H_8)$ (g)	$m(C_8H_6D_2)$ (g)	(D/H)$_{true} \pm \sigma_{(D/H)}$	Rel-err	f
PS-1	0.1078 ± 0.0001	0	$(1.88 \pm 0.06) \times 10^{-4}$	3.2%	1.2
PS-4	1.0397 ± 0.0001	0.0017 ± 0.0001	$(5.76 \pm 0.25) \times 10^{-4}$	4.3%	3.7
PS-8	0.8318 ± 0.001	0.0040 ± 0.0001	$(1.32 \pm 0.08) \times 10^{-3}$	6.1%	8.4
PS-D	0	0.3195 ± 0.0002	$(3.20 \pm 0.09) \times 10^{-1}$	2.7%	2055