

D/H MEASUREMENTS IN ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES USING POLYATOMIC IONS WITH SIMS. N. Bardin¹, G. Slodzian¹, T.-D. Wu², D. Baklouti³, E. Dartois³, C. Engrand¹, R. Brunetto³, J.-L. Guerquin-Kern², J. Duprat¹. ¹CSNSM, CNRS/IN2P3-Univ. Paris Sud, Bat 104, F-91405 Orsay (Noemie.Bardin@csnsm.in2p3.fr), ²INSERM, Institut Curie, Univ. Paris Sud, Bat 110, F-91405 Orsay, ³IAS, CNRS-Univ. Paris Sud, Bat 121, F-91405 Orsay.

Introduction: Micrometeorites (i.e. interplanetary dust particles in the 20-500 microns range) extracted from ultra-clean snow in the central regions of Antarctica are well preserved from terrestrial weathering. In the CONCORDIA collection, we identified ultra-carbonaceous Antarctic micrometeorites (UCAMMs) characterized by a high concentration of organic matter (OM) with extreme deuterium excesses [1]. This OM contains a high nitrogen concentration, suggesting that UCAMMs were possibly formed by irradiation of N-rich ices at the surface of bodies beyond the trans-nepunian region [2]. Most D/H measurements are performed using H⁻ and D⁻ secondary ions emission. However, H-bearing polyatomic species with large secondary ion emission yields could be useful for D/H measurements [3]. We present here new results on the possibility to measure D/H ratios at high mass resolution using polyatomic ions with the NanoSIMS-50 (CAMECA). We designed a calibration protocol of the instrumental mass fractionation (IMF), that was applied to D/H microanalyses of an UCAMM fragment.

Samples & Methods: To correct measurements from the IMF, we used a series of standards: a terrestrial anthracite (DonH8) crushed in a gold foil and a set of four polystyrene (PS) films prepared with different mixing proportions of non-deuterated PS (CH₂-CH(Ph))_n and deuterated D-33% PS (CD₂-CH(Ph))_n, purchased from Polymer Source with a purity of 99%. The PS films were ultra-microtomed (~200 nm) and deposited on a silicon wafer. The D/H ratio of the D-33% PS was monitored by an independent infrared measurement, and the nominal D/H ratios of the PS films were estimated from the mixing ratios: (D/H)_{nominal} = (1.56 ± 0.16) × 10⁻⁴, (5.56 ± 0.30) × 10⁻⁴, (1.32 ± 0.08) × 10⁻³ and (3.33 ± 0.10) × 10⁻¹, i.e. 1, 4, 8 and 2000 times the standard mean ocean water (SMOW) value. These ratios will be measured with accuracy by conventional mass spectrometry in the near future. The UCAMM fragment, DC06-05-94 (DC94) was crushed in a gold foil. To clean the surface before analyses, the samples were pre-implanted over a 200 × 200 μm² area using a defocused 8 keV Cs⁺ primary beam of 300 pA during 30 min (total dose ~1 × 10¹⁶ Cs⁺/cm²). NanoSIMS images were acquired with a 16 keV Cs⁺ primary ion beam on 25 × 25 μm² areas (256 × 256 pixels per frame) on PS samples and 50 × 50 μm² (512 × 512 pixels) on DonH8 and DC94, and with a dwell time of 0.5 ms per pixel. Images of

¹²CH⁻, ¹²CD⁻, ¹²C₂H⁻ and ¹²C₂D⁻ ions were acquired simultaneously with a probe diameter of about 0.25 μm carrying ~12.5 pA obtained by tuning lenses (L0, L1) on the primary beam and using a 300 μm aperture diaphragm (D1#1). The ions were simultaneously collected on the detectors 1 to 4 with the same magnetic field. An entrance slit of 5 μm × 100 μm (ES#5) was used, and an aperture slit of 150 μm × 150 μm (AS#3) reduced the beam divergence. For ¹²C₂D⁻ species, at mass 26 and radius 480 mm, a selection slit (ExS) of 10 μm was used. In these conditions, we measured the isotopic ratios CD⁻/CH⁻ on PS, and C₂D⁻/C₂H⁻ on PS, DonH8 and DC94.

An advanced mass resolution (AMR) protocol was developed to improve the spectrometer mass resolution by characterizing the secondary ion beam and choosing a specific spectrometer entrance axis on which to align the secondary ion beam [4].

Results & Discussion: Fig. 1 shows the spectrum at mass 26 from an ultrathin section of the D-33% PS sample. ¹²C₂D is well separated from ¹²C¹³CH and its separation with ¹²C₂H₂ is sufficient to measure D/H ratios, even at natural abundance levels.

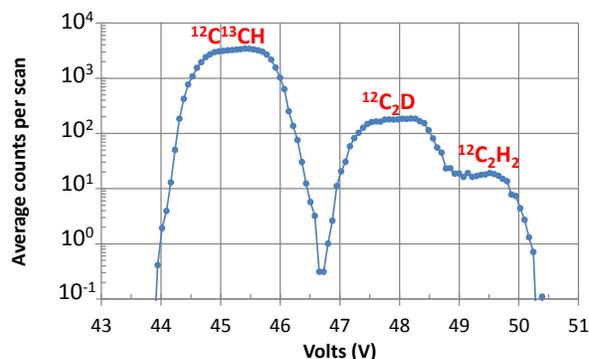


Figure 1: Mass spectrum recorded at mass 26 from an ultrathin section of the D-33% PS sample. The spectrum was averaged over 10 scans. The abscissa scale in volts refers to mass scanning with dedicated deviation plates. Voltage variations are proportional to (ΔM/M), the relative mass difference between mass lines. The built-in voltage scanning step has been here divided by 2.

The relative mass differences (ΔM/M) separating C₂D from ¹²C¹³CH and C₂H₂ are 1/8900 and 1/16800, respectively. Following the conventional definition of the mass resolving power (MRP = 0.5/MLW(10%)), where MLW(10%) is the mass line width - in relative mass units - containing 80% of the total line intensity, a MRP of 24,000 is achieved in the conditions of Fig. 1.

The AMR protocol allows to use the NanoSIMS at high mass resolution without suffering from a substantial loss in signal. For example, on DC94, $\sim 1.6 \times 10^5$ c/s were collected from C_2H^- , resulting in a ratio Γ of the signal produced per primary Cs^+ current of $\sim 1.4 \times 10^4$ c/s.pA $^{-1}$ at high mass resolution, compared to $\Gamma \sim 1.7 \times 10^4$ c/s.pA $^{-1}$ obtained from H^- signals at low mass resolution.

The IMF calibration curves (Fig. 2) show the CD^-/CH^- and C_2D^-/C_2H^- isotopic ratios measured on a series of 4 to 7 acquisitions obtained from different areas on each reference sample.

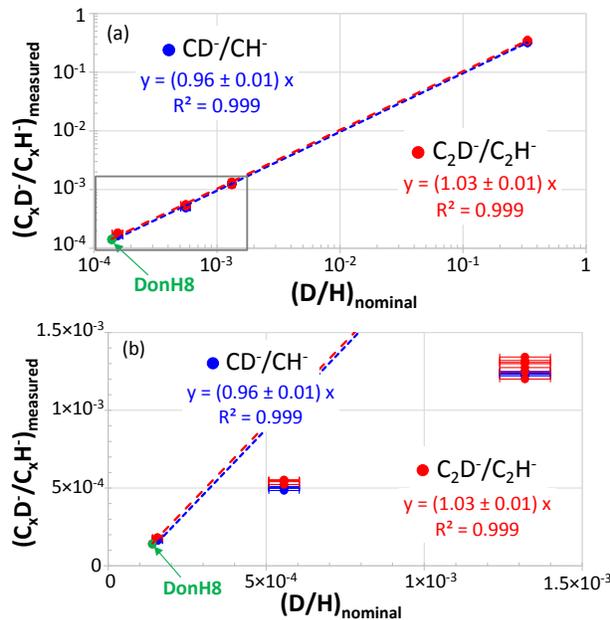


Figure 2: (a) IMF calibration curves of CD/CH (blue line) and C_2D/C_2H (red line) obtained on a series of PS samples and on DonH8 (green dot). 2σ errors are on the order of the dot size; (b) Enlargement in linear scale of the rectangle drawn in Fig. 2a, for $0 < D/H < 1.5 \times 10^{-3}$.

The regression line equation is calculated by the least-squares method. For the measured ratios, the statistical errors (2σ) are close to the counting statistics on each acquisition and the external reproducibility (2σ) between different acquisitions is on average 3% for CD/CH and 4% for C_2D/C_2H . Using either CH or C_2H , the IMF regression curve has a slope close to 1, an intercept compatible with the origin and a linear determination coefficient R^2 close to 1. We obtained an IMF ($\alpha = R_{meas}/R_{nom}$) equal to 0.96 ± 0.01 and to 1.03 ± 0.01 for the CD/CH and C_2D/C_2H ratios, respectively.

The instrumental isotopic fractionation using polyatomic ions (CH^- , C_2H^-) is thus small compared to isotopic analyses using single ions (H^-). This is probably due to the large secondary emission yields of ions like CH^- , OH^- , C_2H^- , related to their high electron affini-

ties (EA) (1.24eV, 1.83eV and 3eV, respectively), compared to that of H^- (EA=0.75eV), entailing lower emission fractionation, and to the small mass difference between C_2D and C_2H compared to that between D and H (lower detection fractionation).

Figure 3 represents the C_2D^-/C_2H^- ratio image from the DC94 fragment. The bulk D/H ratio is $D/H_{bulk} = (5.4 \pm 0.4) \times 10^{-4}$ [$\delta D_{bulk} = 2500 \pm 250$ ‰]. The isotopic distribution is highly heterogeneous, and exhibits extreme deuterium excesses, up to 35 times the SMOW value: $D/H_{max} = (5.4 \pm 0.5) \times 10^{-3}$ [$\delta D_{max} = 34,000 \pm 3000$ ‰].

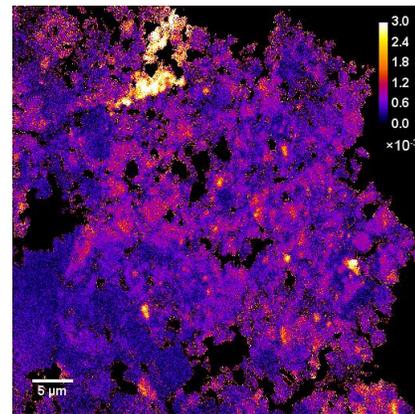


Figure 3: C_2D^-/C_2H^- image (processed with ImageJ) from an UCAMM fragment (DC94) pressed into a gold foil. Field of view $50 \times 50 \mu m^2$ with 512×512 pixels (probe size $\sim 0.25 \mu m$).

Conclusion: At a given magnetic field, ions ranging from ^{12}C to $^{12}C^{15}N^-$ are available for simultaneous measurements in the focal plane of the NanoSIMS, which is not the case for H^- and $^{12}C^{15}N^-$. The AMR protocol [4] provides the mass separation needed for measuring safely isotopic ratios like $^{12}CD^-/^{12}CH^-$ or $^{12}C_2D^-/^{12}C_2H^-$. Thus, using polyatomic ions allows simultaneous measurements of the hydrogen and the nitrogen ($^{12}C^{15}N^-/^{12}C^{14}N^-$) isotopic compositions in extraterrestrial samples. $^{12}C_2D^-/^{12}C_2H^-$ and $^{16}OD^-/^{16}OH^-$ isotopic ratios can also be measured simultaneously, which provides access to the hydrogen isotopic composition of organic matter and of hydrated minerals in extraterrestrial samples, respectively.

Acknowledgements: This study was funded by the ANR project OGRESSE (11-BS56-026-01) and by CNES. The Antarctic micrometeorite collection at CONCORDIA was supported by IPEV and PNRA.

References: [1] Duprat J. et al. (2010) *Science*, 328, 742–745. [2] Dartois E. et al. (2013) *Icarus*, 224, 243–252. [3] Piani L. et al. (2012) *Analytical Chemistry*, 84, 10199–10206. [4] Slodzian G. et al. (2014) *Microscopy & Microanalysis*, in press.