

MEASURING ISOTOPE RATIOS ACROSS THE SOLAR SYSTEM. C. R. Webster¹ and P. R. Mahaffy², ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109; Chris.R.Webster@jpl.nasa.gov ²NASA Goddard Space Flight Center (GSFC), 8800 Greenbelt Rd., Greenbelt, Md., 20771. Paul.R.Mahaffy@nasa.gov

Introduction: Stable isotope ratios in C, H, N, O and S are powerful indicators of a wide variety of planetary geophysical processes that can identify origin, transport, temperature history, radiation exposure, atmospheric escape, environmental habitability and biology [1].

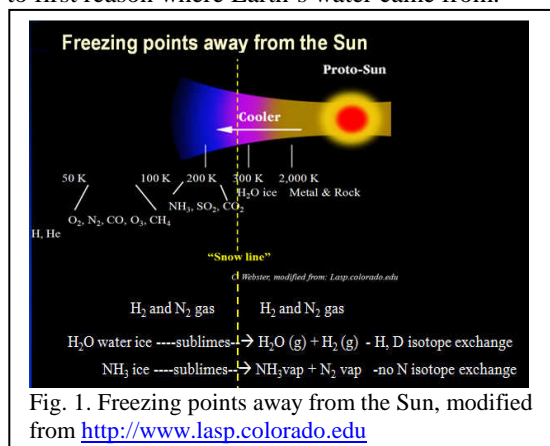
For the Allan Hills 84001 meteorite, for example, the $^{13}\text{C}/^{12}\text{C}$ ratio identifies it as a Mars (SNC) meteorite; the $^{40}\text{K}/^{40}\text{Ar}$ ratio tells us the last time the rock cooled to solid, namely 4 Gya; isotope ratios in ^3He , ^{21}Ne and ^{38}Ar show it was in space (cosmic ray exposure) for 10-20 million years; ^{14}C dating that it sat in Antarctica for 13,000 years before discovery; and clumped isotope analysis of $^{18}\text{O}^{13}\text{C}^{16}\text{O}$ in its carbonate that it was formed at $18 \pm 4^\circ\text{C}$ in a near-surface aqueous environment [2].

Solar System Formation: The conditions of the Big Bang synthesized only the first three elements H, D, ^3He and ^7Li [3]. Three minutes later nucleosynthesis in stars and supernovae [4] produced other elements in various isotopic forms that returned heavy-element enriched elements to interstellar matter for new star formation [5]. During the formation of our solar system 4.5 Gya, collapsing dust and gas first coalesced into a spinning, heating protosun as nuclear reactions fired up the Sun. As the nebula cooled, volatiles condensed out far from the Sun to form outer planets, while closer in, refractory solid material condensation formed the terrestrial planets. Eventually, a period of strong solar wind cleared out the remaining gas from the disk.

The Nice Model [6] has detailed the complex dynamics that led to our current planetary configuration. Initially the four giant planets were in compact circular orbits surrounded by a huge disk of planetesimals out to nearly 40 AU. Jupiter first migrated inward to 1.5 AU, truncating inner planetesimal disk, and then outward with Saturn's pull while the inner planets formed. Jupiter and Saturn's migration into mutual orbital resonances shifted Neptune and Uranus into elliptical orbits to completely destabilized the solar system into a chaotic period of sweeping up planetesimals and scattering comet and asteroids into a one hundred million period of the Late Heavy Bombardment (LHB)[7]. Objects that did not accrete to form large enough bodies to differentiate are believed to retain the chemical composition of the original condensed solar nebula. Thus the oldest meteorites, asteroids and comets must hold clues about the early phases of solar system evolu-

tion, and their isotopic ratios (e.g. D/H, $^{18}\text{O}/^{16}\text{O}$) may reveal their role in bringing volatiles to the Earth during the LHB. In less than 100 Myears, the LHB is estimated [5] to have delivered about 200 tons/m² (!) of extraterrestrial material, with ~3,000 impact structures >100 km in size and ~10 structures larger than the 1,300 km-Imbrium basin on the Moon.

Isotopic ratios offer the key to unraveling the complex dynamics and chemistry associated with the formation and evolution of planetary bodies (planets, satellites and primitive bodies) including differentiation by retaining a fingerprint record of temperature, radiation environment and sun-distance location through equilibrium, disequilibrium, and temperature-dependent chemical processes. In the overly-simplified world of equilibrium temperatures, we begin by identifying condensation temperatures of various elements and gases (Fig. 1) in reference to the "snow line" where water vapor freezes to ice. Transport across this snow line changes isotopic composition of some species (e.g. D/H in water) but not in others (e.g. in H_2 , N_2 gas, or in N when ammonia ice sublimates), and this has been used [8] to first reason where Earth's water came from.



Noble Gas Abundances and Isotopic Ratios:

Noble gas abundances are a powerful discriminators of atmospheric and planetary volatile evolutionary models [9]. Although it is believed that noble gases in our Sun are the same as those present in the solar nebula from which terrestrial planets (and meteorites) were formed, presolar material (grains) were discovered to have survived in primitive meteorites (e.g. Murchison Meteorite) that showed very different (orders of magnitude) Xe, Ne, C, N and O isotope ratios [10]. Equally interesting are Earth observations that our atmosphere has a

ten-fold noble gas excess (Fig. 2) that cannot originate from the strongly degassed mantle, but is believed delivered with other volatiles and organic carbon by impacts from icy planetesimals that trapped noble gases at low temperatures [7].

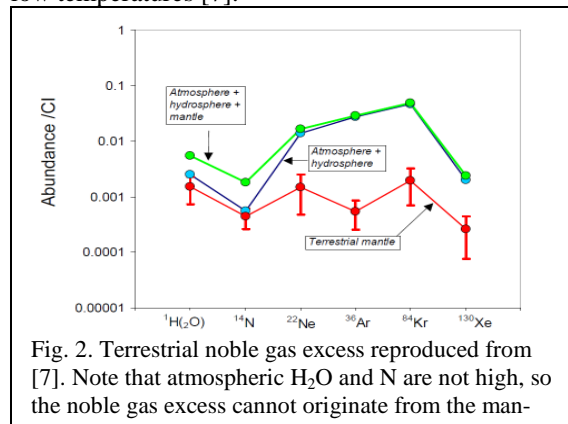


Fig. 2. Terrestrial noble gas excess reproduced from [7]. Note that atmospheric H₂O and N are not high, so the noble gas excess cannot originate from the man-

On Earth, Xenon's nine isotopes are strongly mass-fractionated (4% per amu), and although ¹²⁹Xe is hugely depleted compared to chondrites (implying that most of the Xe escaped), there remains 7% too much ¹²⁹Xe, an anomaly [11] in discord with our fundamental understanding of solar system formation as evidenced from Jupiter observations (Fig. 3).

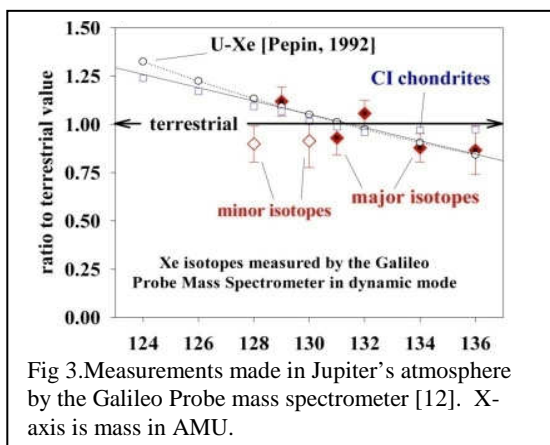


Fig 3. Measurements made in Jupiter's atmosphere by the Galileo Probe mass spectrometer [12]. X-axis is mass in AMU.

Stable Isotope Ratios: For stable isotope ratios in 3-isotope systems, departures from mass-dependent (MD) fractionation have detailed a variety of processes from ozone hole photochemistry (O) to the emergence of life (S) and planetary migrations (O). Unfortunately, neither carbon nor nitrogen have a third stable isotope and cannot be used to study mass-dependent nor mass-independent (MI) processes.

The D/H Ratio. The D/H ratio exhibits a wide range of enrichments and depletions compared with isotopic (SMOW) standards for two reasons: first, adding a neutron to a light element has a larger effect than doing so to heavier elements like C, N, O, S; second,

water undergoes large fractionations during freezing or sublimation due to the large differences in ground state vibrational energy between HDO and H₂O.

On Earth, and in partnership with delta-¹⁸O measurements, the D/H ratio has been used to successfully record rainfall maps, detail cirrus cloud formation [13], identify water salinity, and record the long-term climate record [14]. For our solar system, D/H is a powerful tool for identifying origin, migration and evolution.

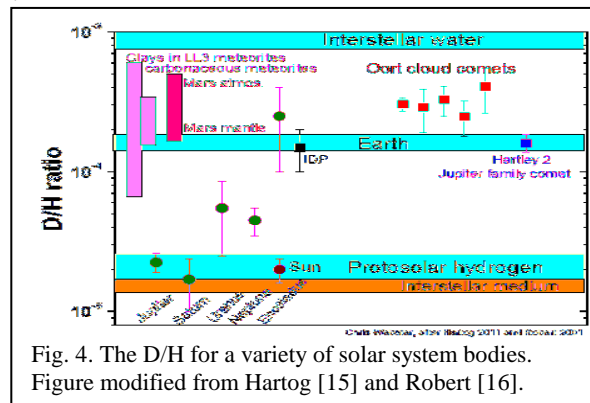


Fig. 4. The D/H for a variety of solar system bodies. Figure modified from Hartog [15] and Robert [16].

The Martian atmosphere is strongly enriched in D/H due to atmospheric escape processes initiated when Mars lost its magnetic field. However, it is expected that the mantle and crust will show increasingly lower D/H values in hydrated minerals formed at earlier times. The Mars Science Laboratory SAM experiment will trace the history of Mars evolution through the sedimentary record of Gale Crater.

Until the very recent and striking observation of Hartley-2 by Hartog et al. [15] from the Herschel Space Observatory, the theory that comets delivered water to Earth was questionable since Oort cloud comets had D/H values three times that of terrestrial SMOW. With the right D/H ratio, Jupiter-family comets look more likely delivery agents (see Fig. 4).

Carbon ¹³C/¹²C isotope ratio. Biological processes are well known to prefer the use of ¹²C (evaporation, diffusion through leaf stomata, enzyme reactions) and produce depletions in delta-¹³C that are typically 2.7% for C₃ plants that use Calvin-Benson photosynthesis pathway, and 1.3% for C₄ plants using the Hatch-Slack pathway [17]. This fractionation has been used in climate change studies to identify sources and sinks of the increasing atmospheric carbon dioxide since its' delta-¹³C values distinguish oceanic and biospheric sources.

With the discovery of methane on Mars [18], experiments are planned [19] by MSL's SAM-TLS instrument to measure the delta-¹³C in methane to determine if sub-surface bacteria (e.g. methanogens) that on Earth produce large depletions in delta-¹³C (to 12%) might

be the source. Lower depletions would indicate non-biological (rock chemistry) production (see Fig. 5).

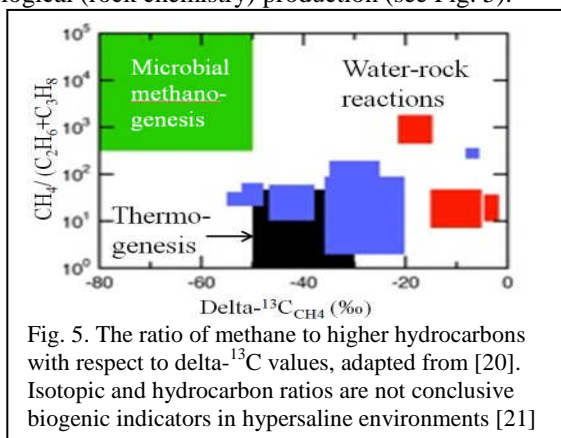


Fig. 5. The ratio of methane to higher hydrocarbons with respect to $\delta^{13}\text{C}_{\text{CH}_4}$ values, adapted from [20]. Isotopic and hydrocarbon ratios are not conclusive biogenic indicators in hypersaline environments [21]

Oxygen $^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$ isotope ratios. Oxygen is highly reactive and produces numerous compounds. Due to isotopic exchange between oxygen-containing rocks (e.g. carbonates) and water (e.g. the terrestrial hydrosphere), the triple isotope system in oxygen compounds is an extremely important identifier of alteration processes (fluid-rock interactions, hydrothermal alteration) and is used to classify solar system material including meteorites [1]. In general, the $\delta^{18}\text{O}$ value is a good proxy for mineral type, and can detail gemstone origin and trade routes.

In the triple isotope plot (Fig. 6) of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ [22], lunar samples fall on the mass-dependent (slope = 0.5) terrestrial fractionation line, and this observation was used as evidence that the Moon formed during the final stages of Earth's accretion 4.5 Gya when Earth collided with another large body (Theia) originating from the same region of the solar nebula [23]. While some meteoritic classes join Earth, Moon and Mars in slopes of 0.5 (although with different offsets and therefore reservoirs), at the big picture of Fig. 6, most solar system bodies (solar oxygen, chondrules, molecular clouds and asteroidal water) lie on the unity mass-independent slope.

The enrichment in ^{16}O of the Sun measured by Genesis and of calcium-aluminum inclusions (CAI) cannot be reconciled with conventional MD fractionation, and a variety of explanations have been put forward (e.g. supernova injection, CO self-shielding, fractionation in the protoplanetary disk, and even heterogeneous chemistry on interstellar dust) [see the review of Dominguez, 2010 [22]].

Clumped isotopes in C and O. As a further constraint on the environment of alteration processes, John Eiler's group developed a method of clumped isotope analysis of $^{18}\text{O}^{13}\text{C}^{16}\text{O}$ in carbonates to identify temperature of formation, used to suggest that carbonates in Allan Hills 84001 were formed at $18 \pm 4^\circ\text{C}$ in a near-

surface aqueous environment [2]. Although clumped or multiply-substituted isotopes are in very low abundances, new techniques like cavity ring-down may help open up this emerging field for planetary exploration.

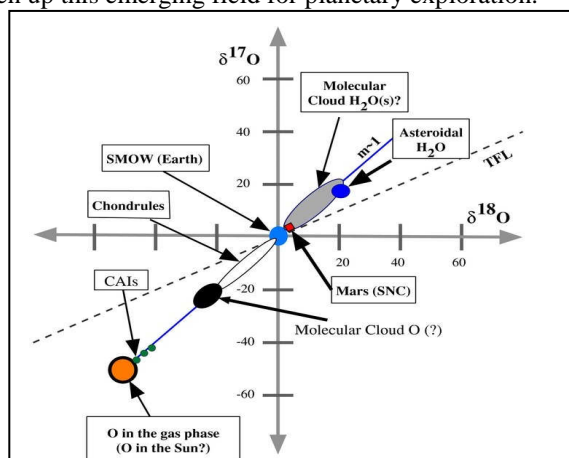


Fig. 6. Reproduction of Fig. 2 in Dominguez (2010), reference [22], summarizing oxygen isotope data.

Sulfur $^{34}\text{S}/^{33}\text{S}/^{32}\text{S}$ isotope ratios. In triple isotope plots, the “ Δ ” value is used to quantify the difference (offset) of a delta-value from the mass-dependent slope, which for $\delta^{33}\text{S}$ vs. $\delta^{34}\text{S}$ would be a slope of 0.5. Isotope ratios in S are very powerful for identifying sources and sinks for atmospheric sulfur, and especially photochemical processes (e.g. Earth and Venus sulfur cycles), and on Earth played a pivotal role in recording the emergence of life some 2.2 Gya: In the absence of O_2 , stratospheric UV photolysis of SO_2 rained out surface sulfates with a large range of $\Delta^{33}\text{S}$ values, but once cyanobacteria became the main source of surface sulfates, the observed spread was very narrow [24].

Nitrogen $^{15}\text{N}/^{14}\text{N}$ isotope ratio. Planetary atmospheric escape processes depend principally on mass differences, and like $^{13}\text{C}/^{12}\text{C}$, D/H and $^{18}\text{O}/^{16}\text{O}$, the nitrogen $^{15}\text{N}/^{14}\text{N}$ ratio shows enrichment in the atmosphere of Mars. Nitrogen is also very important as a potential biomarker, and as a discriminator in the very different physics of fractionation of molecular nitrogen N_2 and ammonia NH_3 , the latter being a significant component of the ice giants. Unlike water, the sublimation of ammonia ice into vapor and N_2 gas results in little or no isotope exchange in nitrogen [8]. Thus, in conjunction with D/H in water, the $^{15}\text{N}/^{14}\text{N}$ ratio is a powerful discriminator of transport across the “snow” lines of water and ammonia [8].

Requirements for Measurement of Planetary Isotope Ratios: The table below provides a guide to the requirements for measuring isotope ratios based on sensitivities identified for planetary science objectives.

Measurement	Requirement
Elemental ratios to solar	2-5%
Noble gas isotope ratios	3%
D/H	1-20%
$\delta^{13}\text{C}$	0.1-2 ‰
$\delta^{13}\text{C}$ biological	5-10 ‰
$\delta^{18}\text{O}$, $\delta^{17}\text{O}$	0.2-2 ‰
$\delta^{15}\text{N}$	0.2-2 ‰
$\delta^{34}\text{S}$, $\delta^{33}\text{S}$	0.2-1 ‰

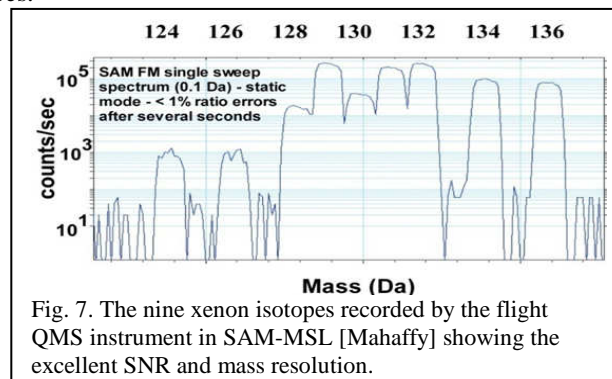
Mass Spectrometry: Mass spectrometry has to date provided a truly enormous wealth of information about our solar system [25], measuring the composition of numerous planets and satellites (e.g. Mars, Jupiter, Titan, Moon, Enceladus, Venus, comets, asteroids) usually for the first time, detailing a wide variety of geophysical and geochemical processes, and with its additional study of meteorites and primitive bodies, is the backbone of measurements behind our fundamental understanding of the solar system and its evolution.

Mass spectrometers are unique in their survey capability and ability to measure the very important noble gases and their isotope ratios that are not accessible by optical means. For stable isotope measurements in C, H, N, O and S, IRMS mass spectrometers are the recognized standards on Earth, where sub-per-mil precision is readily achieved with large, complex laboratory setups. However, for planetary missions where only a few tens of kg are available, this high performance cannot be readily achieved. In particular, mass interferences make measuring isotope ratios in water, ammonia and methane very difficult if these species are in similar abundances, as we saw from the Enceladus plume results [26] from Cassini.

Planetary mass spectrometers flown have included GCMS magnetic sectors (Viking, Rosetta Ptolemy), magnetic sectors (Phoenix), time-of-flight reflectron (Rosetta ROSINA) or secondary-ion (Rosetta COSIMA) mass spectrometers, and linear quadrupole mass spectrometers (Galileo, Huygens, MSL-SAM). Orbitrap mass spectrometers are under development by many groups.

The linear quadrupole mass spectrometer (QMS) developed by NASA GSFC for Galileo, Cassini Orbiter, Cassini Huygens Probe, MSL, Maven, and LADEE missions is able to determine repeatable isotope ratios to better than 1% precision. Examination of the signal levels at 134, 135, 136, and 137 Da in Fig. 7 illustrates that with a precisely fabricated and aligned set of hyperbolic rods and ion focusing optics a crosstalk of

less than 10^{-5} is achieved between adjacent mass channels. The wide dynamic range of the SAM QMS is combined with its gas enrichment, separation techniques and static mass spectrometry to enable measurement of minor ^{124}Xe and ^{126}Xe atmospheric isotopes.



Additional recent advances in mass spectrometry for a future Mars rover [27] allow ions from either a GCMS electron impact source or ions directly laser desorbed from a solid sample (LDMS) at the Mars pressure of 5-7 torr to be introduced into opposite ends of a linear ion trap. In the LDMS mode a fast aperture valve developed at GSFC is opened just before the laser fires one or multiple shots and then immediately closed. Ions pulled into the linear trap by the gas flow are trapped with a low amplitude RF field as the mass spectrometer chamber is pumped until the pressure is sufficiently low to turn on the detectors and initiate a mass scan. Better than unit mass resolution up to ~1000 Da has been demonstrated with a miniature linear trap (3 mm radius, 3 cm long). The ion trap has the additional advantage of tandem mass spectrometry to more definitively identify complex organic species.

IR Tunable Laser Spectroscopy: For light molecules at pressures below ~100 mbar, IR tunable laser spectroscopy offers a direct, non-invasive, unambiguous method for measuring stable isotope ratios to sensitivities of ~1 ‰ for planetary low-mass (<5 kg), all-solid-state instruments. Tunable laser spectrometers are particularly well suited to H_2O , NO, NO_2 , HNO_3 , O_3 , CO, CO_2 , NH_3 , SO_2 , HCl, N_2O and CH_4 .

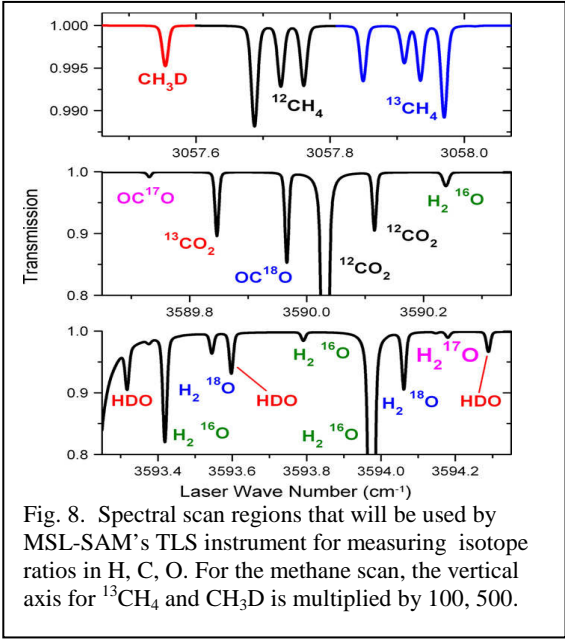
The secret to success for this method lies in the spectroscopy of the IR region (1-30 μm), in which most simple molecules have several vibrational bands (3N-6 for non-linear, 3N-5 for linear molecules) containing about one hundred rotational absorption lines from which key lines can be chosen that are well separated from each other and from other interfering gases. High symmetry in simple molecules like tetrahedral CH_4 can produce degeneracies and a complex ro-vibrational line system, but linewidths for most molecules are typically $<0.02\text{ cm}^{-1}$. With a laser linewidth one twentieth of the

molecular linewidth, high sensitivity is achieved since there is no significant “instrument function” to broaden measured lines and thereby reduce absorption depths.

Isotopic shifts between vibrational bands depend to a first order on reduced mass differences; for HDO and H₂O this is large, while for ¹³C this is more typically about 11 cm⁻¹ (but varies). In methane at 3.3 μm, we are fortunate that the 11-cm⁻¹ shift does not dump the ¹³CH₄ line group ontop of the adjacent ¹²CH₄ group but just to the side (see Fig. 8 and reference [19]).

Unlike mass spectrometers, laser spectrometers are usually not stuck with the mass ratio dynamic range, but can often be tuned to regions where both parent and minor isotope (e.g. ¹²CO₂ and ¹³CO₂ and/or ¹⁸OCO) have absorption lines of similar intensity (see Fig. 8 middle panel). This helps with the precision of the ratio measurement. Because CO₂ and H₂O have numerous overlapping bands, this is readily done, but note that this luxury is not afforded to the isolated CH₄ band at 3.3 μm, and we are stuck with ¹³CH₄ lines that are typically ~90 times weaker than those of ¹²CH₄.

The Mars Science Laboratory (MSL) Curiosity Rover will begin on-surface measurements in Fall 2012, and isotope ratio measurements will be made by the Sample Analysis at Mars (SAM) suite’s [28] quadrupole mass spectrometer (QMS) and the tunable laser spectrometer (TLS). Measurements will be made of the Martian atmosphere and also of gases evolved from pyrolysis, or generated during combustion, of solid samples. Expected capability is given below:



Measurement	SAM Capability	Primary
Noble gas isotope ratios	3%	QMS
D/H in water	1%	TLS, QMS
δ13C in CO ₂	2 ‰	TLS, QMS
δ13C in methane	10 ‰	TLS
δ18O, δ17O in CO ₂ and H ₂ O	2-5 ‰	TLS
δ15N	20 ‰	QMS
δ34S, δ33S in SO ₂	20 ‰	QMS

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