Fundamentals of Isotopic Ratios

Mass Spectrometry

Lionnel MOUNIER
History: key dates

• **1906**: Thompson received the Nobel Prize for his work on charged particles

• **1922**: Aston received the Nobel Prize for the discovery of 212 of the naturally occurring isotopes using three generations of mass spectrographs

• **1930’s**: Urey developed the theory of isotope geochemistry and received the Nobel Prize for the discovery of Deuterium

• **1940’s**: Nier developed the first IRMS, a double-focusing double inlet MS

• **1947**: Jenckel built the first MS at Altas-Werke AG in Bremen and created a new small division: MAT

• **1953**: MAT launched the first commercial IRMS
History: from MAT to Thermo
History: pioneers

Harold C. Urey, Cesare Emiliani, and G.J. Wasserburg in Urey's lab

Photo taken in 1953, University of Chicago archives.
Organic MS vs IRMS: What is the difference?

In **Organic MS** the analyte is the substance of interest and the analytical questions are usually closely related to it (molecular weight, structure, amount)

*In Isotope Ratio MS the analyte in very many cases is only the carrier of information. The analytical question may be quite unrelated.*

In **Organic MS** the result of a single analysis can carry all requested information

*In Isotope Ratio MS the result of a single analysis is basically meaningless. The information hidden in isotope ratios can only be accessed in comparison to other isotope ratios*
Analytical information from a sample

Analysis of the Isotopic Composition: Source, Origin, Fate?

Quantification: How Much?

Substance Identification: What?
What is an isotope?

Frederick Soddy (1877-1956) originated the word *isotope* from the Greek words *isos* meaning “equal” (as in chemically non-separable) and *topos* meaning “place” or of the same place in the periodic table.

An isotope is the same element with the same number of protons but differing number of neutrons.
**What is an isotope?**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Protons</th>
<th>Neutrons</th>
<th>Total</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{16}\text{O}$</td>
<td>8</td>
<td>8</td>
<td>16</td>
<td>99.763%</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>8</td>
<td>9</td>
<td>17</td>
<td>0.0375%</td>
</tr>
<tr>
<td>$^{18}\text{O}$</td>
<td>8</td>
<td>10</td>
<td>18</td>
<td>0.1905%</td>
</tr>
</tbody>
</table>

**Diagram:**
- $^{12}\text{C}$: $6p^+, 6n, 6e^-$
- $^{13}\text{C}$: $6p^+, 7n, 6e^-$
- $^{14}\text{C}$: $6p^+, 8n, 6e^-$
Definitions

• Isotope
  • Nuclides having the same atomic number but different mass numbers, e.g. $^{12}\text{C} (6p + 6n)$, $^{13}\text{C} (6p + 7n)$

• Isotopologue
  • A molecular entity that differs only in isotopic composition (number of isotopic substitutions), e.g. $^{12}\text{CO}_2$, $^{13}\text{CO}_2$

• Isotopomer
  • Isomers having the same number of each isotopic atom but differing in their positions, e.g. $^{15}\text{N-N-O}$, $\text{N}^{15}\text{N-O}$

• Clumped isotopes
  • Molecules with bonds between minor abundant isotopes
    • $^{13}\text{C}^{18}\text{O}$ ($\text{CO}_2$, $\text{CO}$), $^{17}\text{O}^{18}\text{O}$ ($\text{O}_2$), $^{34}\text{S}^{18}\text{O}$ ($\text{SO}_2$), $^{13}\text{C}^{2}\text{H}$ ($\text{CH}_4$)
Type of isotopic systems

**Radioactive:** naturally unstable isotopes that spontaneously disintegrate or decay to form new isotopes or elements.

e.g. $^{87}\text{Rb} \rightarrow ^{86}\text{Sr}$

e.g. $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{Pa} \rightarrow ^{234}\text{U} \text{ ..................................} ^{206}\text{Pb}$

Radioactive isotopes are commonly used to determine age in geology and in archaeology.

**Stable:** naturally stable - so, don’t spontaneously disintegrate or decay.

e.g. Oxygen ($^{16}\text{O}, ^{17}\text{O}, ^{18}\text{O}$), Carbon ($^{12}\text{C}, ^{13}\text{C}$)

Also: Lithium ($^{6}\text{Li}, ^{7}\text{Li}$), Sulfur ($^{32}\text{S}, ^{33}\text{S}, ^{34}\text{S}, ^{36}\text{S}$), Iron ($^{54}\text{Fe}, ^{56}\text{Fe}, ^{57}\text{Fe}, ^{58}\text{Fe}$)...

**Noble:** the elements in the last column of the periodic table: helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe). There are stable and they are called noble because not chemically reactive.
Different types of IRMSs

• TIMS (Thermo Ionization Mass Spectrometer): *Triton Plus*

• MC-ICP-MS (Multi-Collector ICP-MS): *Neptune Plus*

• Uranium Hexafluoride Isotopic Analysis MS: *Uranus*

• SIRMS or Gas-IRMS (Stable Isotope Ratios Mass Spectrometers): *Delta V, MAT 253 & MAT 253 Ultra*

• SVMS or Noble Gas MS (Static Vacuum Mass Spectrometers): *Argus VI, Helix SFT & Helix MC*
Different types of IRMSs

- Delta V
- Argus VI
- Triton Plus
- Neptune Plus
- MAT 253
- Helix SFT
- Uranus
- MAT 253 Ultra
- Helix MC
Anatomy of an IRMS

All the IRMSs have a common anatomy

- **Magnet** to deflect the ions according on their m/z
- **Ionization Source** to produce the ions
- **Multi-collector** for parallel detection of the ion beams
- **Vacuum system**
This combination of sources enable to ionize almost all the Mendeleyev table
Working principle of a magnetic sector field mass analyzer

Lorentz force:

\[ F = q(E + v \times B) \]

\[ r = \frac{m^*v}{e^*B} \]
The Mass Spectrometry Equation

If an ion of mass $M$ and charge $Z$ is accelerated in a potential $V$ and injected into a uniform magnetic field $B$, then the ion experiences a force and moves in a circular orbit of radius $R$. The motion is defined by:

$$\frac{M}{Z} = \frac{B^2 R^2}{2V}$$

For singly-charged ions, the radius is determined by the nature of the magnetic and electric fields.

The combination of fields selects ions of particular mass and forms a mass filter.
Why sector field MS?

• Unique features of magnetic sector field mass analyzers are mandatory for precise isotope ratios analysis:

  • High acceleration voltages give high transmission
    • High sensitivity, mandatory for minor isotopes

  • Ions with different mass are separated in space
    • Ability for parallel detection, mandatory for high precision isotopic ratios

  • Ability for high mass resolution
    • Elimination of interferences, critical in ICP-MS
Why multi-collection? Sequential measurement of isotopes

Precision and accuracy of the ratio depend on signal stability

\[ IR = \frac{I_{\text{isotope1}}(t)}{I_{\text{isotope2}}(t)} \]
Why multi-collection? Parallel measurement of isotopes

\[ IR = \frac{I_{\text{isotope1}}(t)}{I_{\text{isotope2}}(t)} \]

Precision and accuracy of the ratio \textit{independent of signal stability}
Peak Shape

The peak shape is defined by the source and resolving slits because the analyzer is constructed such that the image of the source slit is focused at the resolving slit.

When the resolving slit is much narrower than the source slit, a triangular peak shape is observed. This is the case of analytical MSs.

When the resolving slit is much wider than the source slit, a broad, flat-topped peak is observed. This is the case of IRMSs.
Peak Shape

A pronounced difference between analytical and isotope ratio instruments lies in the peak shape observed by scanning the magnetic or electric fields.

An analytical instrument provides a spectrum of mass peaks that is characteristic of chemical composition. Very narrow peaks are used to distinguish closely spaced masses.

In isotope ratio work, the chemical composition of the sample is known and the fields are held constant. The variation of isotopes in an element is most precisely measured by using broad peaks.

Flat top peaks are mandatory for high precision isotopic measurements.
Peak Shape

CO$_2$

N$_2$
Type of Isotope Ratios Measurements

**Natural abundance**
Natural variations in the isotopic content of substances occur due to the different physico-chemical properties of isotopes.

**Tracer levels**
A chemical containing a ‘high’ dose of a minor isotope is input into a system to enable a process to be followed. (Note: many agricultural and biomedical applications use enriched tracers)

**Isotope dilution**
Isotope spikes are used to determine the concentration of an analyte element.
Anatomy of a Gas-IRMS

On-line or Off-line

Sample Preparation

Pure Gas

Intro. System

Dual Inlet or Cont. Flow

Ref. Gas

Sample

Sample/Reference Gas Comparison (ref. gas calibrated to international standard)

MAGNET

Ionization Source

Vacuum system

Detectors

light masses

heavy masses
How do we get the highest accuracy and precision?

(1) Ratio measurement: measuring ratios makes life easier

Isotope 1 and isotope 2 being measured at the same time, precision and accuracy of the ratios are independent of the signal stability.
How do we get the highest accuracy and precision?

(2) Difference measurement:
measuring the difference between sample and reference makes life easier.

By measuring relative differences, the highest precision can be achieved.
Stable Isotopes

**Hydrogen**
- Mass 1: 99.984%
- Mass 2: 0.0156%

**Carbon**
- Mass 12: 98.892%
- Mass 13: 1.108%

**Nitrogen**
- Mass 14: 99.635%
- Mass 15: 0.365%

**Oxygen**
- Mass 16: 99.759%
- Mass 17: 0.037%
- Mass 18: 0.204%

**Sulphur**
- Mass 32: 95.02%
- Mass 33: 0.76%
- Mass 34: 4.22%
- Mass 36: 0.014%
Natural variations

- Ocean water
- Arctic sea ice
- Marine moisture
- (Sub)tropical precipitation
- Temperate zone
- Polar ice
- Alpine glaciers
- Lake Chad
- Wood cellulose
- Temperate zone
- Clay minerals

- Atmospheric CO₂
- Marine HCO₃⁻
- Marine carbonate
- Marine plankton
- Land plants C₄ type
- Land plants C₃ type
- Groundwater HCO₃⁻
- Fresh-water carbonate
- Wood
- Peat
- Coal
- Oil
- Natural gas
- Bacterial CH₄
- Animal bone
- Diamond
### Most important stable isotopes:

<table>
<thead>
<tr>
<th>Element</th>
<th>Minor Isotope</th>
<th>Natural Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$^2$H (D)</td>
<td>0.01557</td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{13}$C</td>
<td>1,11140</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{15}$N</td>
<td>0.36630</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{18}$O</td>
<td>0.20004</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{34}$S</td>
<td>4.21500</td>
</tr>
</tbody>
</table>

### Delta Notation:

\[
\delta \text{ [‰]} = \left( \frac{R_{\text{Sample}}}{R_{\text{Reference}}} - 1 \right) \times 1000
\]
Delta Notation

- The delta notation was introduced by geochemists to represent small variations of the isotopic ratio in natural abundance materials.

- Mostly, stable isotope ratios are measured relative to a reference, and reported in the $\delta$ - notation in ‰:

$$
\delta \left[ \% \right] = \frac{R_{\text{Sample}} - R_{\text{Reference}}}{R_{\text{Reference}}} \times 1000 = \left( \frac{R_{\text{Sample}}}{R_{\text{Reference}}} - 1 \right) \times 1000
$$

- Arguments:
  - measuring absolute isotope abundances is difficult
  - consequently, the isotope abundance ratio of a sample is always measured versus a reference material
  - by measuring relative differences, the highest precision can be achieved
Primary Reference Standards

- The reference standard materials are available from the International Atomic Energy Agency (IAEA) in Vienna. This also includes all the NBS isotope standards.

<table>
<thead>
<tr>
<th>Element Ratio</th>
<th>Primary Reference Standard</th>
<th>Isotope Ratio, R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{2}H/^{1}H$</td>
<td>SMOW ( (\text{Standard Mean Ocean Water}) )</td>
<td>155.76 ± 0.10</td>
</tr>
<tr>
<td>$^{13}C/^{12}C$</td>
<td>PDB ( (\text{Pee Dee Belemnite}) )</td>
<td>11237.2 ± 2.9</td>
</tr>
<tr>
<td>$^{15}N/^{14}N$</td>
<td>Air Nitrogen</td>
<td>3676.5 ± 8.1</td>
</tr>
<tr>
<td>$^{18}O/^{16}O$</td>
<td>SMOW</td>
<td>2005.2 ± 0.43</td>
</tr>
<tr>
<td>$^{34}S/^{32}S$</td>
<td>CDT ( (\text{Canyon-Diabolo-Triolit}) )</td>
<td>45004.5 ± 9.3</td>
</tr>
</tbody>
</table>
Reference Material

• Primary standards are only available in small quantities.

• Many original primary standards have become exhausted and have been replaced by similar materials (V-SMOW, V-PDB, . . .).

• From the IAEA and other agencies a number of reference materials for calibrating measurements are available.

• There is lack of reference material because the reference material cannot be analyzed by all peripherals (GC).

• Isotope laboratories calibrate their own working standards using reference material. The final results should be reported against the international standard in order to compare data with other laboratory.
Dual Inlet

Automated Sample Preparation
i.e: Kiel IV carbonate system

Off-line Sample Preparation
i.e: fluorination

Alternates
Sample/Ref. Introduction

Direct comparison of a pure sample gas to a calibrated reference gas
Dual Inlet

The change over valve allows to alternately switch within in a couple of seconds between two gases.
Dual Inlet

The inlet system is operated by pneumatic valves with a nominal closing pressure of 4 bar. Material used as components of the valves must be carefully selected for maximum inertness and with no cavities. The highest quality valves are of ‘all-metal’ design.

The COV allows the system to alternately switch within in a couple of seconds between two gases which enter in turn into a vacuum chamber. While one gas flows to the vacuum chamber, the other is directed to a vacuum waste pump so that flow through the capillaries is never interrupted.
Dual Inlet

The precision of a measurement using the changeover technique often depends upon the quality of the pressure matching between the variable bellows reservoirs to reach identical signal intensity.

The smallest amount of sample that can be analyzed using DI is limited by the requirement to maintain viscous flow conditions. To achieve viscous flow gases are fed from a reservoir (bellow) to the Changeover Valve by capillaries of 0.1 mm i.d. and about 1 m length. This prevents isotopic diffusion.
Continuous Flow

Sample as a transient signal, reference gas injected as a gas pulse

He Flux

Ref. → ConFlo IV Universal Interface → Pure Sample → Automated Sample Preparation [i.e: Elemental Analyzer]

He Flux

ConFlo IV Universal Interface

Pure Sample

Automated Sample Preparation

Vacuum system

MAGNET

Detectors

Ionization Source

Sample as a transient signal, reference gas injected as a gas pulse
Continuous Flow

The reference gas inlet and open split in continuous flow peripherals (e.g. GC).

Reference gas inlet

Open split for sample gas
Dual Inlet vs Continuous Flow

The Continuous Flow technique offer an alternative, which is faster, simpler and more cost-effective than the classical Dual Inlet technique.

The Dual Inlet offer the ultimate analytical precision and the ability to run samples prepared off-line.

Courtesy Gilles St Jean Ottawa Univ.
Advantages of Continuous Flow IRMS

• Comparison of Continuous Flow with Dual Inlet Technique
  • Less Sample preparation
  • Smaller sample size
  • Multiple Isotope Ratios
  • Speed of Preparation
  • Speed of Analysis
  • Automated Sample clean up by GC
  • Direct access to international standards
Ion Source: Ionization of Sample Gas

The sample gas is ionized by a beam of electrons produced from a heated filament.

The ionization housing is held at a very high potential voltage whilst the rest of the mass spectrometer is at ground potential. This potential difference accelerates the positive ions out of the source into the mass analyzer.
Electron Impact Ion Source

- Electrons produced from a heated filament wire are accelerated through a chamber where they undergo inelastic collisions with the molecules of the gas to be analyzed. The gas molecules ionized as a result of these collisions are drawn out of the ionization chamber, focused, and injected into the mass analyzer by a series of electrically charged plates. The source may also contain charged plates to mop up excess electrons as well as grounded plates for defining the size of the merging ion beam.

- The filament (W, Rh) is resistively heated by passing a relatively large current through it. Electrons are released from the hot surface by thermal emission. The electrons are accelerated toward the ion volume by applying a voltage known as the electron energy voltage (eV) between the trap and the filament.

- The ionization housing is held at a very high potential voltage—the accelerating voltage—whilst the source slit and the rest of the mass spectrometer is at ground potential. This potential difference accelerates the positive ions out of the source into the mass analyzer.
Electron Impact Ionization

- Electron impact ionization is characterized by the following reactions:

For atoms:
- Ionization: \[ A + e^- \rightarrow A^{n+} + (n+1) e^- \]

For molecules
- Ionization: \[ AB + e^- \rightarrow AB^+ + 2e^- \]
- Ionization and dissociation: \[ AB + e^- \rightarrow A^+ + B^+ + 2e^- \]

- Ionization can imply dissociation and can produce fragments. For instance, the ionization of \( \text{N}_2\text{O} \) produces 3 types of ions, \( \text{N}_2\text{O}^+ \), \( \text{NO}^+ \) and \( \text{N}_2^+ \).
## Gas Species in IRMS

<table>
<thead>
<tr>
<th>Gas</th>
<th>Minor Isotopes</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>$^{13}$C, $^{17}$O, $^{18}$O</td>
<td>44, 45, 46, 47, 48, 49</td>
</tr>
<tr>
<td>N₂O</td>
<td>$^{15}$N, $^{17}$O, $^{18}$O</td>
<td>44, 45, 46</td>
</tr>
<tr>
<td>SO₂</td>
<td>$^{33}$S, $^{34}$S, $^{36}$S, $^{17}$O, $^{18}$O</td>
<td>64, 65, 66, 67, ..., 72</td>
</tr>
<tr>
<td>N₂</td>
<td>$^{15}$N</td>
<td>28, 29, 30</td>
</tr>
<tr>
<td>CO</td>
<td>$^{13}$C, $^{17}$O, $^{18}$O</td>
<td>28, 29, 30, 31</td>
</tr>
<tr>
<td>O₂</td>
<td>$^{17}$O, $^{18}$O</td>
<td>32, 33, 34, 35, 36</td>
</tr>
<tr>
<td>Ar</td>
<td>$^{36}$Ar, $^{38}$Ar</td>
<td>36, 38, 40</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>$^{37}$Cl</td>
<td>50, 51, 52, 53</td>
</tr>
<tr>
<td>SiF₄</td>
<td>$^{29}$Si, $^{30}$Si</td>
<td>85, 86, 87</td>
</tr>
<tr>
<td>SF₆</td>
<td>$^{33}$S, $^{34}$S, $^{36}$S</td>
<td>127, 128, 129, 131</td>
</tr>
<tr>
<td>Xe</td>
<td>$^{128}$Xe, ..., $^{134}$Xe, ...</td>
<td>128, ..., 134, 136</td>
</tr>
</tbody>
</table>
Isotope Ratio MS Strategy

• Ions analyzed in CO₂
  • m/z 44 \( ^{12}\text{C}^{16}\text{O}^{16}\text{O} \)
  • m/z 45 \( ^{13}\text{C}^{16}\text{O}^{16}\text{O} + ^{12}\text{C}^{17}\text{O}^{16}\text{O} \)
  • m/z 46 \( ^{12}\text{C}^{18}\text{O}^{16}\text{O} + ^{13}\text{C}^{17}\text{O}^{16}\text{O} + ^{12}\text{C}^{17}\text{O}^{17}\text{O} \)
    → the international CO₂ standard PDB has a 6 % contribution at mass 45 from \( ^{12}\text{C}^{17}\text{O}^{16}\text{O} \). Similarly, 0.2 % of mass 46 is derived from the species \( ^{13}\text{C}^{17}\text{O}^{16}\text{O} \). A correction formula must be used. Species with masses higher than 46 have negligible abundances.

• Ions analyzed in H₂
  • m/z 2 \( ^1\text{H}^1\text{H} \)
  • m/z 3 \( ^2\text{H}^1\text{H} \)
    → \( ^2\text{H}/^1\text{H} \)
Ionic optic

Main Turbo Molecular Pump

Inlet Manifold with front panel control

Precision-fixed Magnet

Ion Source

Differential Turbo Molecular Pump (optional)

Collector Assembly

Up to 10 Amplifiers
Universal CNOSH Detector

- m/z 2 (H₂)
- m/z 3 (HD)
- m/z 4, 5, 6 (CO₂)
- m/z 28, 29, 30 (N₂, CO)
- m/z 32, 33, 34 (O₂)
- m/z 64, 66 (SO₂)
Why Faraday Collectors?

- **Secondary Electron Multiplier**
  - One Ion $\approx 10^6$ electrons
  - High amplification
  - Low linear range

- **Faraday Cup**
  - One Ion = one electron
  - Very high linear range
  - Excellent quantification
Faraday Collectors – HD Collector

- Rejection of $^4\text{He}^+$ ions by a retardation lens
History of Multi-collection of CO$_2$ in IRMS

1970s
- 44
- 45

1980s
- 44
- 45
- 46
- 29,31, 33,45
- 30 - 46

1990s
- 44
- 45
- 66

2000s
- 44
- 45
- 46
- 47
- 48
- 49
Collector Configurations – Standard Sets

- Universal Triple Collector + HD (3kV system)

<table>
<thead>
<tr>
<th>Chip no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ampl.-Channel:</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Gases/Masses:</td>
<td>C\textsubscript{2}H\textsubscript{2}, N\textsubscript{2}O</td>
<td>44</td>
<td>45</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N\textsubscript{2}, CO</td>
<td>28</td>
<td>29</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{2}</td>
<td>32</td>
<td>33</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO\textsubscript{2}</td>
<td>64</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>2</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Resistors:</td>
<td>CO\textsubscript{2}, N\textsubscript{2}, ...</td>
<td>3\times10^8</td>
<td>3\times10^{10}</td>
<td>1\times10^{11}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{2}</td>
<td>3\times10^8</td>
<td>3\times10^{11}</td>
<td>1\times10^{11}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IID</td>
<td>1\times10^9</td>
<td>1\times10^{12}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Collector Configurations – Isotopomers

- Isomers with the same number of each isotopic atom but at different positions, for instance:
  - $^{15}\text{N}_\beta$-N-O vs. N-$^{15}\text{N}_\alpha$-O
Collector Configurations – Isotopologues

- Deconvolution of Isotopologues using Fragment Ions

- $\text{CO}_2^+ \rightarrow \text{CO}^+$
  
  $\begin{array}{cccc}
  28 & 29 & 44 & 45 \\
  \text{□} & \text{□} & \text{□} & \text{□}
  \end{array}$

  $(2^*) \quad R^{29} = R^{13} + R^{17}$

  $- \quad R^{45} = 2R^{13} + 2R^{17}$

  $2R^{29} - R^{45} = R^{13}$

- $\text{N}_2\text{O}^+ \rightarrow \text{N}_2^+$
  
  $\begin{array}{cccc}
  28 & 29 & 44 & 45 \\
  \text{□} & \text{□} & \text{□} & \text{□}
  \end{array}$

  $(-) \quad R^{29} = 2R^{15}$

  $R^{45} = 2R^{15} + R^{17}$

  $R^{45} - R^{29} = R^{17}$

- $\text{SO}_2^+ \rightarrow \text{SO}^+$
Collector Configurations – Isotopologues

• Deconvolution of Isotopologues using Fragment Ions

\[ \text{CO}_2^+ \rightarrow \text{CO}^+ \]  
\[
\begin{array}{cccc}
28 & 29 & 44 & 45 \\
\hline
\end{array}
\]

\[ \text{N}_2\text{O}^+ \rightarrow \text{N}_2^+ \]  
\[
\begin{array}{cccc}
28 & 29 & 44 & 45 \\
\hline
\end{array}
\]

• \( \text{SO}_2^+ \rightarrow \text{SO}^+ \)  
\[
\begin{array}{cccc}
48 & 50 & 64 & 66 \\
\hline
\end{array}
\]

\[
(2^*) \quad R^{50} = R^{34} + R^{18} + 2R^{33}R^{17} + (R^{17})^2 \\
( - ) \quad R^{66} = R^{34} + 2R^{18} + R^{33}R^{17} \\
2R^{50} - R^{66} = R^{34}
\]

\[
\begin{array}{cccc}
48 & 49 & 64 & 65 \\
\hline
\end{array}
\]

\[
(2^*) \quad R^{49} = R^{33} + R^{17} \\
( - ) \quad R^{65} = R^{33} + 2R^{17} \\
2R^{49} - R^{65} = R^{33}
\]
Collector Configurations – “Clumped Isotopes”

- Collector for “Clumped Isotopes” of CO₂, O₂ and CO
  - Up to 12 ion beams
  - Computer controlled switching of the amplifier gains

<table>
<thead>
<tr>
<th>Meßkanal:</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<td>CO₂/N₂O</td>
<td>44</td>
<td>45</td>
<td>46</td>
<td>47</td>
<td>48</td>
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<tr>
<td></td>
<td>N₂ / CO</td>
<td>28</td>
<td>29</td>
<td>30</td>
<td>31</td>
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<td>32</td>
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<th>Widerstand:</th>
<th>CO₂/N₂O</th>
<th>3*10⁸</th>
<th>3*10¹⁰</th>
<th>1*10¹¹</th>
<th>1*10¹²</th>
<th>1*10¹²</th>
<th>1*10¹²</th>
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<tr>
<td></td>
<td>N₂ / CO</td>
<td>3*10⁸</td>
<td>3*10¹⁰</td>
<td>1*10¹¹</td>
<td>3*10¹¹</td>
<td>1*10¹²</td>
<td>1*10¹²</td>
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<tr>
<td></td>
<td>NO</td>
<td>3*10⁸</td>
<td>1*10¹¹</td>
<td>3*10¹¹</td>
<td>1*10¹¹</td>
<td>1*10¹²</td>
<td>1*10¹²</td>
<td>1*10¹²</td>
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<tr>
<td></td>
<td>O₂</td>
<td>3*10⁸</td>
<td>3*10¹¹</td>
<td>1*10¹¹</td>
<td>3*10¹¹</td>
<td>1*10¹²</td>
<td>1*10¹²</td>
<td>1*10¹²</td>
</tr>
</tbody>
</table>
Isotope Ratio MS Strategy

Precision of Isotope Ratios based on:

- Conversion to simple Gases e.g. CO\textsubscript{2}
- Special Gas Ion Source (EI, gas tight)
- Magnetic Sector MS
- Multi-Collector
- Faraday Cups Isotope Ratio Determination
- Sample / Standard Comparison
Conversion to Simple Gases

- Acid Reaction Carbonates, Foraminifera, Speleothem ... Gas Bench, Kiel
- Combustion Sediments, Soils, Tree rings... EA, GC
- Pyrolysis Sediments, Soils, Tree rings, Phosphates, Water, Ice... EA, GC
- Equilibration Water, Ice... Gas Bench

- Fluorination Mainly S and Si Off-line preparation and Dual Inlet
- Chemical Oxidation
- Reduction
- Biochemical Reaction
Inlet Systems for Gas-Isotope Ratio MS

- GC Isolink
- Kiel device
- LC Isolink
- Gas Bench
- PreCon
- TC/EA
- Elemental Analyzers
Kiel IV Carbonate Preparation Device - with individual acid dose per sample.

Carbonate sample preparation device with acid dosing valve and 46 separate sample vials for individual acid reaction of each sample. The system is fully automatic and microprocessor-controlled.
Kiel IV Carbonate Preparation Device

**External Precision MAT 253**

\(^{13}\text{C (CO}_2\text{)}\) 0.04 ‰ at sample size >20 µg  
\(^{18}\text{O (CO}_2\text{)}\) 0.08 ‰ at sample size >20 µg

**External Precision DELTA V Advantage/Plus**

\(^{13}\text{C (CO}_2\text{)}\) 0.04 ‰ at sample size >40 µg  
\(^{18}\text{O (CO}_2\text{)}\) 0.08 ‰ at sample size >40 µg
Kiel IV Carbonate Preparation Device

Specification

20µg
δ13C 0.04 ‰
δ18O 0.08 ‰

≥ 10 µg
δ13C 0.02 ‰
δ18O 0.04 ‰

Isotope Analysis of 6 – 130 µg samples with the KIEL IV Carbonate Device

Jens Radke, Peter Haubold, Andreas Hilbert, Thermo Fisher Scientific, Bremen, Germany

Introduction
Isotopic analysis of small (6-130 µg) samples of CaCO3 is increasingly important in paleoclimatic reconstructions. The requirement for isotopic analysis of small samples of carbonate arose in studies of biogenic carbonates (e.g. foraminifera, bivalves, brachiopods, otoliths, corals). Studies of carbonates from growth zones of individual organisms and high resolution studies of microfossils from drill cores require an analytical system which can provide both high throughput and high performance in precision.

Large dynamic range between 6 µg and 130 µg
δ13C 0.05 ‰
δ18O 0.1 ‰
Kiel IV: throughput

Average 9,954 samples/year


Samples analyzed:
- 1993: 10,000
- 1994: 10,000
- 1995: 10,000
- 1996: 10,000
- 1997: 10,000
- 1998: 10,000
- 1999: 10,000
- 2000: 10,000
- 2001: 10,000
- 2002: 5,000 (128 day fire)
- 2003: 10,000
- 2004: 15,000
- 2005: 10,000
- 2006: 10,000
- 2007: 10,000
- 2008: 10,000

Courtesy of Dorinda Ostermann,
Woods Hole Oceanographic Institution, MA, USA
H/Device

**H/Device** for automated reduction of aqueous and organic samples to hydrogen by manual injection of micro liter samples

**External Precision**

$^2\text{H} (\text{H}_2) \leq 0.5 \, \%$ at sample size $\leq 1 \, \mu\text{L}$
H/Device

Defining the Standard for combining

- Highest Precision
- High Throughput
- Small Sample Size

\[ \delta D_{\text{VSMOW}} < \pm 0.5 \% \]
Tools for water analysis

Specifications for System Acceptance

TC/EA

- $< 0.5 \mu L$
- $\delta^{18}O < 0.2 \%$
- $\delta D < 2.0 \%$

GasBench II

- $< 200 \mu L$
- $\delta^{18}O < 0.08 \%$
- $\delta D < 2.0 \%$

Performance Data

- $\delta^{18}O$ 0.07 \%
- $\delta D$ 0.4 \%

- $\delta^{18}O$ 0.06 \%
- $\delta D$ 0.87 \%
Elemental Analyzers

Flash HT Plus

TC/EA
Thermo Scientific FLASH HT *Plus* Elemental Analyzer

Fully automated multi-element isotope analysis

- **Customer Need**
  - 5 elements + 5 isotopes in 1 system
  - High productivity
  - Small footprint

- **Our Response**
  - Full automation for CNSOH
  - 2 fully integrated autosamplers
  - Dynamic Flash Combustion and High Temperature Conversion in 1 EA

Industry leading Isotope Ratio Mass Spectrometry

**Food Testing**
**Forensics**
**Environmental Analysis**
**Earth Sciences**
FLASH HT *Plus* – fully automated EA for IRMS

- 2 MAS 200R Autosampler for solids
- Dynamic Flash Combustion furnace
- High Temperature Conversion furnace
- Status Display
- Water trap and GC cabinet
  - column for N$_2$/CO$_2$/SO$_2$ separation
  - column for H$_2$/CO separation
  - TCD Thermal Conductivity Detector.

- 5 elements and 5 isotope ratios – CNSOH
- ASV for automated switching between both EA modes
- Full software control
- 2 auto-samplers – full automation
- Sulfur-ready with sulfur-resistant tubing making extra fittings and modifications obsolete
Principle of the Thermo Scientific FLASH Plus

1 Elemental Analyzer → 2 Analyses → 5 Isotopes
NCS-Triple Measurement with smartEA™ option

- One analysis
- Three elements
- Three reference gases
- Fast N/C jump
- Slow C/S jump
- Individual sample dilution of N₂, CO₂, SO₂

FlashEA 1112 HT
Single reactor setup WO₃ filling
- Reactor: 1020°C
- GC: 70°C (PP-QS 50/80)
Flow: 90 mL/min
0.259 mg Sulfanilamide
(16.3% N, 41.8% C, 18.6% S)
< 18 minutes
Operation Modes and Switching Time

- < 35 min for 5 isotopic ratios
- < 22 min for $\delta D$, $\delta^{18}O$ and $\delta^{15}N$, $\delta^{13}C$
- Switching time HO $\rightarrow$ NCS: 260 s
- Equilibration time NCS $\rightarrow$ HO: 130 s
- Source conditioning during FlashEA equilibration time
  - Two analysis per samples
  - Fully automated operation
Elemental Analyzers

**External Precision**

\(^{13}\text{C} (\text{CO}_2) 0.15 \permil, \text{sample size} 50 \mu\text{g} \ \text{C} \\
^{15}\text{N} (\text{N}_2) 0.15 \permil, \text{sample size} 50 \mu\text{g} \ \text{N} \\
^{2}\text{H} (\text{H}_2) 3 \permil, \text{solid sample size} 25 \mu\text{g} \ \text{H} \ or \ \\
^{2}\text{H} (\text{H}_2) 2 \permil, \text{liquid sample size} 0.5 \mu\text{L} \\
^{18}\text{O} (\text{CO}) 0.4 \permil, \text{solid sample size} 50 \mu\text{g} \ \text{O} \ or \\
^{18}\text{O} (\text{CO}) 0.2 \permil, \text{liquid sample size} 0.5 \mu\text{L} \\
^{34}\text{S} (\text{SO}_2) 0.2 \permil \text{ at sample size} 50 \mu\text{g}
Why Compound Specific Isotope Analysis?

- To extract the isotope information diluted in complex mixtures
- To access to sources, fluxes and metabolism at molecular level
GC IsoLink II

**GC IsoLink II for C and N** for the accurate and precise on-line determination of $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ isotope ratios in organic mixtures.

The GC IsoLink is directly connected to the gas chromatograph.

A unique micro combustion furnace converts the sample into CO$_2$ and N$_2$. Combustion water is removed by a non-cryogenic phase separator. For N$_2$ measurements CO$_2$ is quantitatively removed by an on-line cold trap.
GC IsoLink II

**H/D-Reactor for GC IsoLink II** – by high temperature conversion (TC) of GC eluates providing the accurate and precise on-line determination of hydrogen isotope ratios in organic mixtures.

**Option for $^{18}$O analysis of GC eluates** – for GC IsoLink II providing the accurate and precise on-line determination of oxygen isotope ratios in organic mixtures.

The high temperature conversion reactor can be placed in parallel to the oxidation reactor in the GC IsoLink II.
GC Combustion / HT Conversion Flow Scheme

- Automated Switch from $\text{CO}_2 \rightarrow \text{H}_2 \rightarrow \text{CO}_2 \rightarrow \ldots$
- Switch by 4-port Valco valve
- Valve is behind the reactors
- Valve is in the cold zone
GC IsoLink II Micro Channel Devices

- Attain Higher Resolution and Sensitivity by Full Connectivity to Reactors
  - Unleash true capillary GC for GC-IRMS by connecting reactors with the GC system via micro channel devices.
GC IsoLink II CO₂ → H₂ → CO₂ → ….

- FID Mix: C14 data

\[ \delta^{13}C \quad \delta^{2}H \]

\[ \text{ca. 5 h} \quad H_3^+ \text{ settlement} \]

- 7.5 – 30 ng: ± 0.16‰
  - 7.5 ng: ± 0.09‰  
  - n = 5

- 7.5 – 30 ng: ± 0.17‰
  - 7.5 ng: ± 0.09‰  
  - n = 5

- 300 ng: ± 1.86‰
  - n = 10
ConFlo IV: Auto-Dilution Technology for GC IsoLink II

Sample Gas Inlet

Dilution Off

Reference Gas Inlet

Dilution On

Reference Gas On

Adjustable He Flow

MS

EA

ThermoFisher Scientific
GC IsoLink II

**External Precision**

\(^{13}\text{C}\) 0.2 ‰ (SD 1 σ; n = 5)

using \(n\text{-C}_{14}\) to \(n\text{-C}_{16}\) alkanes at natural abundance, 0.8 nmol C on column (10 ng C or 12 ng alkane or 60 pmol alkane)

**External Precision**

\(^{2}\text{H}\) 3.0 ‰ (SD 1 σ; n = 5)

using \(n\text{-C}_{14}\) to \(n\text{-C}_{16}\) alkanes at natural abundance, 15 nmol \(\text{H}_2\) on column (30 ng H or 200 ng alkane or 0.8 nmol alkane)
Hyphenation of GC-IRMS with GC-MS

- Structures and isotope ratios in One Run
GC/MS-IRMS Solutions

• Simultaneous GC-IRMS and GC/MS application

• Thermo Scientific ISQ QD
• Thermo Scientific ISQ LT
• Thermo Scientific ITQ 900
LC IsoLink

**LC IsoLink Interface** – High sensitivity interface for the reproducible and accurate on-line determination of $^{13}\text{C}/^{12}\text{C}$ isotope ratios under aqueous conditions (patented). The LC IsoLink interface allows compound specific isotope analysis from complex sample mixtures by coupling HPLC systems to Thermo Scientific Stable Isotope Ratio Mass Spectrometers.
A unique chemical micro-oxidation under aqueous LC conditions converts the sample into CO$_2$, which is subsequently transferred into a helium carrier gas stream. Residual water vapor is removed by a non-cryogenic phase separator. The purified CO$_2$ is conducted to the IRMS ionization source for $^{13}$C/$^{12}$C isotopic ratios measurements.
Non volatile compounds only accessible by liquid chromatography can now be isotopically analyzed even in complex matrices.

The method still presents limitations, it is only applicable to $^{13}\text{C}/^{12}\text{C}$ and under aqueous LC conditions.

**External Precision**

$\delta^{13}\text{C} < 0.3 \, \%$ (1 $\sigma$, n=5), demonstrated by flow injection of 3 nmol benzoic acid.
GasBench II – Interface and Sample Preparation Device. Automated sample preparation device for the precise determination of the isotope ratios of gases like CO$_2$ from air or CO$_2$ released from carbonates, CO$_2$ from dissolved inorganic carbon (DIC), $^{18}$O and D analysis of aqueous samples by CO$_2$/H$_2$O and H$_2$/H$_2$O equilibration. (Determination of isotope ratios on other gases like N$_2$, N$_2$O, SO$_2$ on request.)
GasBench II

The gases entrained in a helium carrier gas stream are fed to a GC column via an automated sample loop. Water is removed by a non-cryogenic phase separator (Nafion).

A high dynamic range is accomplished by the unique auto-dilution mode leaving the sample integrity untouched. High precisions are reached due to multiple loop injections.
GasBench II

High Precision & Ease of Use
GasBench II Water

- Place 200 μL of the sample in the vial
- Add the Platinum Catalyst
- Close the vial
- Place all sample vials in the autosampler tray
- All vials are automatically flushed

D transfer from H₂O into H₂ in the headspace
- Equilibrate for 40 min

Analysis
- Start the Sequence Acquisition

<table>
<thead>
<tr>
<th>IAEA accepted value [%]</th>
<th>GasBench II Results</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mean [%]</td>
</tr>
<tr>
<td>Vostok Snow</td>
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<tr>
<td>IAEA GISP</td>
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<td>OCEAN 2</td>
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<tr>
<td>IAEA SLAP</td>
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<td>ANST 4</td>
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<td>HBW-2 Tap</td>
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<tr>
<td>IAEA VSMOW</td>
<td>0</td>
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<tr>
<td>HL-1</td>
<td>-363.3</td>
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<tr>
<td>PAN 5</td>
<td>-293.3</td>
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<tr>
<td>GISP 379</td>
<td>-192.3</td>
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</table>
GasBench II Water

Vostok (Antarctic ice), -56.64‰ ± 0.02‰

Wine A: -2.45 ± 0.02‰
Wine B: -0.29 ± 0.02‰
Wine C: 3.35 ± 0.07‰

Ocean2, seawater, -0.84 ± 0.03‰

Measured δ¹⁸O = -56.64 ± 0.02‰
Measured δ¹⁸O = -0.84 ± 0.03‰

GasBench II-DELTA™
Analyst: A. Hilkert 9/99
GasBench II Dissolved Inorganic Carbon
GasBench II Dissolved Inorganic Carbon

Place 30 μl H₃PO₄ conc. in an open 10 ml Exetainer (3 - 4 drops)

Flush with Helium in a glovebag

Close Exetainer while flushing

Inject 600 μl of sample using a 1 ml syringe (for single use)

Shake exetainer
Wait for 1 h

Place sample in the autosampler tray
Start acquisition sequence
GasBench II Carbonates

- In situ sample preparation (acid dosing)
GasBench II Carbonates

- Enhanced Dynamic Range
GasBench II

External Precision

\(^{13}\text{C (CO}_2\text{)}\) 0.08 ‰ using \(\geq 0.3\%\) \(\text{CO}_2\) in He

\(^{18}\text{O (CO}_2\text{)}\) 0.08 ‰ using \(\geq 0.3\%\) \(\text{CO}_2\) in He

\(^2\text{H (H}_2\text{)}\) 2 ‰ using \(\geq 1.0\%\) \(\text{H}_2\) in He

\(^{13}\text{C (CO}_2\text{)}\) 0.1 ‰ at sample size of 100 µg

\(^{18}\text{O (CO}_2\text{)}\) 0.1 ‰ at sample size of 100 µg
PreCon

**Trace Gas Pre-Concentrator PreCon** – System for the automatic, computer-controlled pre-concentration and preparation of trace gases (N$_2$O, CH$_4$) in atmospheric air.

The device consists of an assembly of chemical traps, cryogenic traps and oxidation reactor including all necessary valve controls in order to facilitate isotope ratio determination from one of the above mentioned trace gas components. The system enables direct gas injection into any appropriate GC system.
PreCon

External Precision

$^{13}$C (CH$_4$) 0.5 ‰ at sample size 100 mL
$^{15}$N (N$_2$O) 0.5 ‰ at sample size 100 mL
$^{18}$O (N$_2$O) 1.0 ‰ at sample size 100 mL

from ambient air with 1.7 ppm CH$_4$ and 300 ppb N$_2$O
“A tool for exploring the isotopic anatomy of volatile molecules”

MAT 253 Ultra Development

MAT 253 Ultra:
Combination of
• MAT 253 Gas IRMS with
• NEPTUNE Plus MC-ICPMS
MAT 253 Ultra main characteristics

- **Modified Neptune/Triton analyzer**
  - 23 cm radius magnet
  - 2x magnification at image plane
  - Dispersion quadrupole
  - ‘Zoom’ optic capability (±5 % mass range)

- **Modified Neptune/Triton collector array**
  - 7 collectors, 6 moveable
  - Switchable FC/EM at every position
  - RPQ retardation lens before central collector

- **Modified MAT-253 front end**
  - 4 bellows and carrier-gas port
  - e- bombardment source (5-150 eV)
  - 5 kV initial acceleration
  - Entrance slits from 250 to 5 µm
Why Clumped Isotopes of Methane?

Origin of methane

- in **natural gas reservoirs** might be generated by the decomposition of **organic matter**, by **bacteria** or by **chemical reactions** in rocks.
- in air comes from natural **gas wells**, from **landfills**, from **cows** and from thawing **permafrost** in the Arctic.
- on **Mars** - might be geological or biological.

Questions addressed:

- how fast is permafrost melting?
- how long will natural gas deposits last?
- is there life on other planets?

Source of methane? isotopic signature
Clumped Isotopes of Methane – Complex peak

Mass 17 methane
Nominal resolving power ~ 19,000 (5%/95% definition)
Clumped Isotopes of Methane – Complex peak

With the MAT 253 Ultra very small isotope signatures can be explored.
Inventory of measurements made to-date by the Ultra

- Methane
  - $^{13}$CH$_4$
  - $^{12}$CH$_3$D
  - $^{13}$CH$_3$D
- Ethane
  - $^{13}$C$^{12}$CH$_6$
  - $^{13}$C$_2$H$_6$
- Propane
  - $^{13}$C of methyl fragment
  - $^{13}$C of C$_2$ fragment
  - $^{13}$C of full molecule
- Oxygen
  - $^{18}$O$^{16}$O
- Nitrous oxide
  - $^{15}$N$^{14}$N$^{16}$O
  - $^{14}$N$^{15}$N$^{16}$O
  - $^{14}$N$_2$$^{17}$O
  - $^{14}$N$_2$$^{18}$O
  - $^{15}$N$^{14}$N$^{18}$O
  - $^{14}$N$^{15}$N$^{18}$O
- Molecular hydrogen
  - HD
  - D$_2$
- Helium
  - $^3$He/$^4$He
- O Fragment from CO$_2$
  - $^{18}$O
  - $^{17}$O
Clumped-isotope thermometry of carbonates

- Clumped-isotope thermometry (Ghosh et al., 2006; Eiler, 2007) has emerged as a new tool for paleotemperature reconstructions and is attracting growing interest in a variety of different applications in geology.

- The thermometer is solely based on thermodynamic properties and does not depend on the bulk carbon and oxygen isotope composition of the carbonate.
Clumped-isotope thermometry of carbonates

• Bonds between two rare isotopes are more stable. (Eiler, 2007). This leads to a slightly higher abundance of these bonds than would be observed for a purely stochastic isotope distribution. As the abundance of these bonds is temperature-dependent, the difference between the measured and the stochastically expected bond abundance can be used as a thermometer.

• The best studied species for clumped-isotopes so far is CO2. Ghosh et al. (2006) were the first to show that this excess bond abundance of 13C-18O in carbonates can be used as a thermometer for the formation of carbonate, where the carbonate is converted to CO2 by reaction with phosphoric acid.
Clumped-Isotope Measurements on Small Carbonate Samples with a Kiel IV Carbonate Device and a MAT 253 Mass Spectrometer

Thomas W. Schmidt¹, Jens Radke², Stefano M. Bernasconi²
¹Geologisches Institut, ETH Zurich, Switzerland, ²Thermo Fisher Scientific, Bremen, Germany

The MAT 253- Kiel IV is capable of:
- fully automated measurement of carbonate clumped-isotopes,
- routine precision of 0.01 to 0.02 ‰,
- simultaneous measurement of δ13C and δ18O.
Noble Gas Mass Spectrometry
Noble Gases

The Noble Gases are here in the Periodic table.
Noble Gas MS, what is different?

The sample size is extremely small, imagine how much gas is contained in rocks…

Because of this very small sample size, noble gas instruments operate with a static vacuum, pumps are switch off during the analysis.

Again for the same reason, the background levels in Noble gas systems are absolutely critical to the successful analysis. Noble Gas MSs often need to be baked at high temperature.
About Noble Gases

*What’s important in Noble Gas MS:*

- Multi-collection for high throughput and high precision
- High sensitivity for very small samples (gases from rocks!)
- Minimum internal volume (sensitivity)
- High resolution, to tackle a number of interference issues
- Highest quality pumping and vacuum technology (static vacuum)
- High quality electronics (small signals)
- Automation capability

**Application specific instruments**
The table below outlines the Noble gases and their relative abundances.

<table>
<thead>
<tr>
<th></th>
<th>Helium</th>
<th>Neon</th>
<th>Argon</th>
<th>Krypton</th>
<th>Xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 - 0.0001%</td>
<td>20 – 90.48%</td>
<td>36 – 0.33%</td>
<td>78 – 0.35%</td>
<td>124 – 0.09%</td>
<td></td>
</tr>
<tr>
<td>4 - 99.999%</td>
<td>21 – 0.27%</td>
<td>37 - Radioactive</td>
<td>80 – 2.28%</td>
<td>126 – 0.09%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22 – 9.25%</td>
<td>38 – 0.06%</td>
<td>82 – 11.58%</td>
<td>128 – 1.92%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39 - Radioactive</td>
<td>83 – 11.49%</td>
<td>129 – 26.44%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 – 99.6%</td>
<td>84 – 57%</td>
<td>130 – 4.08%</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>86 – 17.3%</td>
<td>131 – 21.18%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>132 – 26.89%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>134 – 10.44%</td>
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<tr>
<td>136 – 8.87%</td>
<td></td>
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</tr>
</tbody>
</table>

Measuring noble gas isotopic ratios can be quite challenging.
Noble Gas MS: ARGUS VI

- Multicollector Noble Gas Mass Spectrometer, ability to measure all 5 Argon isotopes simultaneously and with very high sensitivity

Major applications
- Geochronology
- Thermochronology
- Geochemistry
Noble Gas MS: **HELIX SFT**

- High Resolution Multi collector Split Flight tube Noble gas MS, unique ability to measure both Helium isotopes simultaneously

**Major applications:**
- Groundwater dating
- Geochemistry
- Geochronology
- Cosmochemistry
Noble Gas MS: HELIX MC

- High Resolution Multi collector Noble gas MS, ability to measure the isotopes of Neon, Argon, Nitrogen, Krypton (5) and Xenon (5) simultaneously. No peak jumping required

Major applications:
- Geochemistry
- Geochronology
Thermo Ionization Mass Spectrometry (TIMS) & Multi-Collector ICP-MS (MC-ICP-MS)
NEPTUNE Plus & TRITON Plus

Thermal Ionization Mass Spectrometry (TIMS)

Multi-collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS)
Ion Source: **TIMS vs. (MC-)ICPMS**

- **Thermal Ionization (TI)**
  - Ionization takes place by contact with the heated surface of a metal filament.

- **Inductively Coupled Plasma (ICP)**
  - Ionization takes place in an Ar plasma, a partly ionized gas generated by RF magnetic fields.
**Periodic Table: MC-ICP-MS**

![Periodic Table Image](image-url)

*Lanthanide Series*

<table>
<thead>
<tr>
<th>58 Ce</th>
<th>59 Pr</th>
<th>60 Nd</th>
<th>61 Pm</th>
<th>62 Sm</th>
<th>63 Eu</th>
<th>64 Gd</th>
<th>65 Tb</th>
<th>66 Dy</th>
<th>67 Ho</th>
<th>68 Er</th>
<th>69 Tm</th>
<th>70 Yb</th>
<th>71 Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>140.12</td>
<td>143.92</td>
<td>144.24</td>
<td>150.35</td>
<td>151.96</td>
<td>152.54</td>
<td>158.92</td>
<td>158.92</td>
<td>162.55</td>
<td>164.93</td>
<td>167.26</td>
<td>168.93</td>
<td>173.04</td>
<td>174.97</td>
</tr>
</tbody>
</table>

*Actinide Series*

<table>
<thead>
<tr>
<th>90 Th</th>
<th>91 Pa</th>
<th>92 U</th>
<th>93 Np</th>
<th>94 Pu</th>
<th>95 Am</th>
<th>96 Cm</th>
<th>97 Bk</th>
<th>98 Cf</th>
<th>99 Es</th>
<th>100 Fm</th>
<th>101 Md</th>
<th>102 No</th>
<th>103 Lr</th>
</tr>
</thead>
<tbody>
<tr>
<td>232.036</td>
<td>238.03</td>
<td>238.03</td>
<td>237.03</td>
<td>237.03</td>
<td>243.04</td>
<td>247.05</td>
<td>247.05</td>
<td>249.04</td>
<td>253.04</td>
<td>253.04</td>
<td>256.04</td>
<td>256.04</td>
<td>257.05</td>
</tr>
</tbody>
</table>
# TIMS vs. MC-ICPMS: pro’s & con’s

<table>
<thead>
<tr>
<th></th>
<th>TIMS</th>
<th>MC-ICPMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization Efficiency</td>
<td>good for some, bad for most up to 2%</td>
<td>good for almost all elements 0.1 to 1%</td>
</tr>
<tr>
<td>Interferences</td>
<td>hardly low</td>
<td>many can be high</td>
</tr>
<tr>
<td>Background</td>
<td>low</td>
<td>can be high</td>
</tr>
<tr>
<td>Mass Fractionation</td>
<td>changes during run fractionation laws</td>
<td>stable fractionation laws or sample-standard</td>
</tr>
<tr>
<td>Correction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>very good down to 1ppm</td>
<td>bad 10ppm can be reached</td>
</tr>
<tr>
<td>Precision</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Preparation</td>
<td>time consuming</td>
<td>various</td>
</tr>
<tr>
<td>Speed of Analysis</td>
<td>relatively slow</td>
<td>fast</td>
</tr>
<tr>
<td>In-situ Interfaces</td>
<td>possible (Microdrilling) not possible</td>
<td>possible (Laser Ablation, Microdrilling) GC, HPLC, Laser …</td>
</tr>
</tbody>
</table>
## Typical precision

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>MC-ICP-MS</th>
<th>TIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>External</td>
<td>External</td>
</tr>
<tr>
<td></td>
<td>Precision</td>
<td>Precision</td>
</tr>
<tr>
<td></td>
<td>(1 sigma)</td>
<td>(1 sigma)</td>
</tr>
<tr>
<td>$^{87}\text{Sr}/^{86}\text{Sr}$</td>
<td>20 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>$^{143}\text{Nd}/^{144}\text{Nd}$</td>
<td>20 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>$^{207}\text{Pb}/^{206}\text{Pb}$</td>
<td>20 ppm</td>
<td>5 ppm</td>
</tr>
<tr>
<td>$^{206}\text{Pb}/^{204}\text{Pb}$</td>
<td>100 ppm</td>
<td>5 ppm</td>
</tr>
<tr>
<td>$^{235}\text{U}/^{238}\text{U}$</td>
<td>300 ppm</td>
<td>20 ppm</td>
</tr>
<tr>
<td>$^{234}\text{U}/^{238}\text{U}$</td>
<td>0.2 %</td>
<td>&lt; 0.2%</td>
</tr>
</tbody>
</table>
Sample Size

A glass of water
200mL x 15ppb = 3,000 ng Pb

A meteorite inclusion
1.000 - 0.050 ng Pb

3000 - 60,000 times less Pb than in a glass of water ....

US standard for drinking water = 15 ppb
Laboratory contamination should be less than 0.5 pg
Thank you for your listening
Questions?