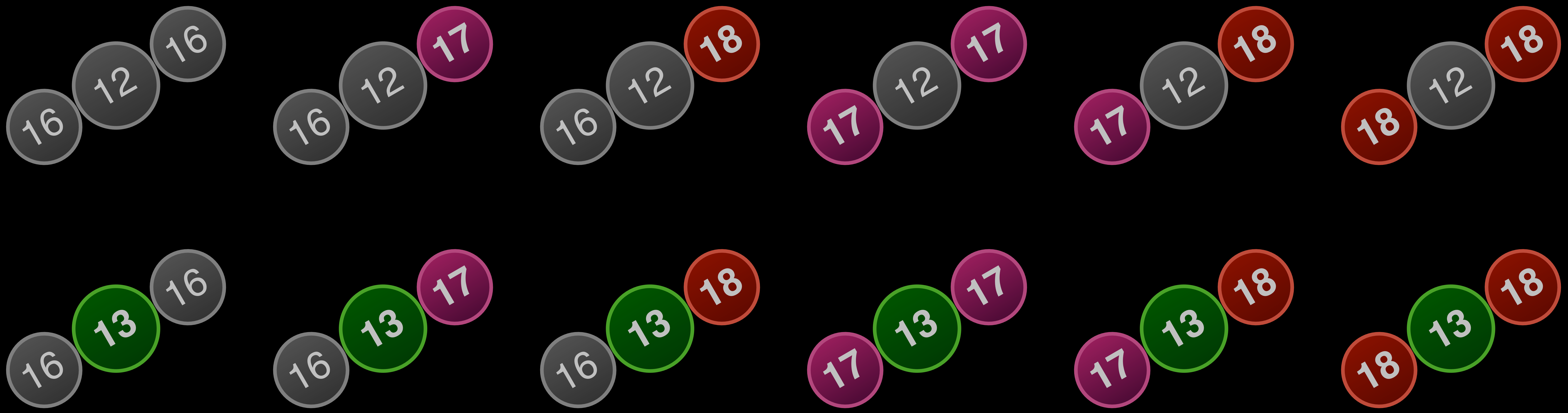
Accélération contre rovibrations

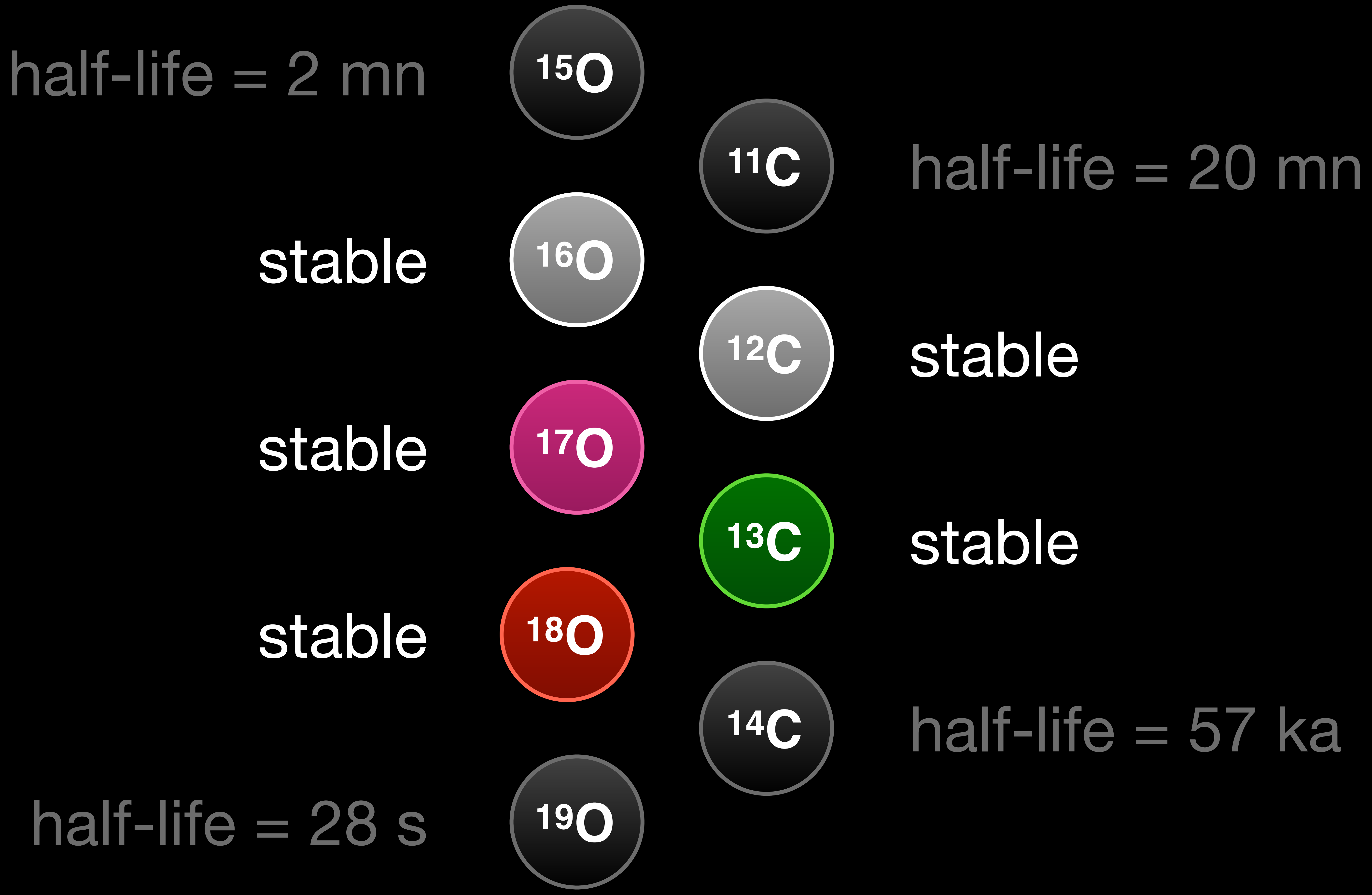
quand la spectroscopie infra-rouge vient bousculer la géochimie

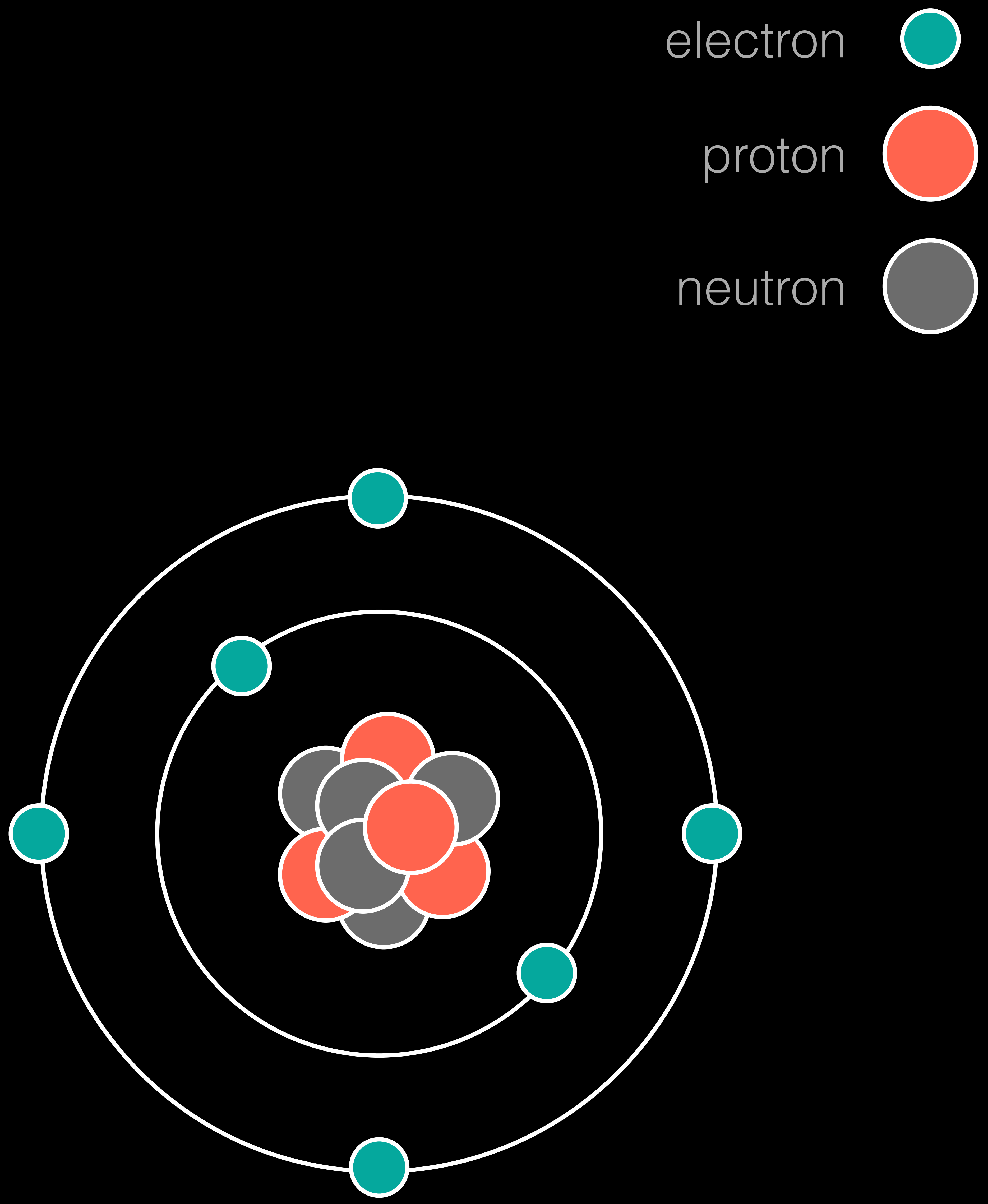


M. Daëron

Centre National de la Recherche Scientifique
Laboratoire des Sciences du Climat et de l'Environnement

Stable vs radiogenic isotopes





Géochimie des isotopes stables: pourquoi ?

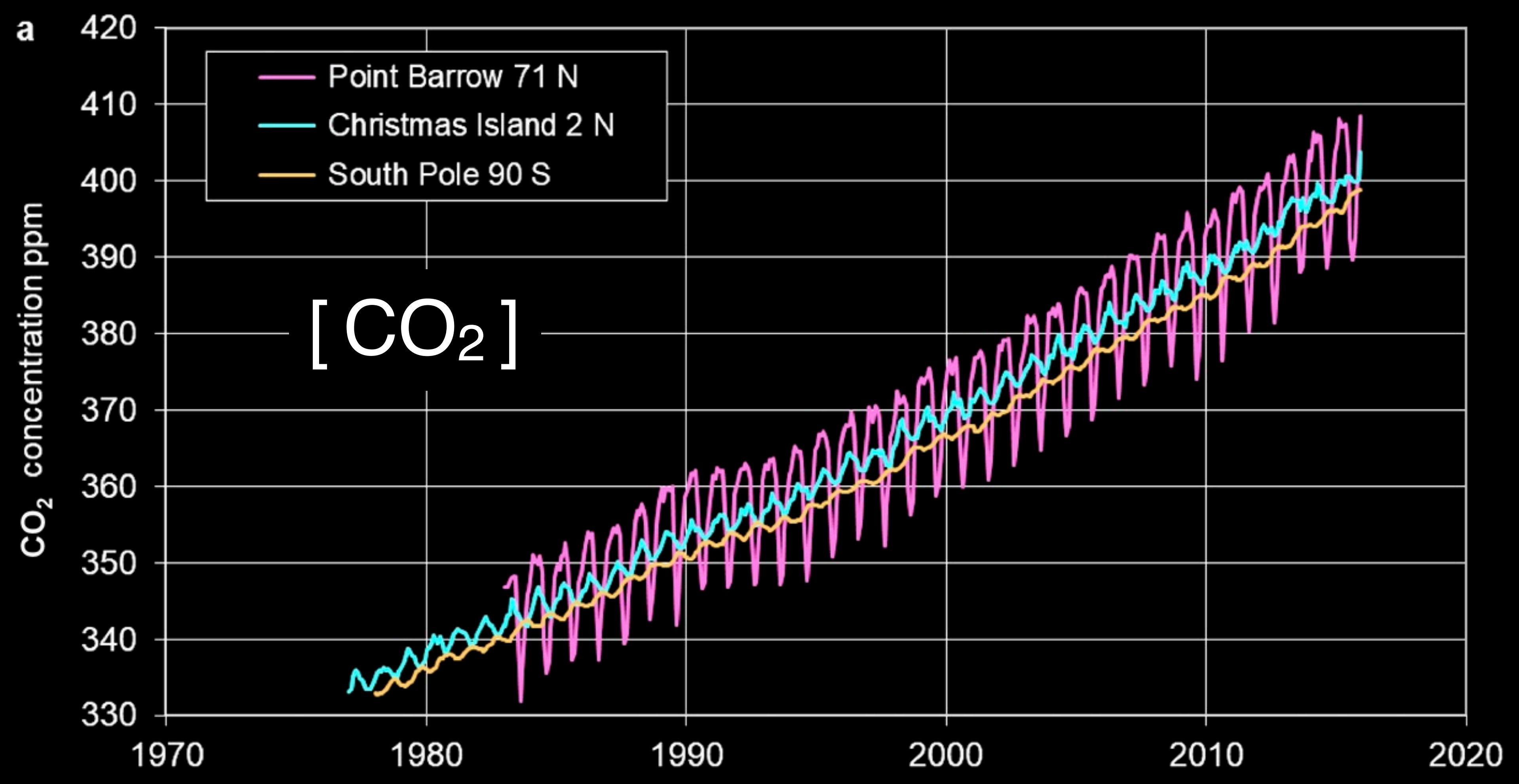
CO_2 atmosphérique

matière organique

– 330 millions d'années

CO_2 atmosphérique

2025



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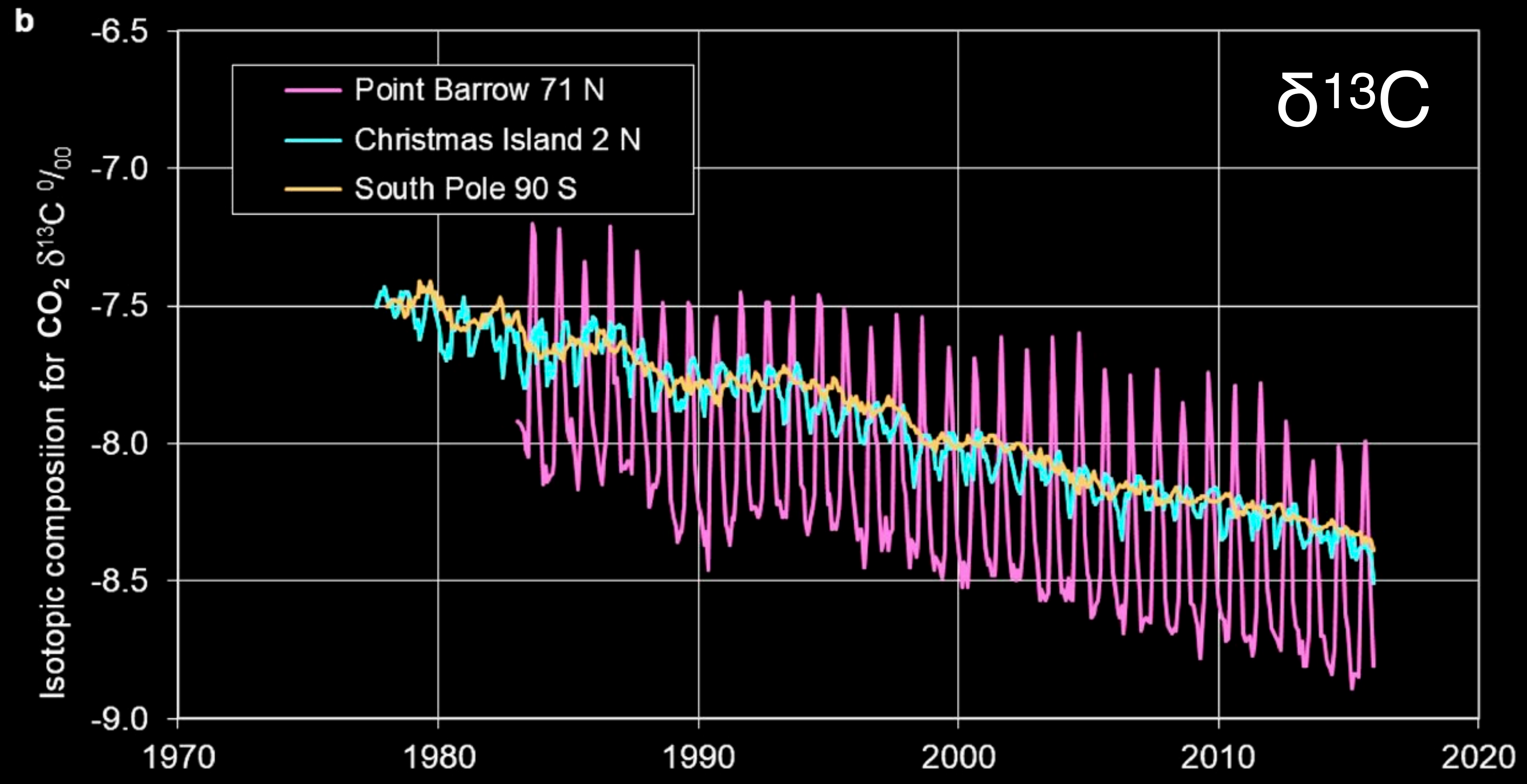
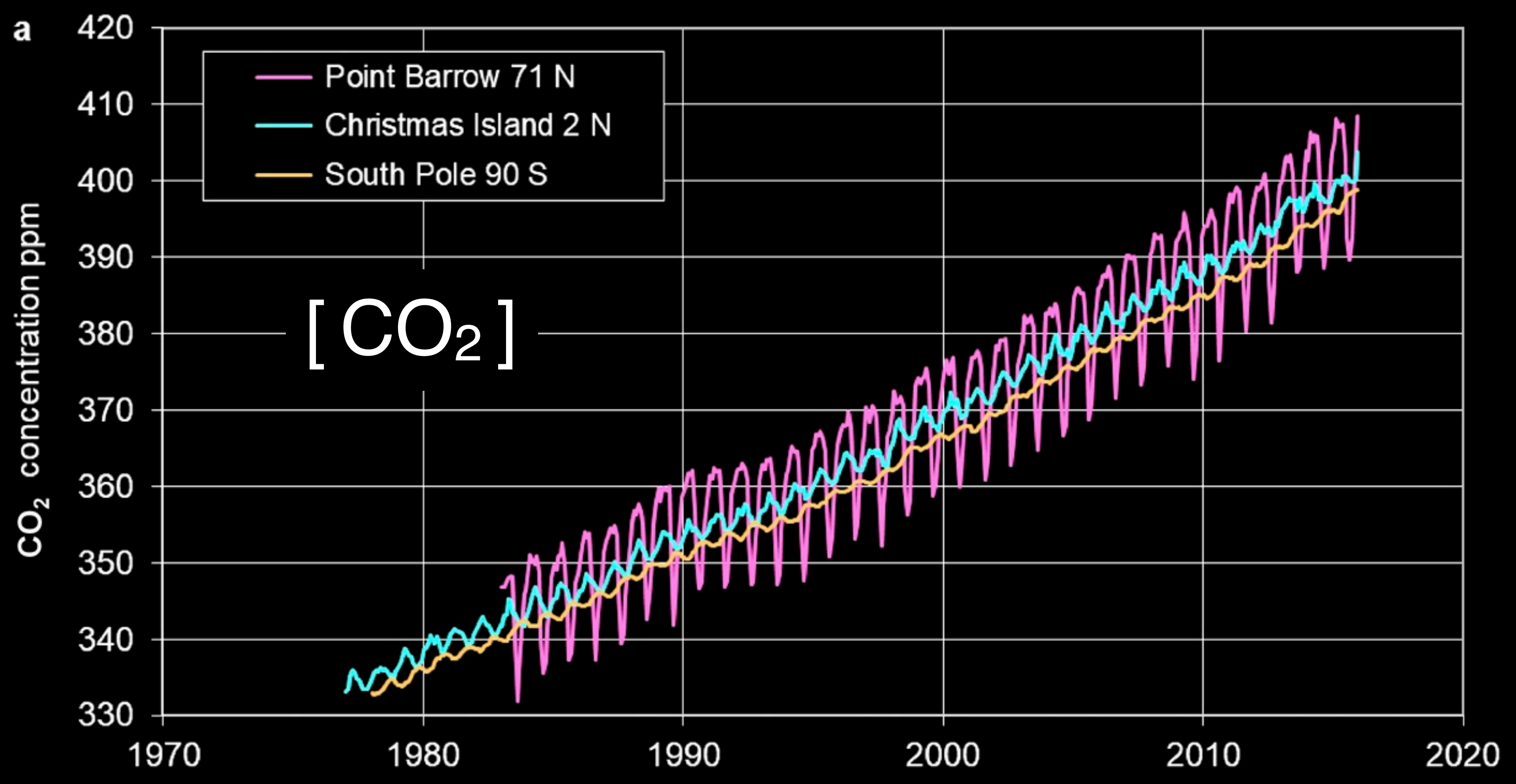
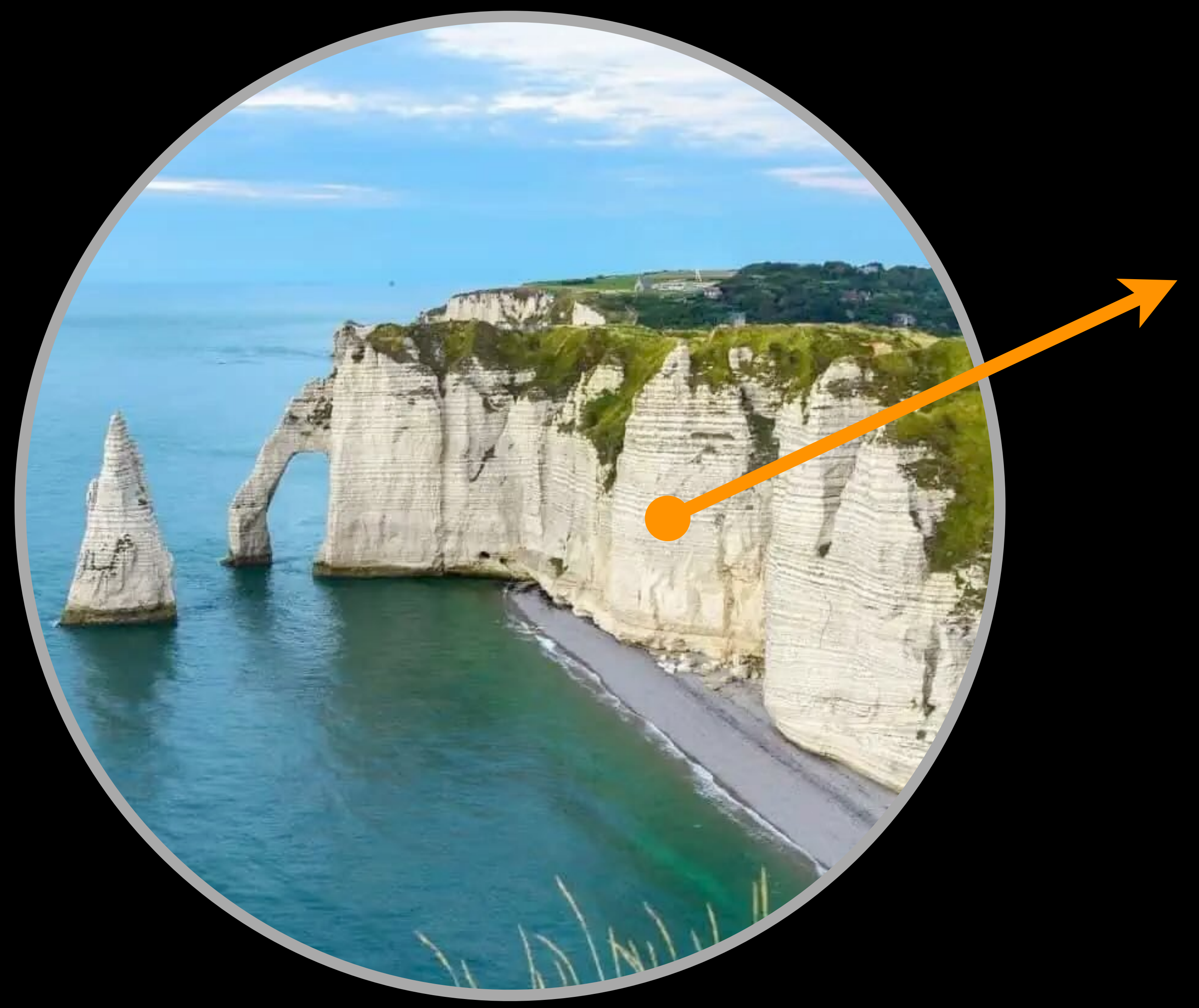
2025







$$\delta^{18}O_{carbonate} = \frac{(^{18}O\ /\ ^{16}O)_{carbonate}}{(^{18}O\ /\ ^{16}O)_{reference}} - 1$$

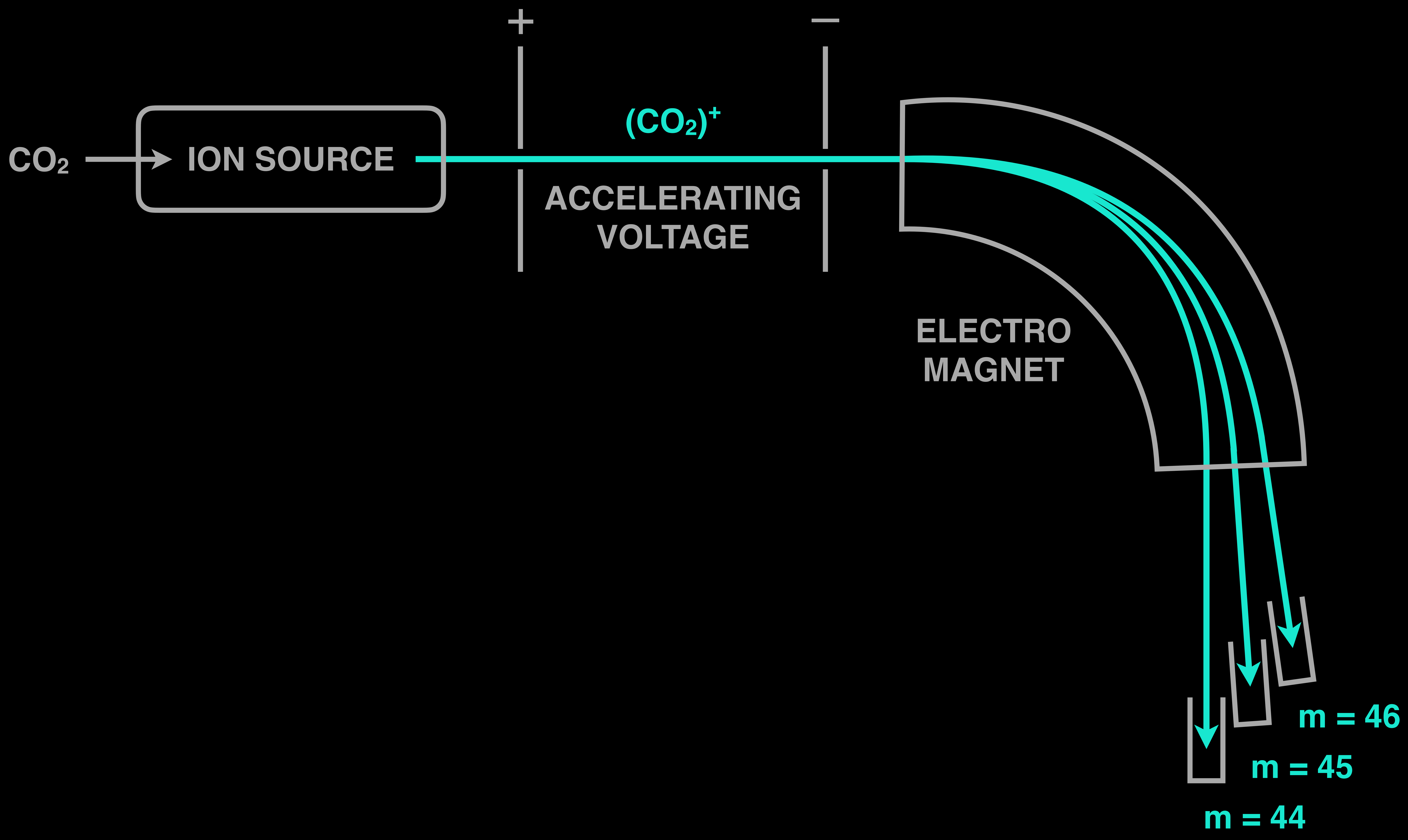
$$\delta^{18}O_{carbonate} = \frac{(^{18}O\ /\ ^{16}O)_{carbonate}}{(^{18}O\ /\ ^{16}O)_{reference}} - 1 \approx \delta^{18}O_{seawater} - b\,T + a$$

période glaciaire : ↑ $\delta^{18}O_{sw}$ ↓ T ⇒ ↑ $\delta^{18}O_{c}$

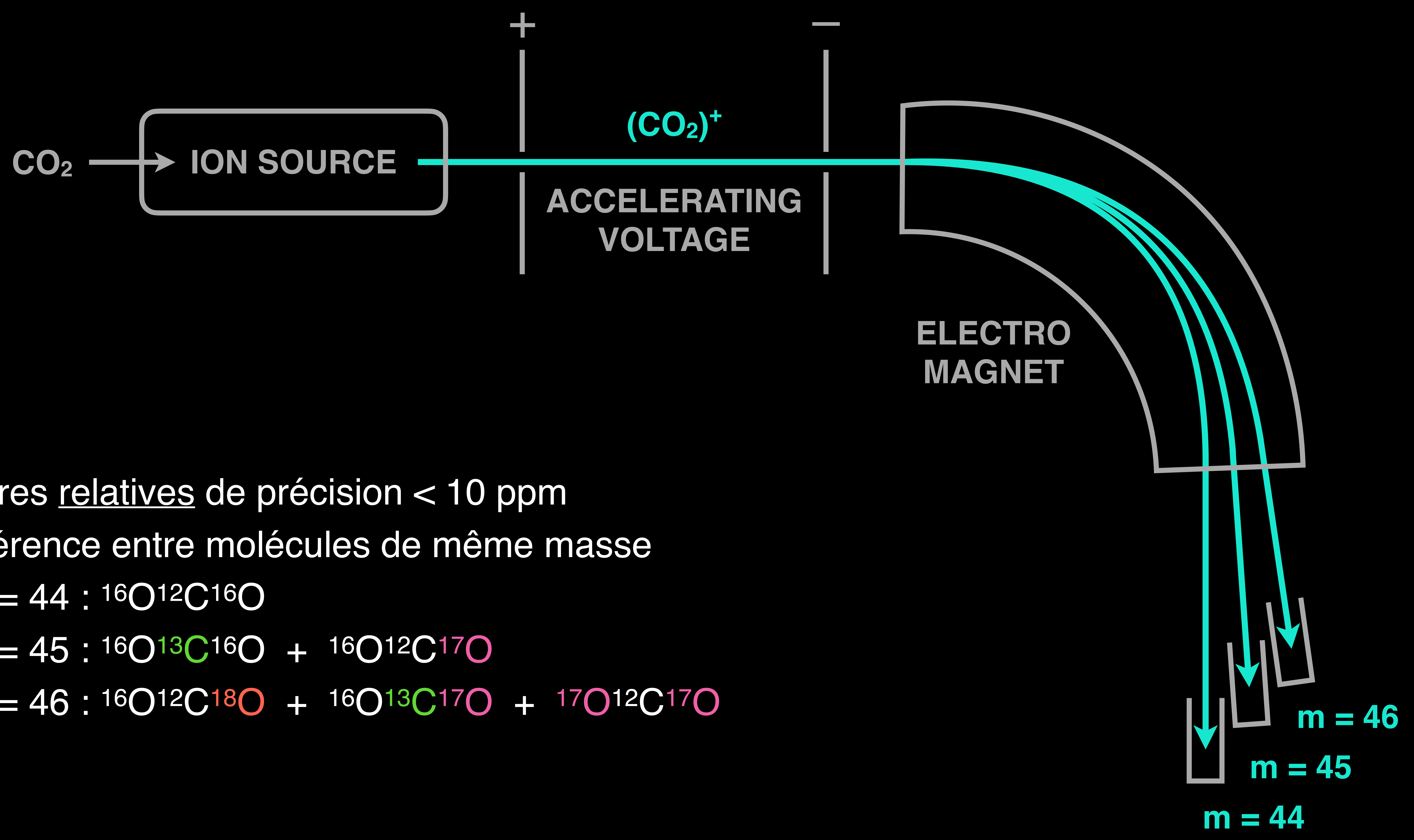
période inter-glaciaire : ↓ $\delta^{18}O_{sw}$ ↑ T ⇒ ↓ $\delta^{18}O_{c}$

Validation de la théorie de Milanković : variations d'insolation ⇒ cycles glaciaires

IRMS: Isotope Ratio Mass Spectrometry



IRMS: Isotope Ratio Mass Spectrometry



- mesures relatives de précision < 10 ppm
- interférence entre molécules de même masse
  - m = 44 : $^{16}O^{12}C^{16}O$
  - m = 45 : $^{16}O^{13}C^{16}O$ + $^{16}O^{12}C^{17}O$
  - m = 46 : $^{16}O^{12}C^{18}O$ + $^{16}O^{13}C^{17}O$ + $^{17}O^{12}C^{17}O$

Stable isotope quantities of interest for CO_2

16 13 16 — m = 45, $x \approx 1 \cdot 10^{-2}$
16 12 18 — m = 46, $x \approx 4 \cdot 10^{-3}$
} $\delta^{13}C$ + $\delta^{18}O$ (since ~1950, σ = 10–50 ppm)

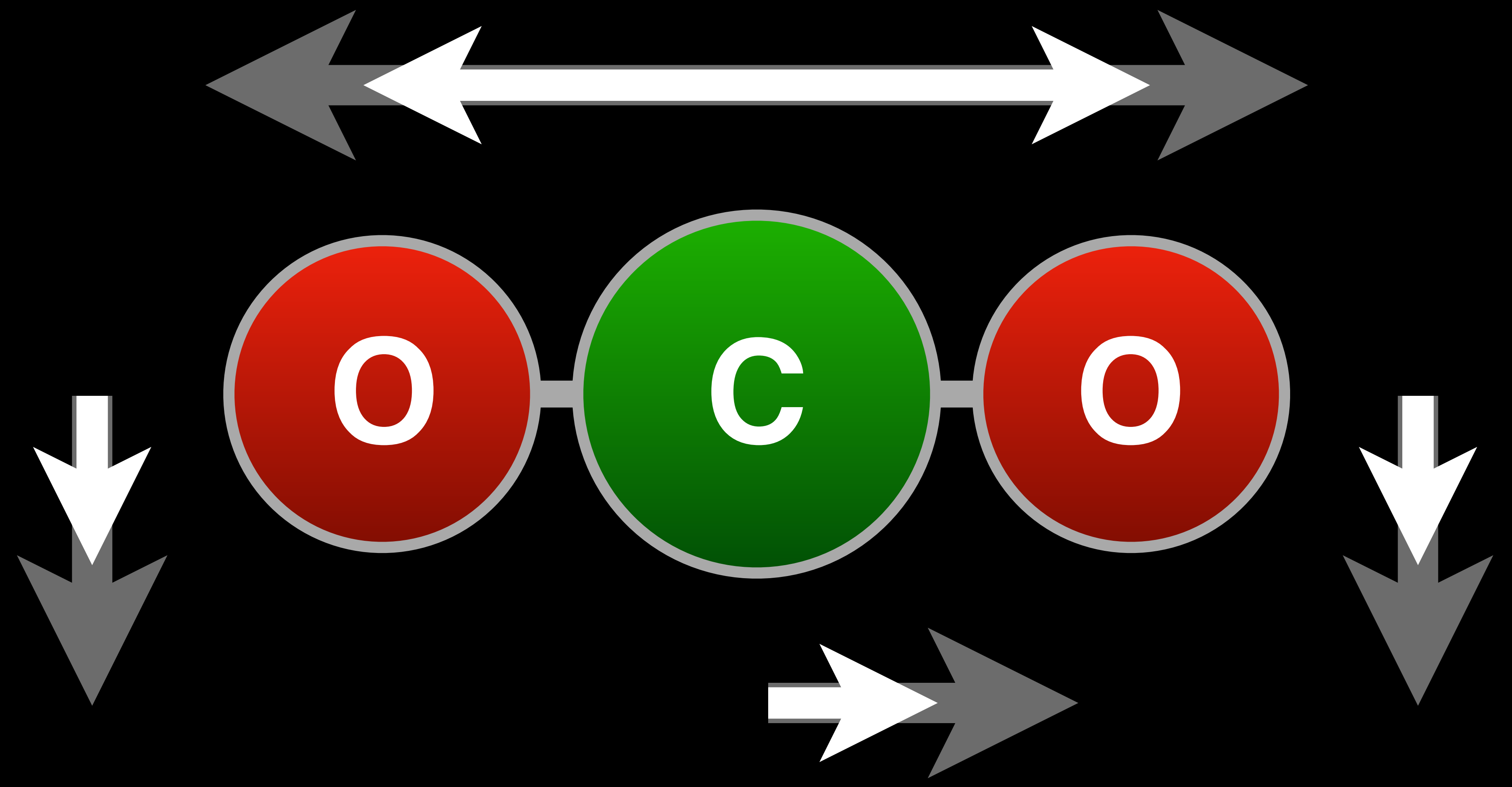
16 12 17 — m = 45, $x \approx 8 \cdot 10^{-4}$ — $\Delta^{17}O$ (since ~2010, σ ≈ 10 ppm)

16 13 18 — m = 47, $x \approx 5 \cdot 10^{-5}$ — Δ_{47} (since ~2010, σ ≈ 10 ppm)

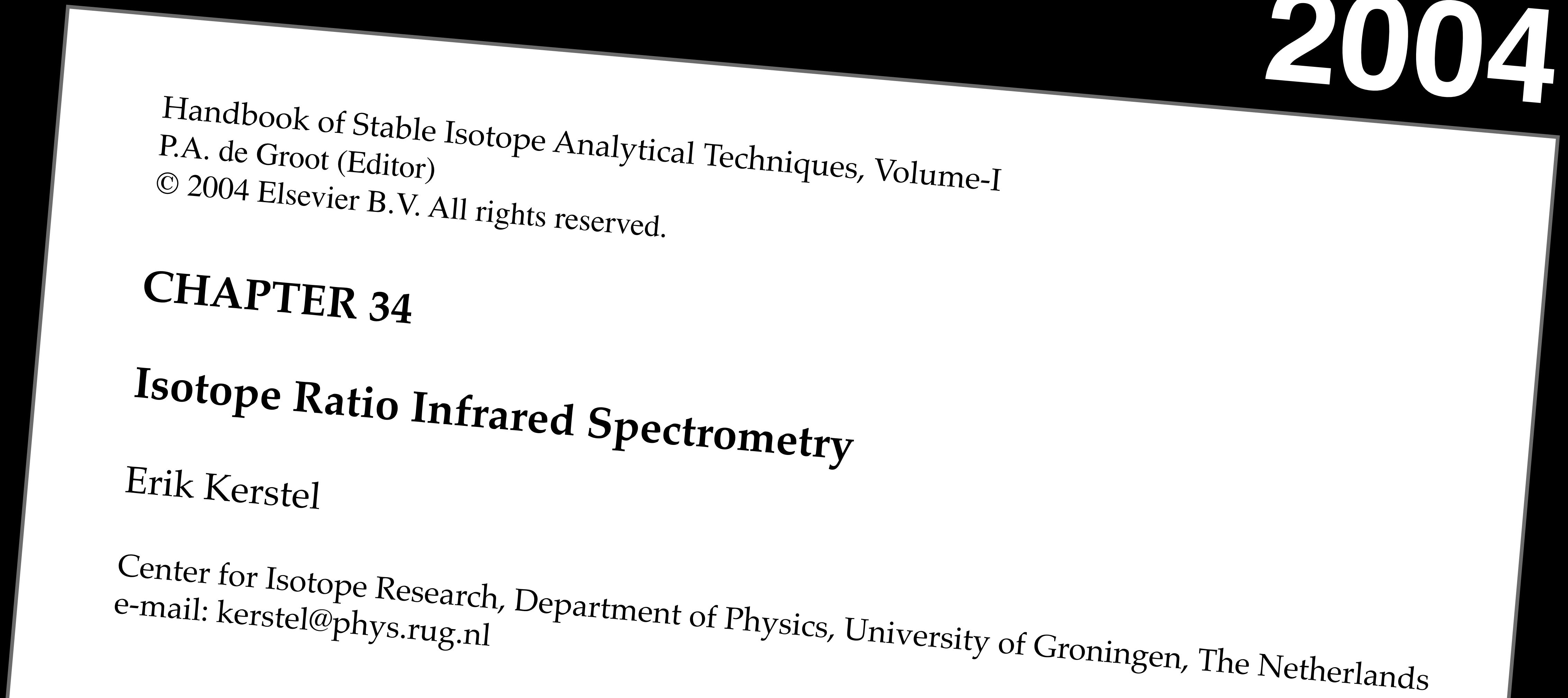
18 12 18 — m = 48, $x \approx 4 \cdot 10^{-6}$ — Δ_{48} (since ~2020, σ ≈ 30 ppm)

Spectroscopic measurements of isotopic abundances

- Many molecules absorb infra-red photons with quantified energy levels.
- These levels corresponding to transitions between rovibrational modes of excitation.
- Absorbed wavelengths depend on the <u>distribution of mass</u> rather than total molecular mass.



2004


Handbook of Stable Isotope Analytical Techniques, Volume-I
P.A. de Groot (Editor)
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CHAPTER 34

Isotope Ratio Infrared Spectrometry

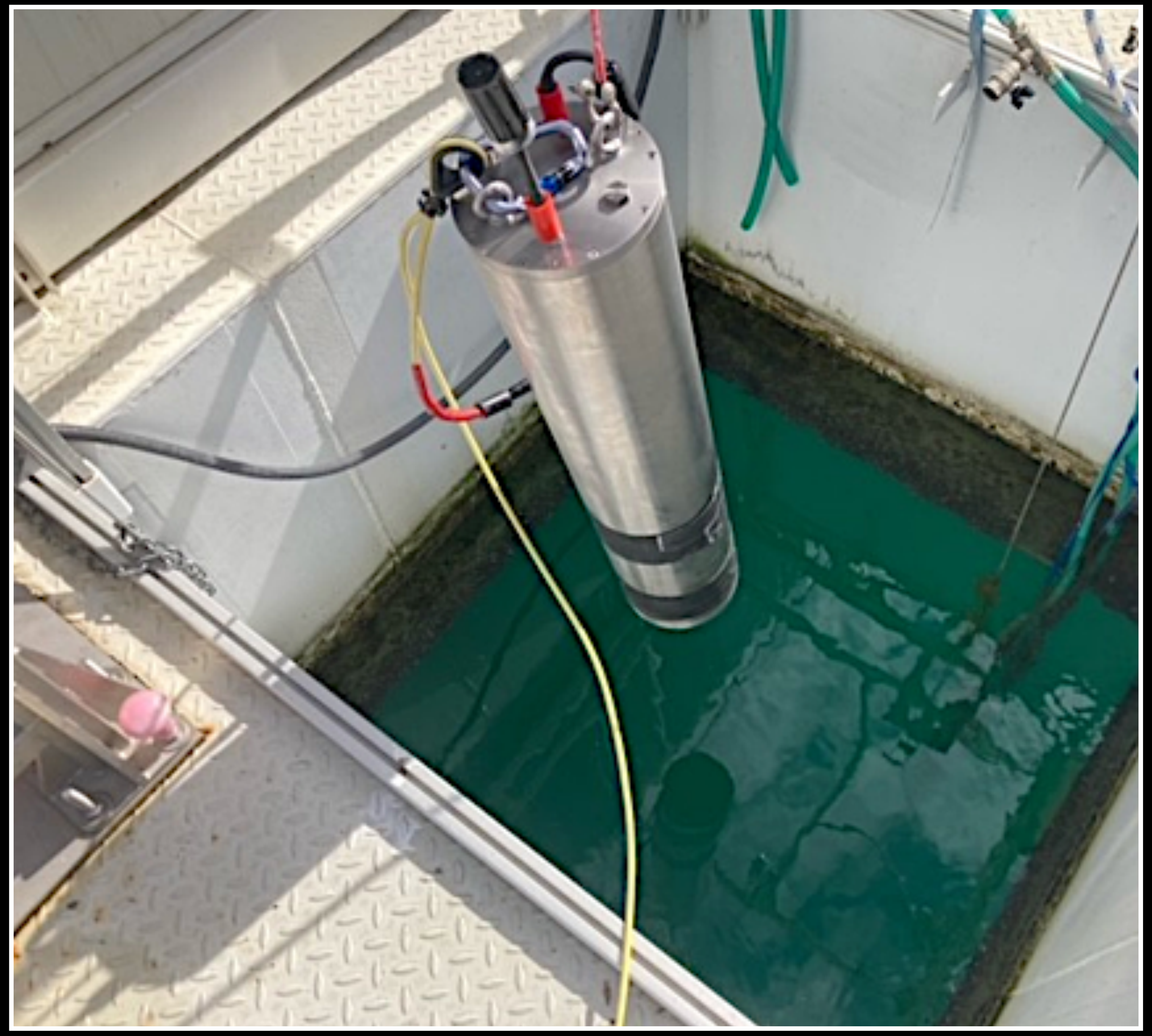
Erik Kerstel

Center for Isotope Research, Department of Physics, University of Groningen, The Netherlands
e-mail: kerstel@phys.rug.nl

Direct measurements in the field

$\delta^{13}C$, $\delta^{18}O$, $\delta^{2}H$...

Infrastructure européenne d'observation
des gaz à effet de serre



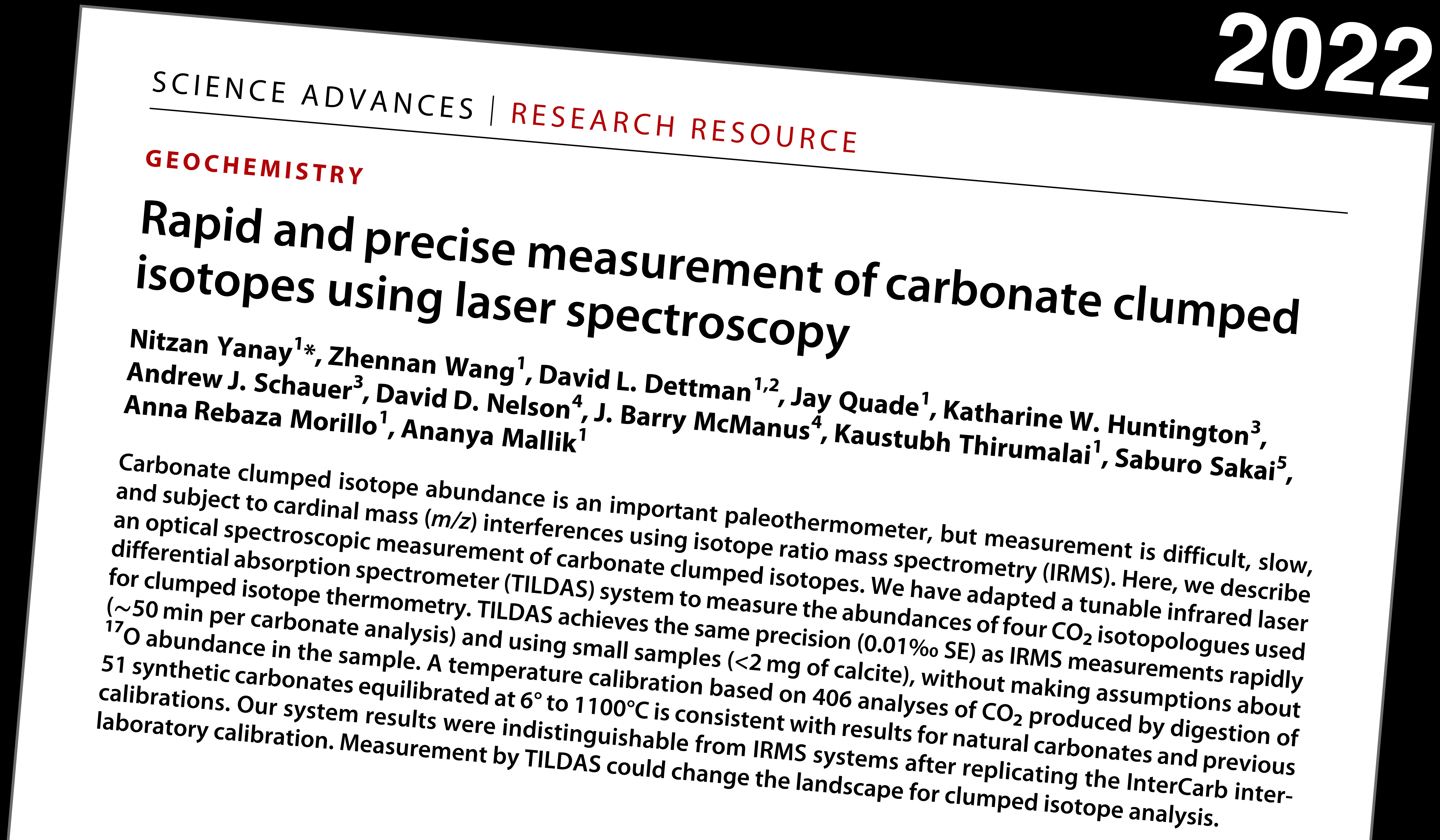
cf présentation d'Axel Wohleber
cet après-midi

Faster measurements in the lab

16 13 18

Tunable Infrared Laser
Direct Absorption Spectroscopy
(TILDAS, Aerodyne)

2022



SCIENCE ADVANCES | RESEARCH RESOURCE

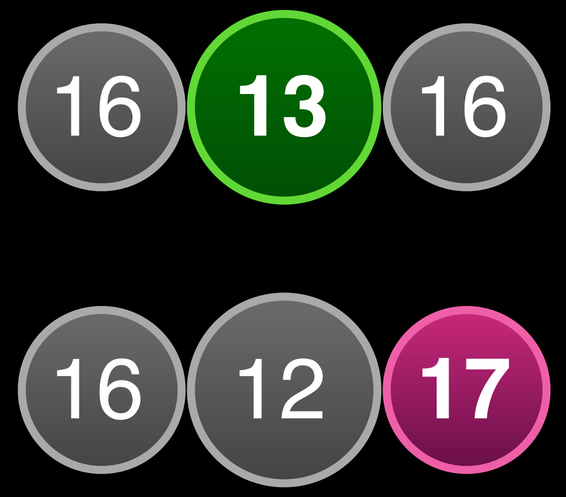
GEOCHEMISTRY

Rapid and precise measurement of carbonate clumped isotopes using laser spectroscopy

Nitzan Yanay[1]*, Zhennan Wang[1], David L. Dettman[1,2], Jay Quade[1], Katharine W. Huntington[3], Andrew J. Schauer[3], David D. Nelson[4], J. Barry McManus[4], Kaustubh Thirumalai[1], Saburo Sakai[5], Anna Rebaza Morillo[1], Ananya Mallik[1]

Carbonate clumped isotope abundance is an important paleothermometer, but measurement is difficult, slow, and subject to cardinal mass (*m/z*) interferences using isotope ratio mass spectrometry (IRMS). Here, we describe an optical spectroscopic measurement of carbonate clumped isotopes. We have adapted a tunable infrared laser differential absorption spectrometer (TILDAS) system to measure the abundances of four CO_2 isotopologues used for clumped isotope thermometry. TILDAS achieves the same precision (0.01‰ SE) as IRMS measurements rapidly (~50 min per carbonate analysis) and using small samples (<2 mg of calcite), without making assumptions about ^{17}O abundance in the sample. A temperature calibration based on 406 analyses of CO_2 produced by digestion of 51 synthetic carbonates equilibrated at 6° to 1100°C is consistent with results for natural carbonates and previous calibrations. Our system results were indistinguishable from IRMS systems after replicating the InterCarb interlaboratory calibration. Measurement by TILDAS could change the landscape for clumped isotope analysis.

Previously challenging measurements (e.g., $\Delta^{17}O$ of CO_2)



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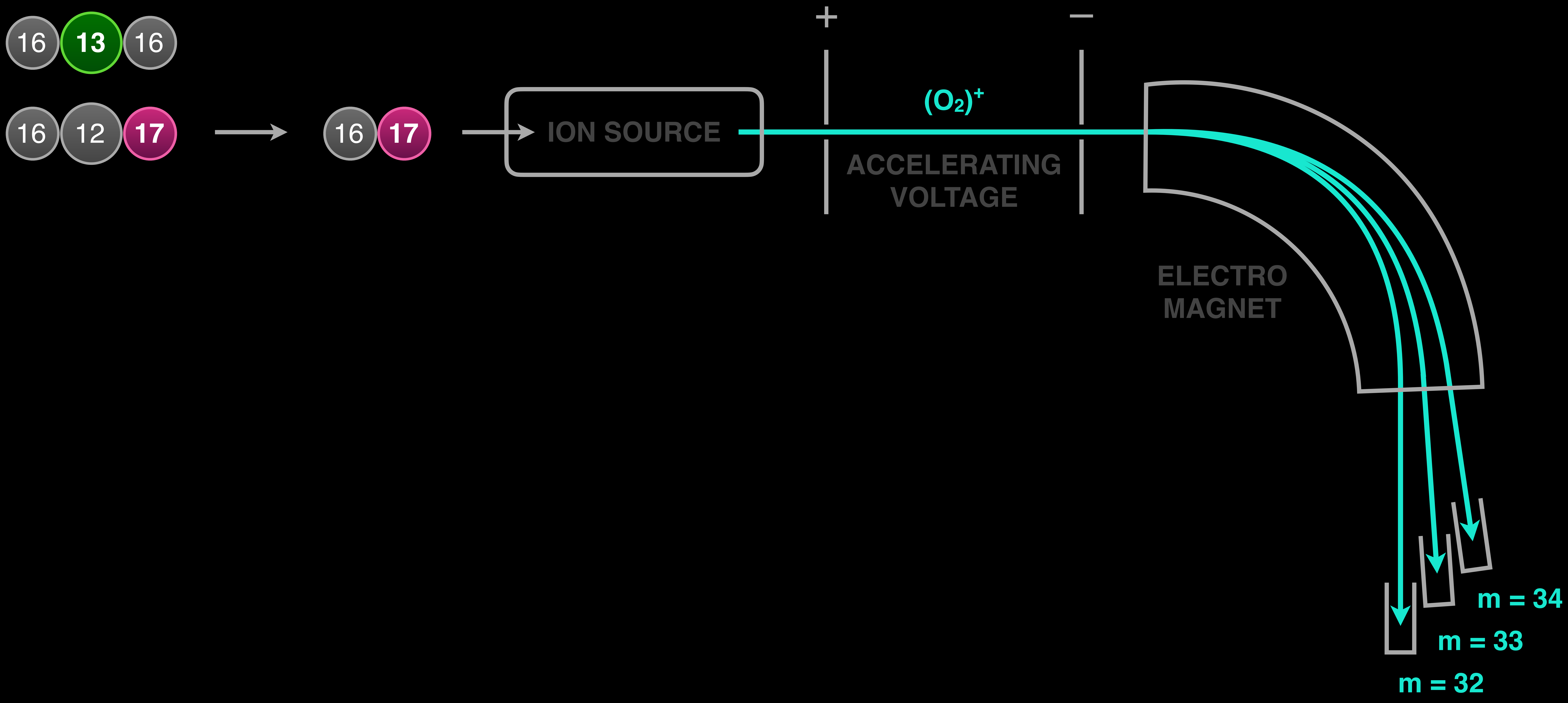

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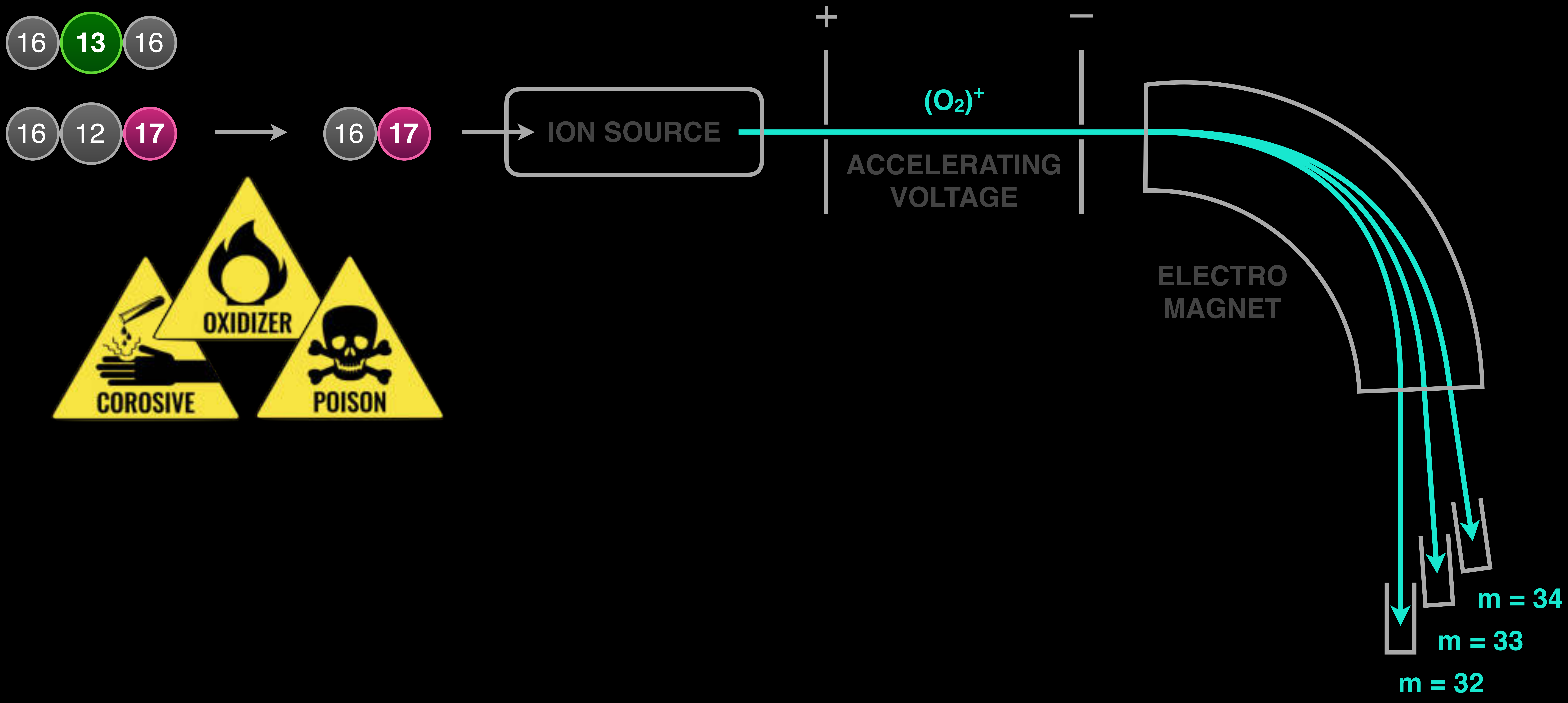
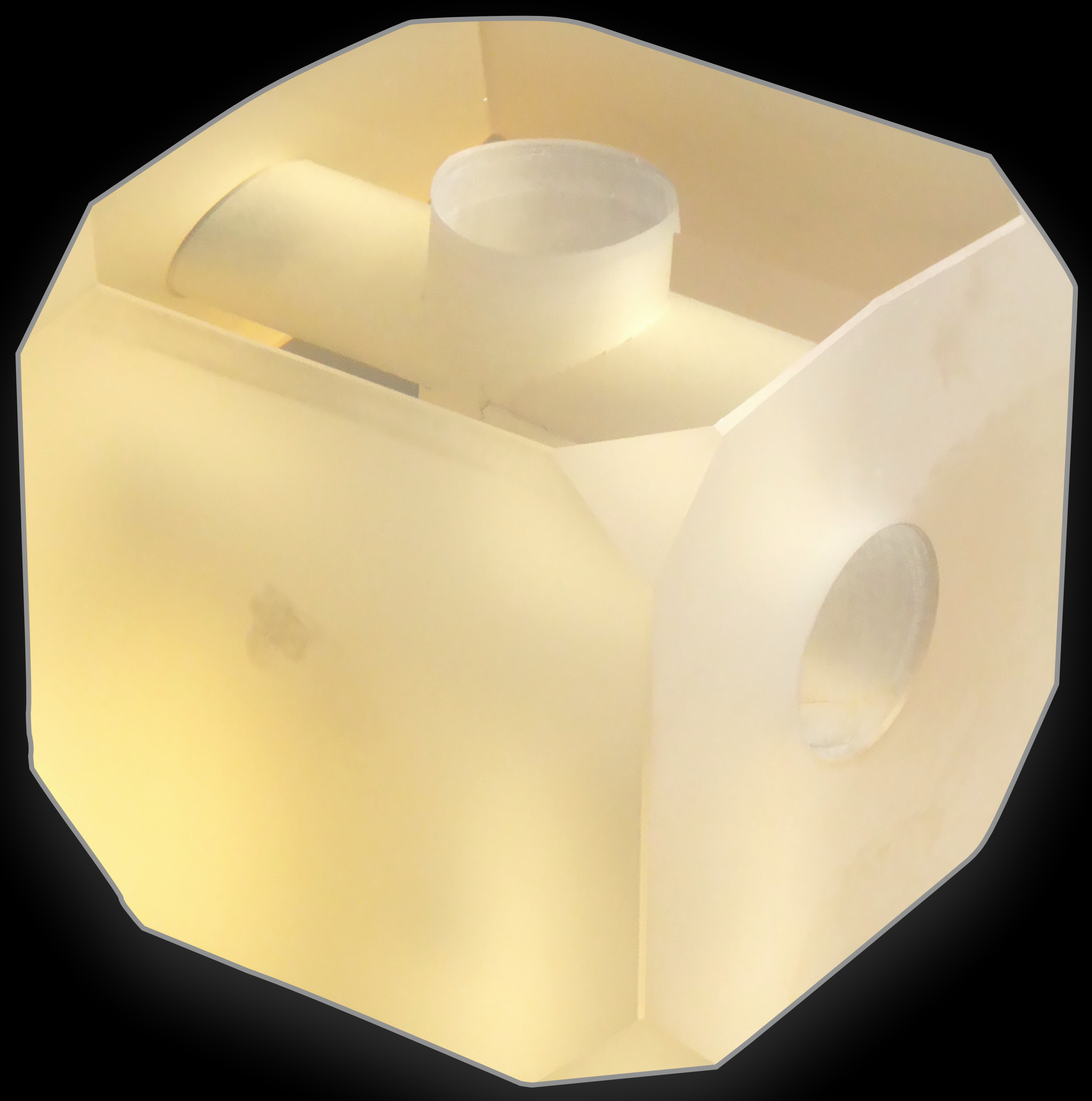


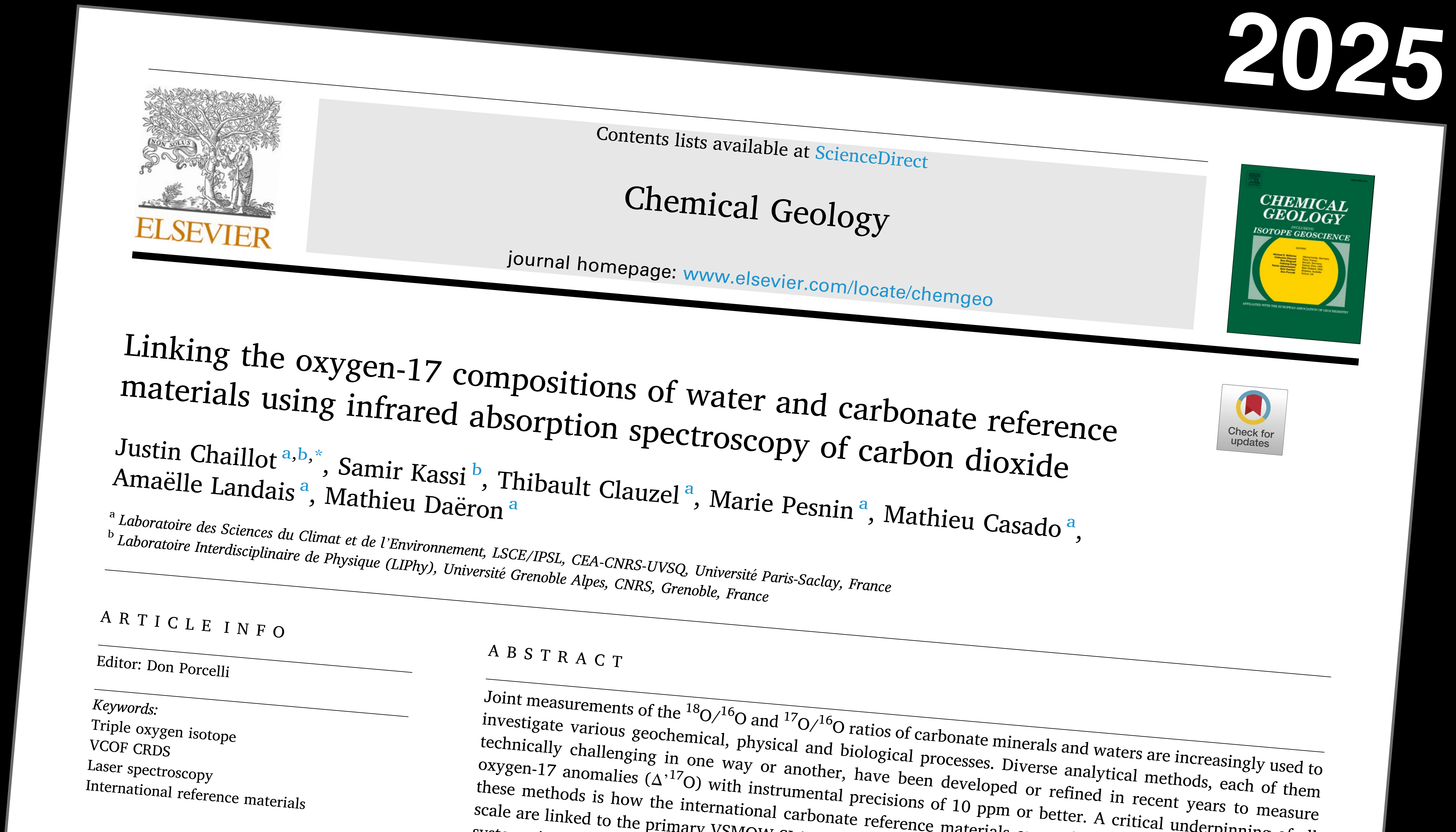
Previously challenging measurements (e.g., $\Delta^{17}O$ of CO_2)

16 12 17



V-Cavity Optical Feedback
Cavity Ring-Down Spectroscopy
(VCOF-CRDS, LIPhy-LSCE)

2025


Contents lists available at ScienceDirect
Chemical Geology
journal homepage: www.elsevier.com/locate/chemgeo

Linking the oxygen-17 compositions of water and carbonate reference materials using infrared absorption spectroscopy of carbon dioxide

Justin Chaillot [a,b,*], Samir Kassi [b], Thibault Clauzel [a], Marie Pesnin [a], Mathieu Casado [a], Amaëlle Landais [a], Mathieu Daëron [a]

[a] Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, France
[b] Laboratoire Interdisciplinaire de Physique (LIPhy), Université Grenoble Alpes, CNRS, Grenoble, France

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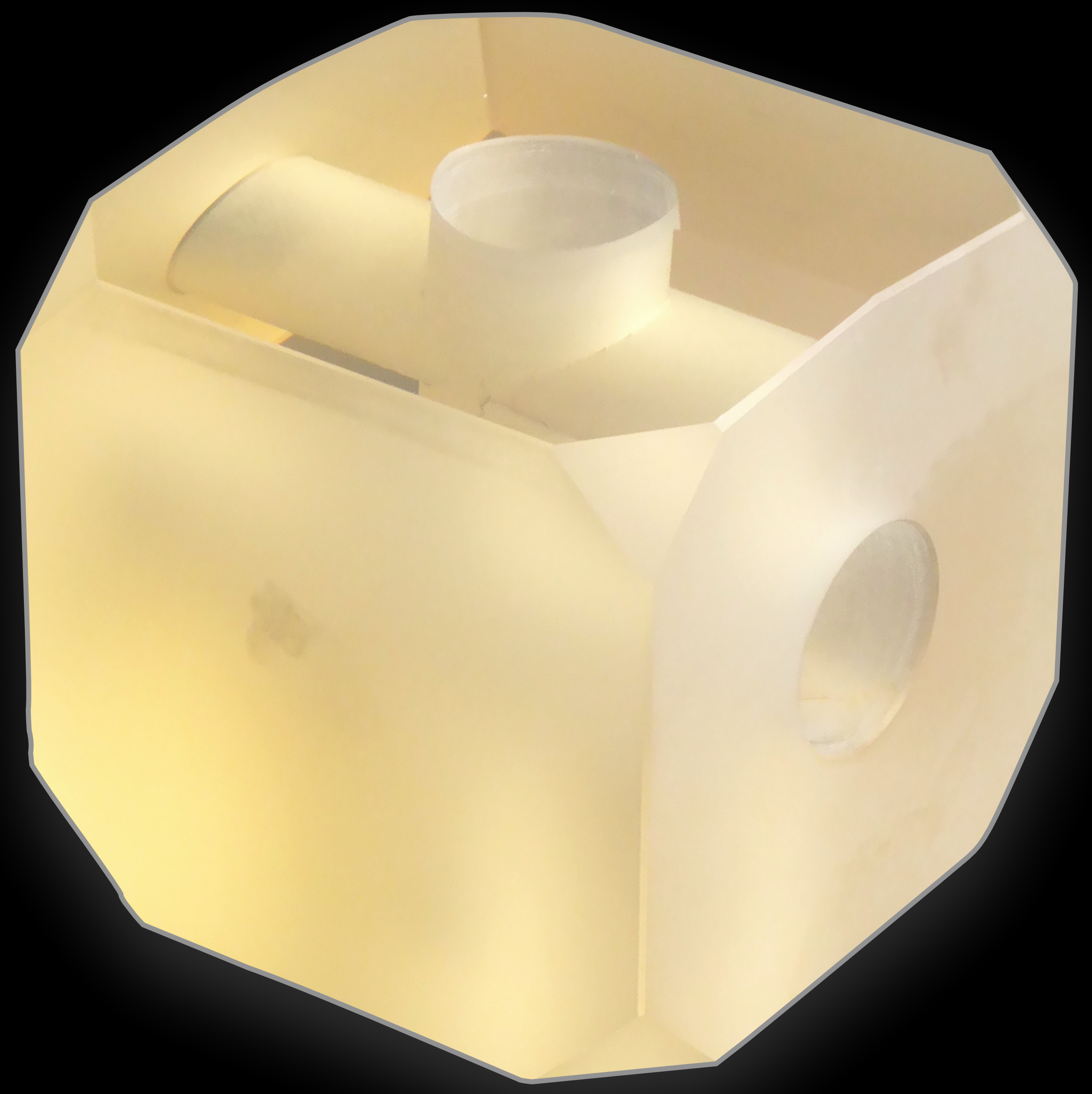
ABSTRACT

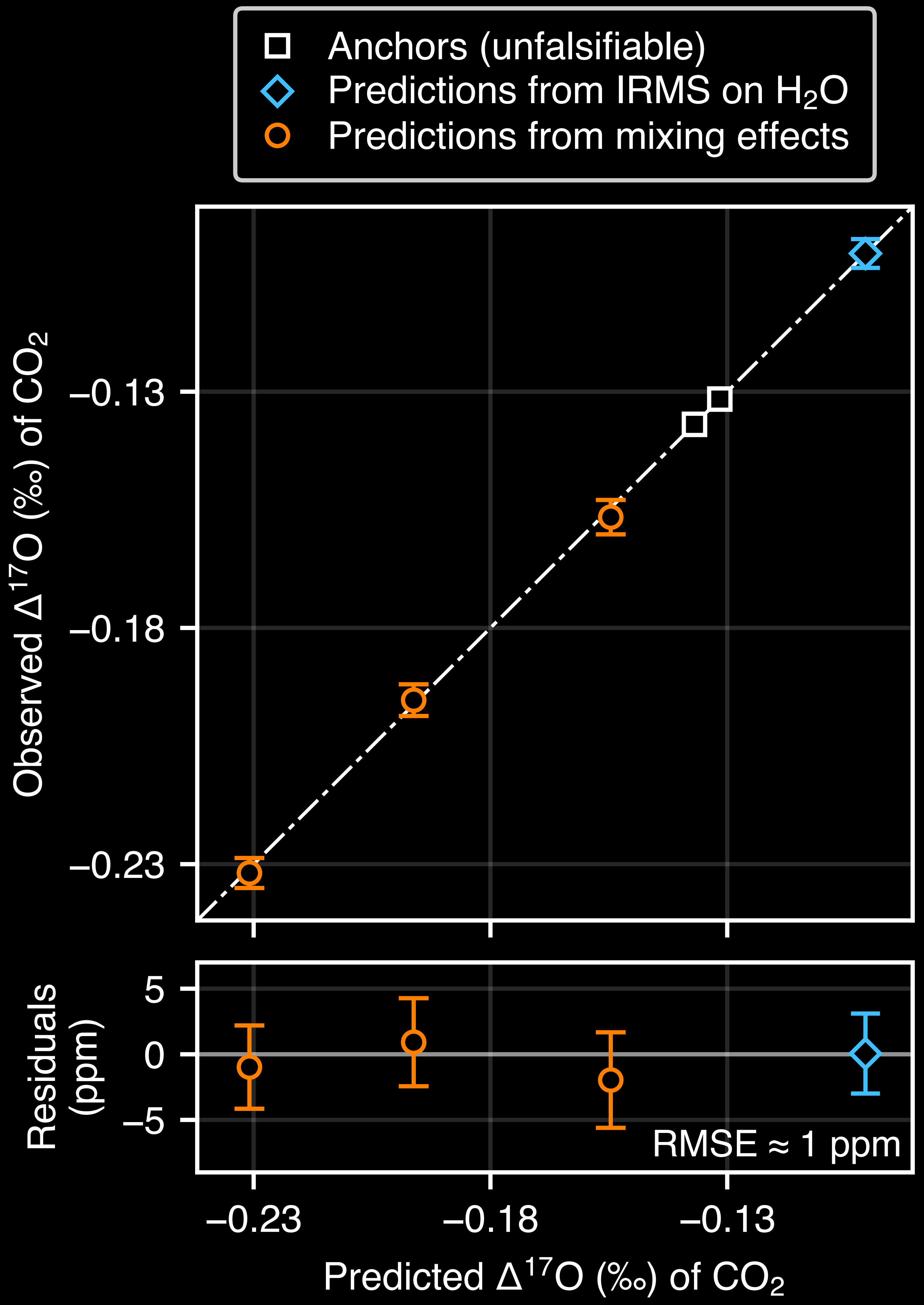
Joint measurements of the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios of carbonate minerals and waters are increasingly used to investigate various geochemical, physical and biological processes. Diverse analytical methods, each of them technically challenging in one way or another, have been developed or refined in recent years to measure oxygen-17 anomalies ($\Delta'^{17}O$) with instrumental precisions of 10 ppm or better. A critical underpinning of all these methods is how the international carbonate reference materials ... scale are linked to the primary VSMOW ...

Previously challenging measurements (e.g., $\Delta^{17}O$ of CO_2)

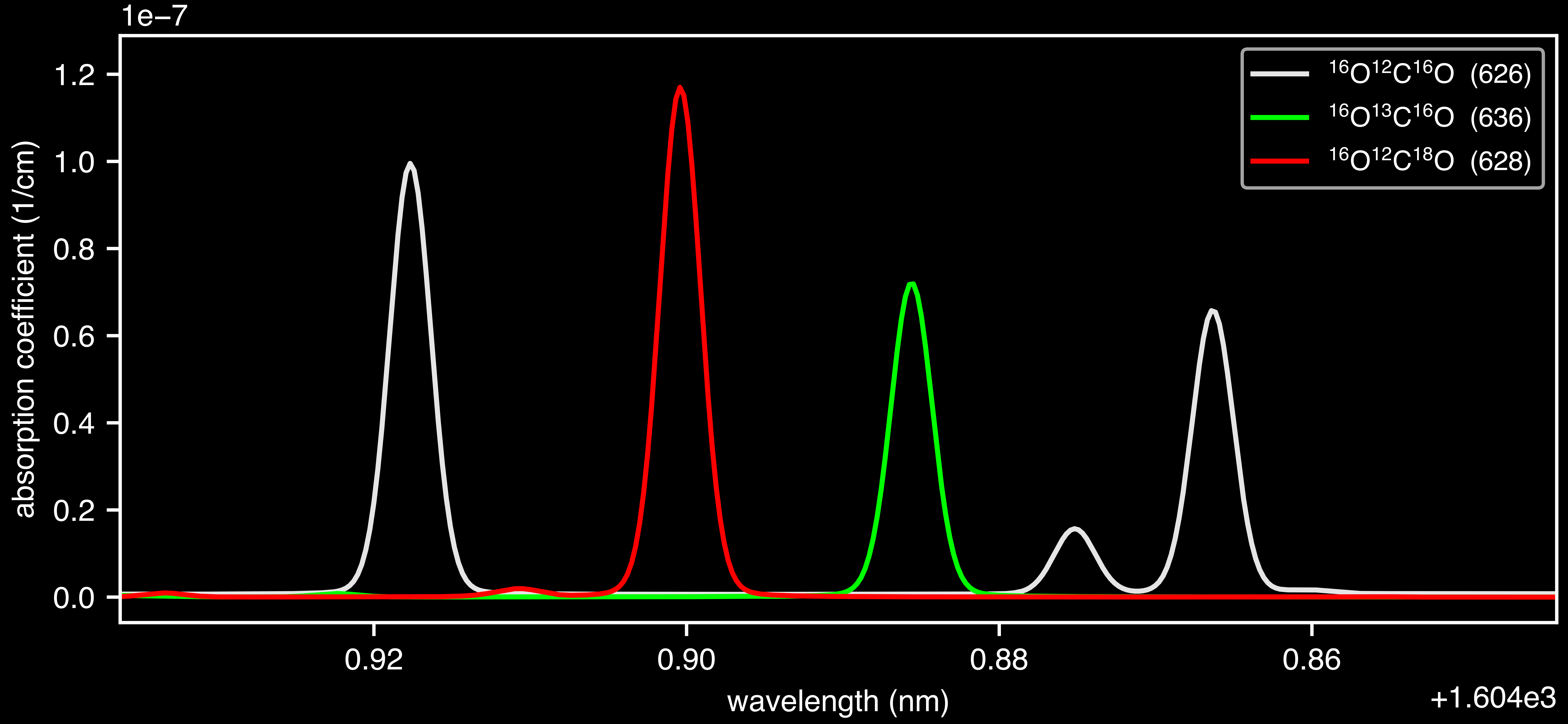
16 12 17



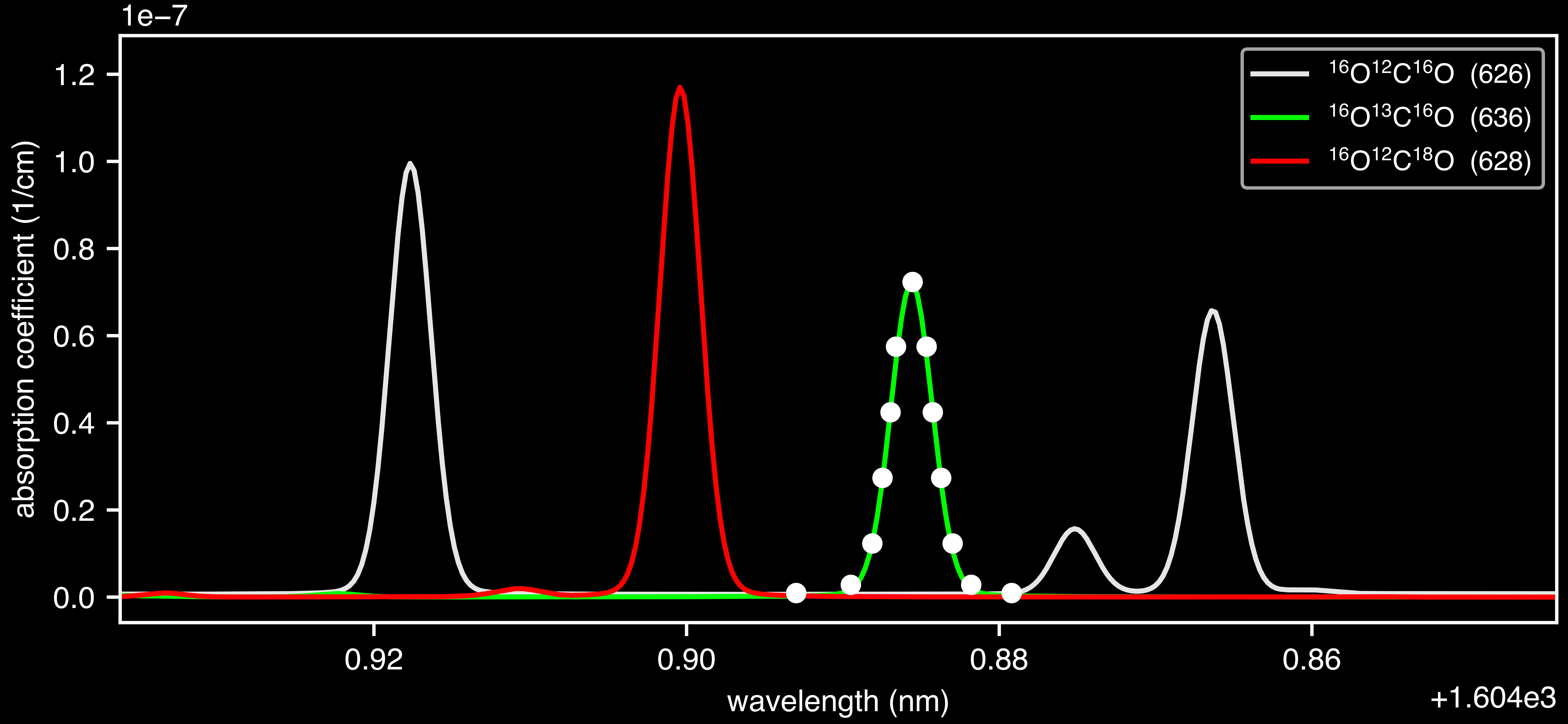
V-Cavity Optical Feedback
Cavity Ring-Down Spectroscopy
(VCOF-CRDS, LIPhy-LSCE)



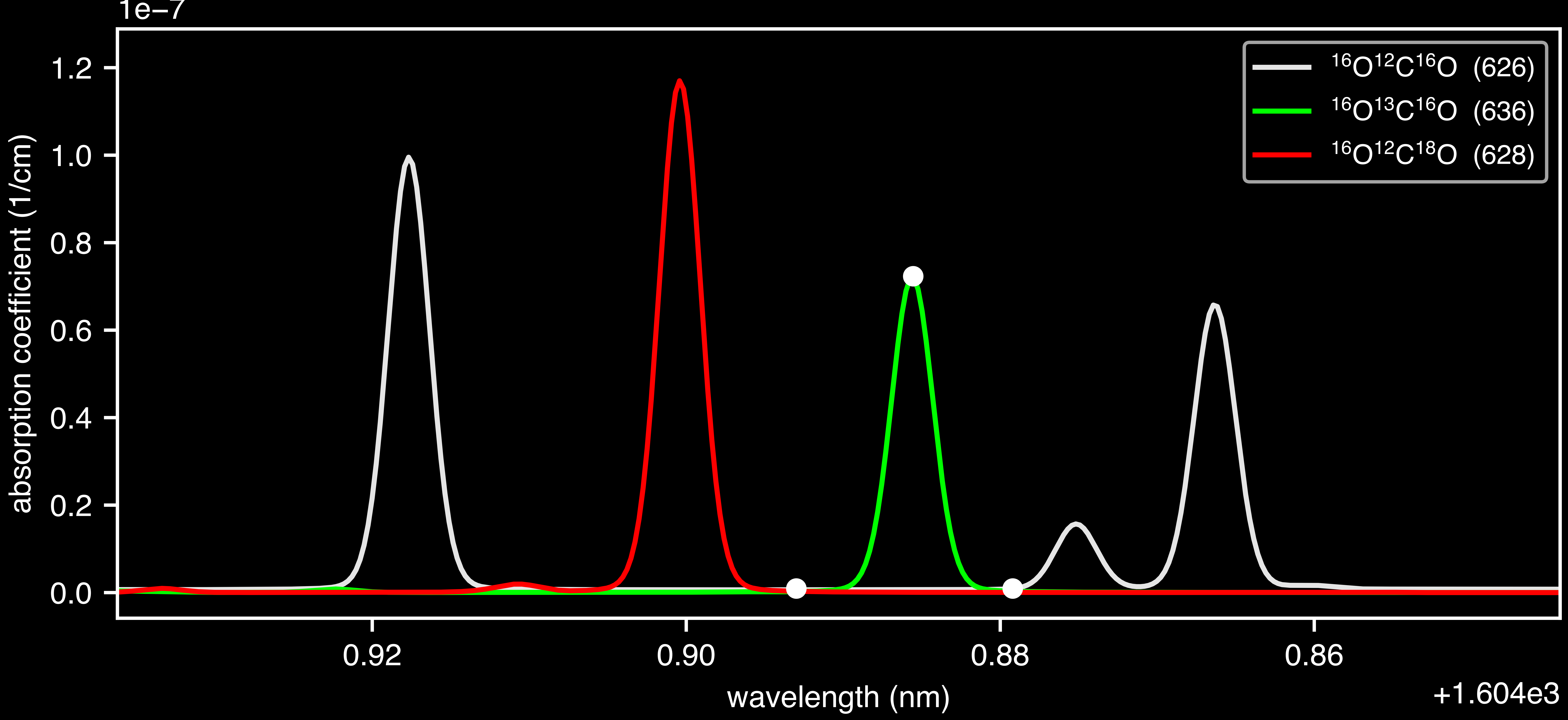
Factors limiting accuracy?



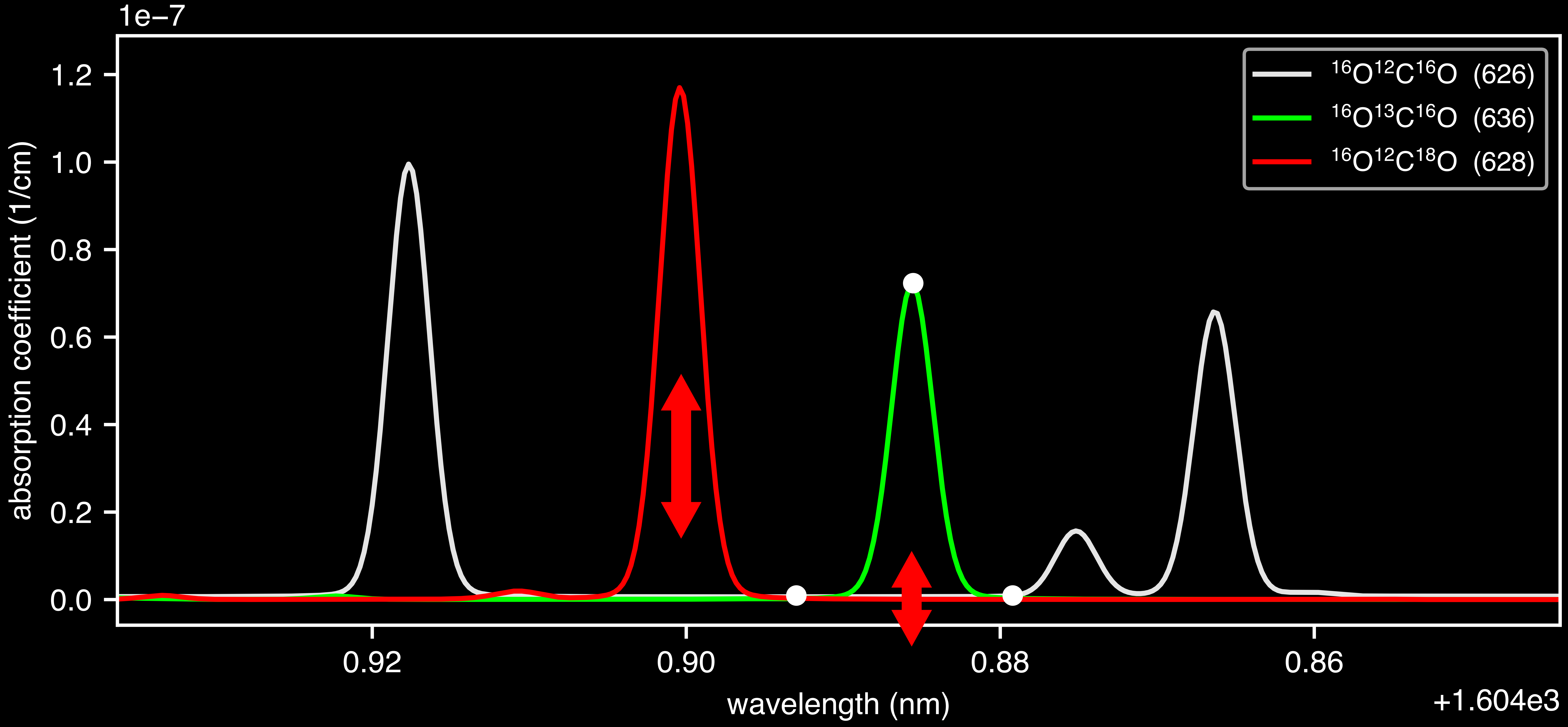
Factors limiting accuracy?



Factors limiting accuracy?



Factors limiting accuracy?

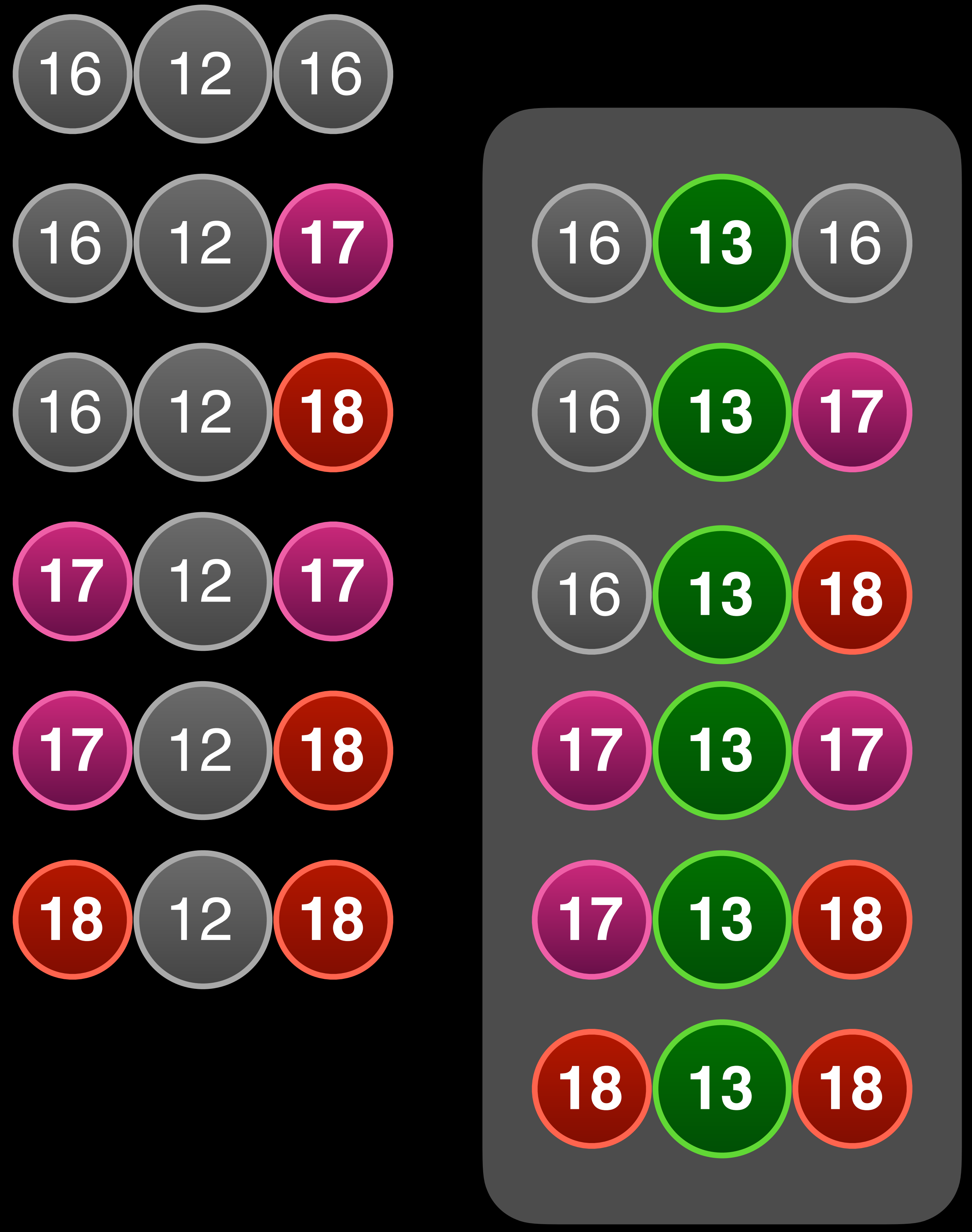


Metrological issues

Example: 3 different definitions of $\delta^{13}C$

Metrological issues

Example: 3 different definitions of $\delta^{13}C$



Textbook definition

$$\delta^{13}C = \frac{(^{13}C\ /\ ^{12}C)}{(^{13}C\ /\ ^{12}C)_{ref}} - 1$$

Metrological issues

Example: 3 different definitions of $\delta^{13}C$

Spectroscopic measurement

$$\delta^{13}C = \frac{(^{636}/_{626})}{(^{636}/_{626})_{ref}} - 1$$

Textbook definition

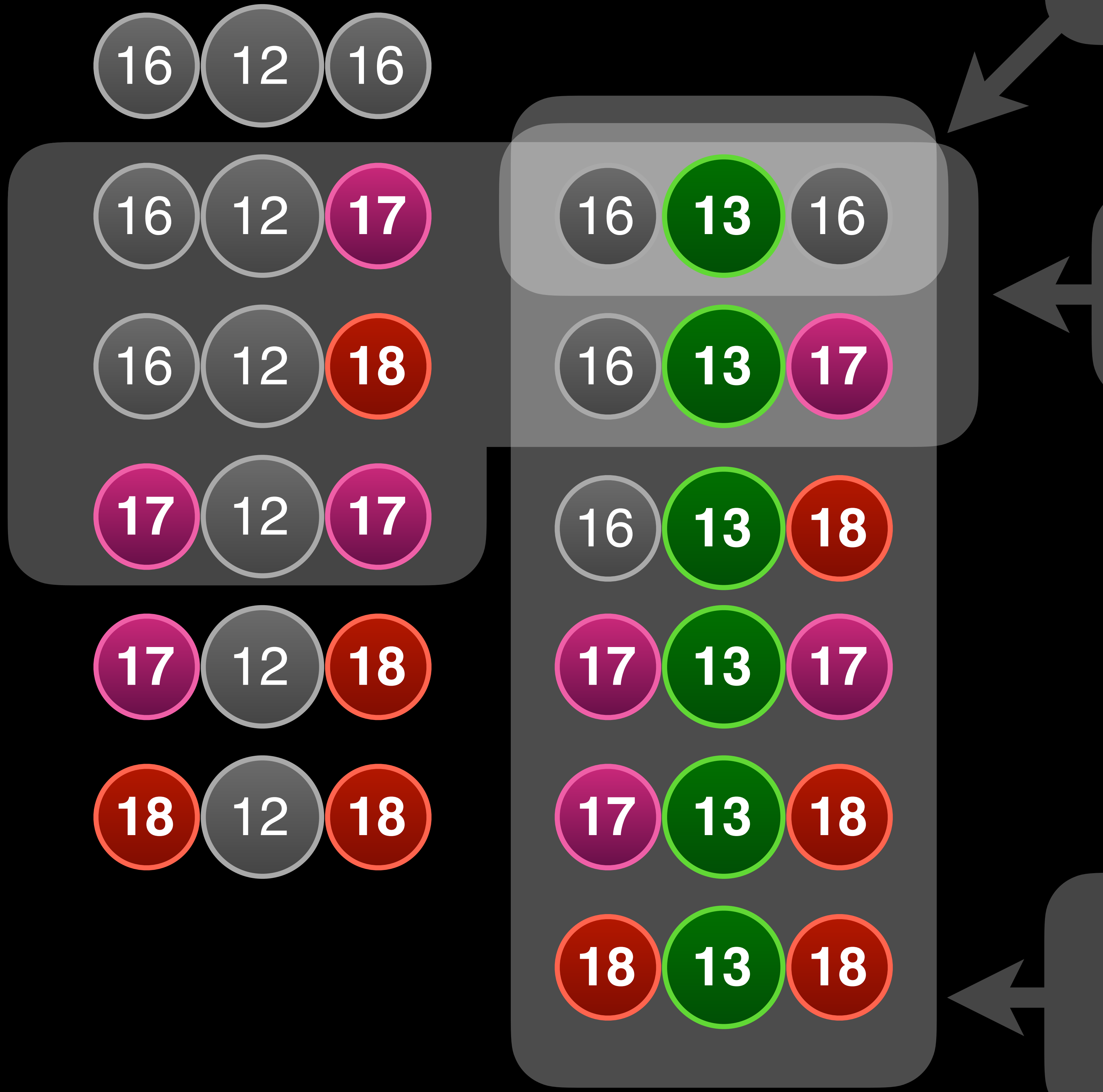
$$\delta^{13}C = \frac{(^{13}C\ /\ ^{12}C)}{(^{13}C\ /\ ^{12}C)_{ref}} - 1$$

Metrological issues

Example: 3 different definitions of $\delta^{13}C$

Spectroscopic measurement

$$\delta^{13}C = \frac{\left({}^{636}/_{626}\right)}{\left({}^{636}/_{626}\right)_{ref}} - 1$$



$$\delta^{13}C = f\left({}^{45}/_{44}, {}^{46}/_{44} \right)$$

assuming $\Delta^{17}O = 0$

IRMS measurement

Textbook definition

$$\delta^{13}C = \frac{\left({}^{13}C \,/\, {}^{12}C\right)}{\left({}^{13}C \,/\, {}^{12}C\right)_{ref}} - 1$$

Conclusions:

Dialogue between spectroscopists and geochemists is useful and rewarding.

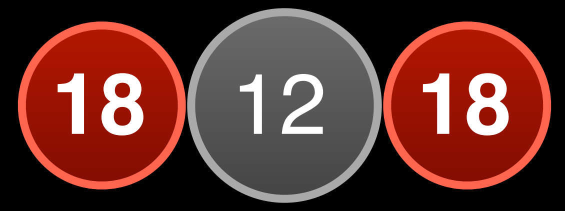
Looming metrological issues

Earth-science applications are demanding but have critical implications for us all.

Earth-science labs will soon need a new generation of engineers & researchers.

Three geochemists comparing the performances of their laser instruments (artistic representation)

Overcome "hard" limits of IRMS? (e.g., Δ_{48} of CO_2)



- IRMS of very rare species is limited by Poisson counting statistics
  (count N ions $\Rightarrow$ $\sigma \approx N^{1/2}$)
- Even after 80+ years of development, ion sources remain not very efficient
- By contrast, precision of infra-red spectroscopy bumps against "soft" limits
  (thermal stability, optical fringes, saturation effects...)