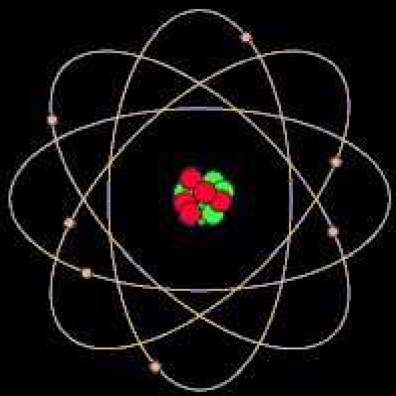
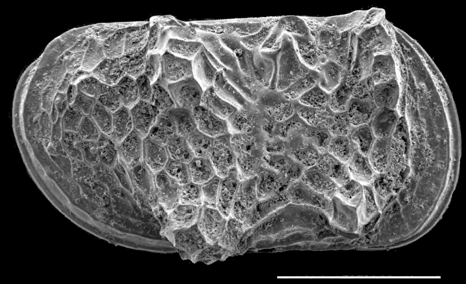
Isotopes: theory, principles and practicalities





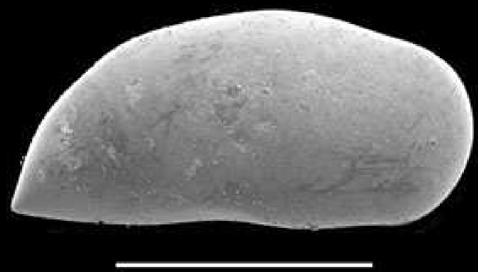
Ian Boomer

Stable Isotope & Luminescence Laboratory,
(SILLA) University of Birmingham

(http://www.gees.bham.ac.uk/research/facilities_silla.shtml)

Stable-Isotopes

Overview

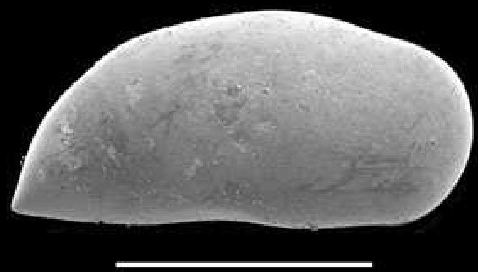


Geochemistry and stable-isotope analysis of lacustrine and marine carbonates provides information on environmental variability in temperature, salinity, isotope composition of the host water and carbon cycling.

Ostracod calcite provides a geochemical snapshot of (largely bottom-water) hydrochemical conditions at the time of (rapid) shell calcification.

Stable-Isotopes

Overview

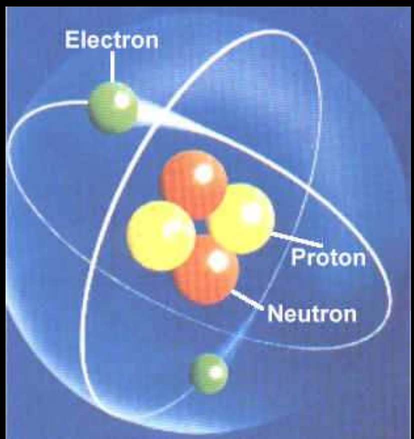


- What are isotopes ?
- What controls isotope composition of water & carbonates?
- How do we deal with isotope results ?
- How do we analyse isotope samples ?

What are isotopes ?

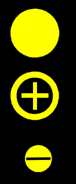
Most element atoms (e.g. Oxygen, Nitrogen, Carbon etc..) may exist as one of a number of isotopes

All isotopes of an element are *Chemically* the same with the same number of **Protons** but have different *Physical* properties due to different numbers of **Neutrons** and therefore different atomic masses.



e.g. *Hydrogen has three isotopes* ***1****, 2, 3*

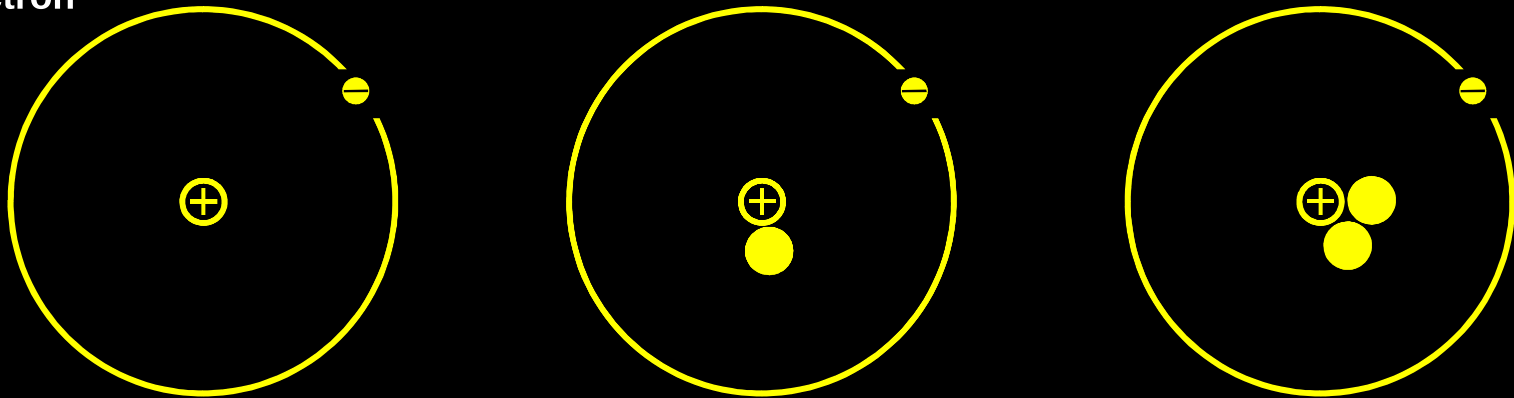
Hydrogen (H) – the simplest element



(Mass = Neutrons + Protons)

(Number = No of Protons)

$^{\text{mass}}_{\text{number}}\text{Element}$ $\quad {}^{1}_{1}\text{H}$



Hydrogen ${}^{1}_{1}\text{H}$	**Deuterium** ${}^{2}_{1}\text{H}$	**Tritium** ${}^{3}_{1}\text{H}$
1 Proton 1 Electron	1 Proton 1 Electron 1 Neutron	1 Proton 1 Electron 2 Neutrons

Three isotopes of Hydrogen: each with 1 Proton in nucleus and 1 Electron in orbit.

Each Isotope has same no. of Protons but a different no. of Neutrons in the nucleus

All isotopes of an element have the same ***atomic number*** but different ***atomic mass***

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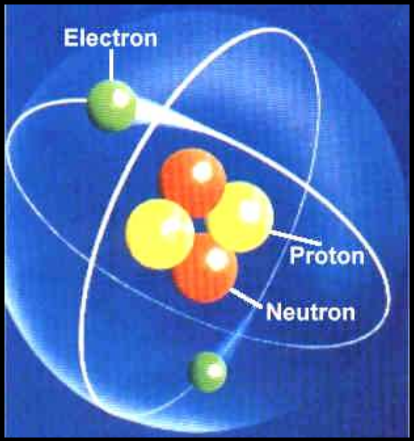

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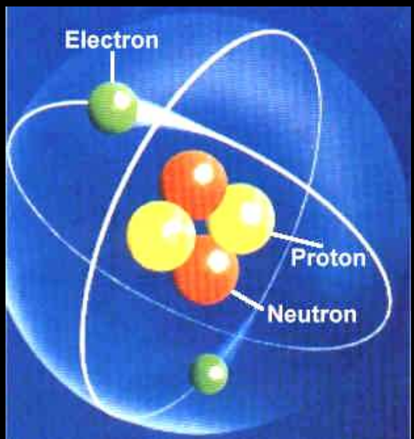


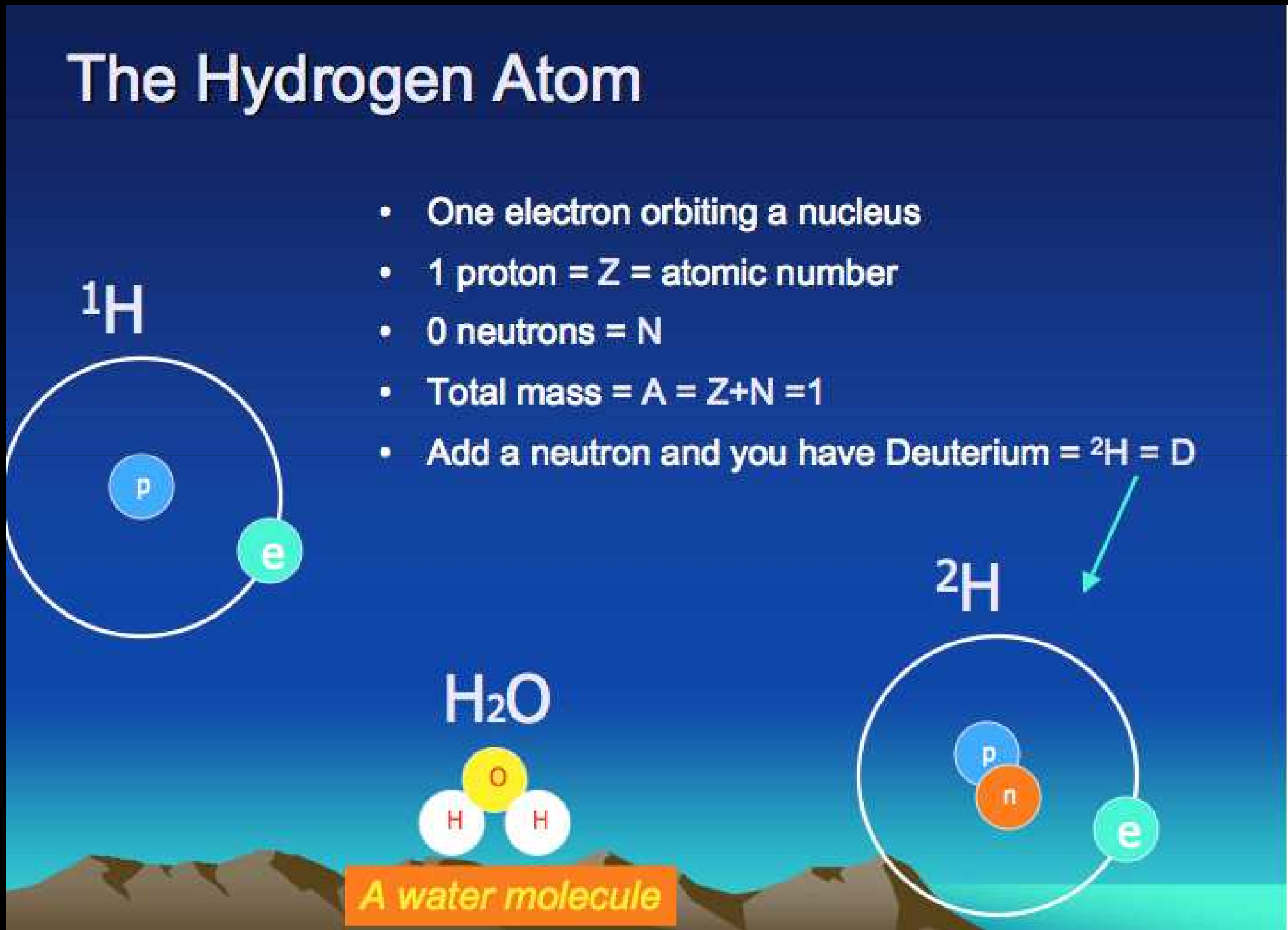
e.g. *Hydrogen has three isotopes* ***1****, 2, 3*

Carbon has three isotopes ***12****, 13, 14*

Oxygen has three isotopes ***16****, 17, 18*

Lightest Isotope, generally >99.8%, is more easily influenced by physical and biological processes

Atoms and Isotopes



All isotopes available for inclusion in environmental molecules
One very common, the other(s), very rare

Stable-Isotopes

Sources – *Where do the isotopes come from?*

From water to $CaCO_3$

Calcium – dissolved as Ca^{2+} ions in water

Carbon – as DIC or DOC (dissolved inorganic carbon, dissolved organic carbon)

HCO_3^- - Bicarbonate ions dissolved in water (formed by interaction between rocks, soils and groundwater in the catchment)

Stable-Isotopes

Sources – *What controls the isotope composition of the water?*

Oxygen – strongly controlled by isotopic composition of input, P:E rates and residence time

$^{18:16}$O ratio $\delta^{18}O$

Carbon – Largely the result of carbon cycling and especially CO2 respiration by plants in lake and catchment, nature of bedrock

$^{13:12}$C ratio $\delta^{13}C$

What is a delta value?

Understanding Isotopes

Delta values

Isotope are generally reported as ‘delta’ values (δ)

These are ratios that relate the isotopic composition of the sample to that of a standard

Delta values are said to be either heavier (enriched) or lighter (depleted) than a standard

For example, if a sample is said to have a delta value of **+5 ‰** $\delta^{18}O$ then it is 5 parts in 1000 *enriched* in ^{18}O compared with the standard

If it has a delta value of **-5 ‰** $\delta^{18}O$ then it is 5 parts in 1000 *depleted* in ^{18}O

Results and Standards

Calculating the delta value

Given as per mil (‰) difference (δ) compared to a standard

For Oxygen this is calculated as :

$$\delta^{18}O = 1000 \times \frac{{}^{18}O/{}^{16}O_{(sample)} - {}^{18}O/{}^{16}O_{(standard)}}{{}^{18}O/{}^{16}O_{(standard)}}$$

The result is multiplied by 1000 simply to make the resulting ratio more ‘meaningful’.

Stable-Isotopes

Isotope standards

PDB – Pee Dee Belemnite (from Cretaceous Pee Dee Formation, Urey et al., 1951) used as a *carbonate standard* (carbon & oxygen). The original soon ran out and was replaced by artificial V-PDB (Vienna PDB, a marble). The IAEA in Vienna now control the creation and distribution of all isotopic standard materials

SMOW – Standard Mean Ocean Water, a *water standard*, used for all fresh, brackish and marine water (hydrogen & oxygen)

Obviously oxygen can be reported on either scale, but generally against V-SMOW for water analyses and V-PDB for carbonates

The IAEA in Vienna now control the creation and distribution of all isotopic standard materials

Understanding Isotopes

We are going to be dealing primarily with carbonate isotopes

The measurement of carbonates is undertaken on CO_2 liberated by acidification (using >99 % phosphoric acid, H_3PO_4), generally at 25˚C.

$$CaCO_3 + 2H^+ \rightarrow CO_2 + H_2O + Ca^{2+}$$

This reaction is *quantitative* for carbon, if all carbon is recovered then the $\delta^{13}C$ of the gas will be the same as the $\delta^{13}C$ of the calcite.

BUT, since one of the oxygen atoms is lost from the carbonate there will be fractionation and the $\delta^{18}O$ will be different – this is temperature dependent and fixed for a given temperature – *fractionation*

This temperature effect also differs between carbonate minerals (calcite, aragonite, dolomite, etc.)

Understanding Isotopes

Fractionation

When molecules change phase (e.g. oxygen from water to calcite, or water to vapour) they do not keep the same isotopic composition.

Heavier isotopes are less mobile (more difficult to 'shift')

They need more energy this results in a change in isotopic composition of the two phases as the physical process proceeds.

Understanding Isotopes

Fractionation

Equilibrium Isotope Fractionation - between materials that are in chemical equilibrium but have different molecular structures (water -> calcite)

Inversely proportional to temperature (forms the basis of palaeothermometry)

Kinetic Isotope Fractionation – occurs during relatively fast, unidirectional processes such as diffusion or where only partial exchange occurs.

Independent of temperature, largely biological (e.g. Photosynthesis or Bacterial oxidation)

For detailed information on fractionation within ostracods see Xia et al., 1997

Understanding Isotopes

Fractionation factor (α)

The difference in Isotopic composition between 2 phases at equilibrium at equilibrium is the *fractionation factor*. This is a fixed value.

The fractionation factor is different for different carbonate minerals.

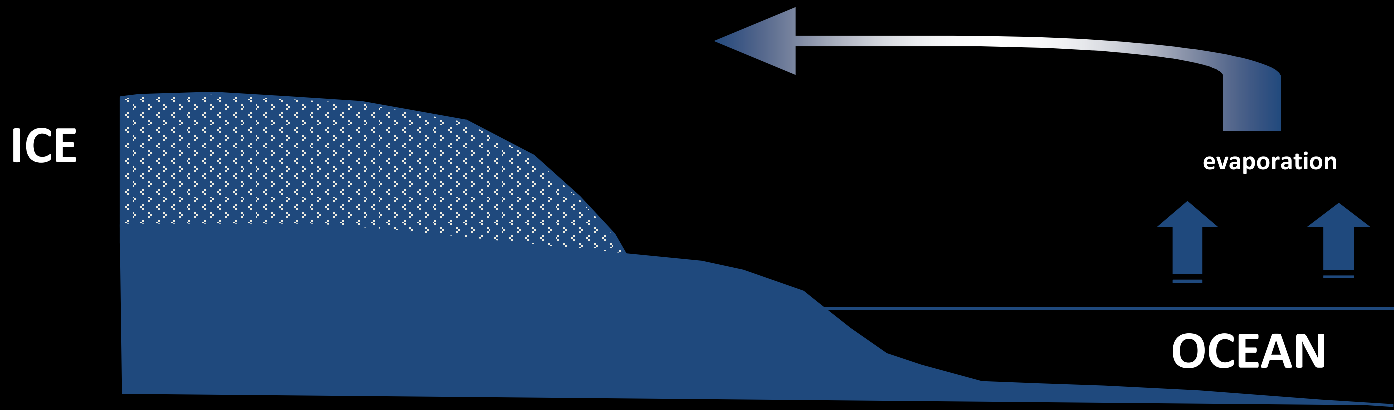
If you know the fractionation factor then you can determine the temperature of precipitation (or re-crystallisation for minerals)

or

If you can constrain the temperature independently (e.g. through shell chemistry) then it is possible to reconstruct the changing $\delta^{18}O$ of the source water

Stable-Isotopes

Common example of isotope enrichment and depletion

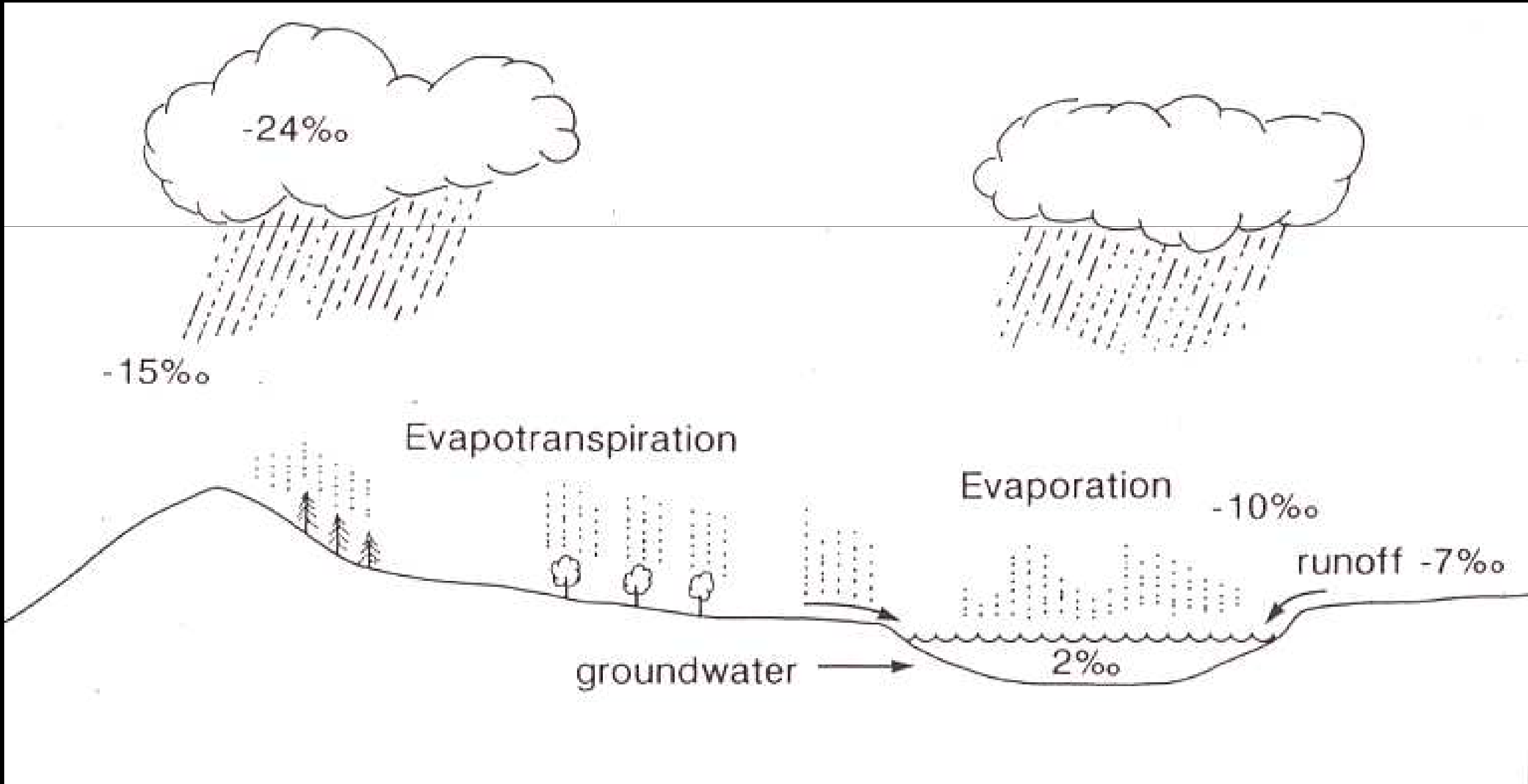


$\delta^{18}O$ –40‰	Glacial	$\delta^{18}O$ +5‰
$\delta^{18}O$ –35‰	Interglacial	$\delta^{18}O$ +3.5‰

Climate	$\delta^{18}O$ ice	$\delta^{18}O$ ocean
Cool period	Light	Heavy
Warm period	Heavy	Light

Stable-Isotopes

Common example of isotope enrichment and depletion



Stable-Isotopes

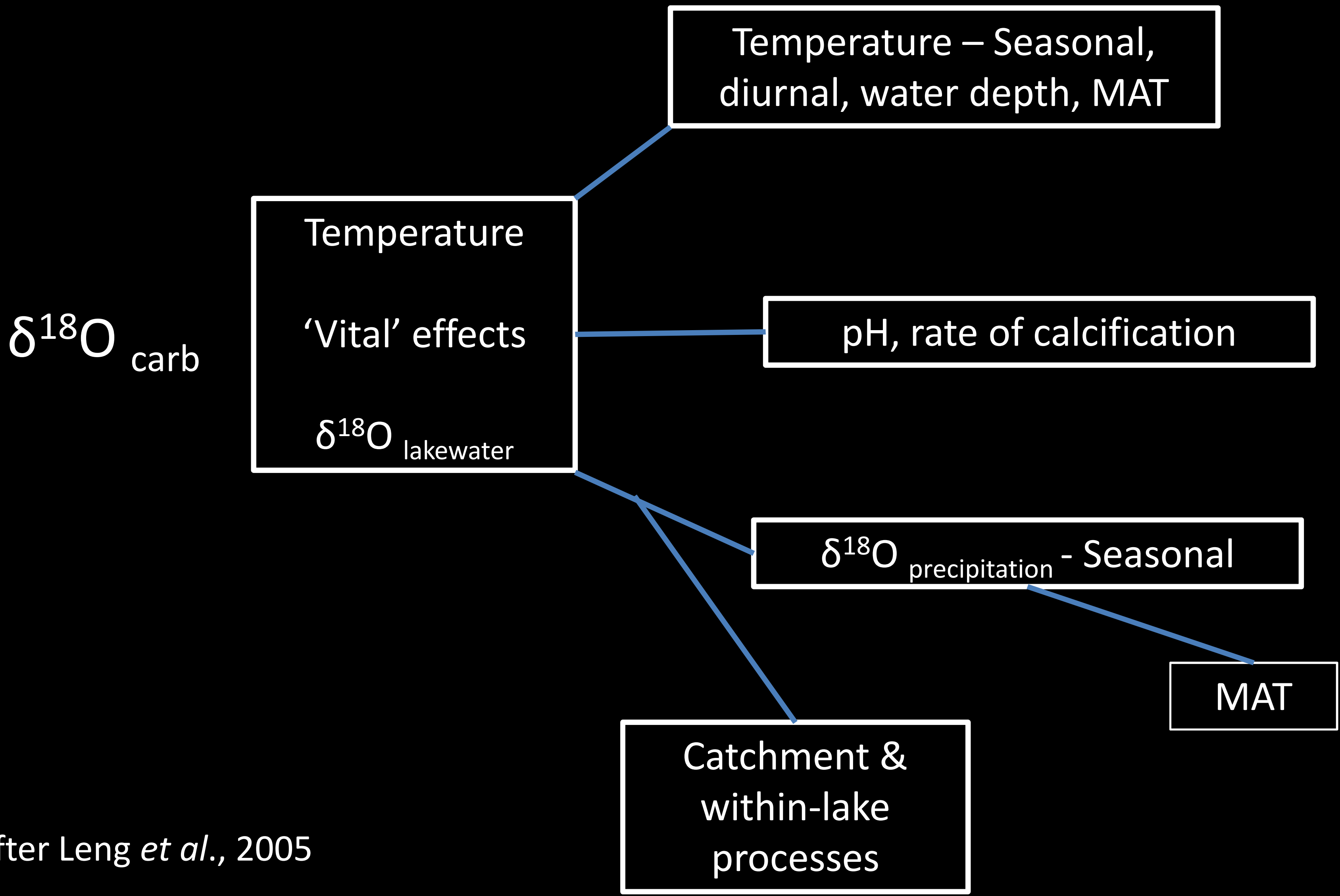
Not a simple story…

Difficult to link any observed changes in isotopic composition of calcite with one particular environmental variable :- e.g. change temperature and…

- Shift equilibrium oxygen-isotope composition in the water
- Change isotopic composition of rainfall in catchment*
- Change rate of evaporation from the lake and the catchment*

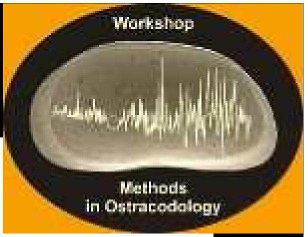
*These are particularly true for OXYGEN

Stable-Isotopes

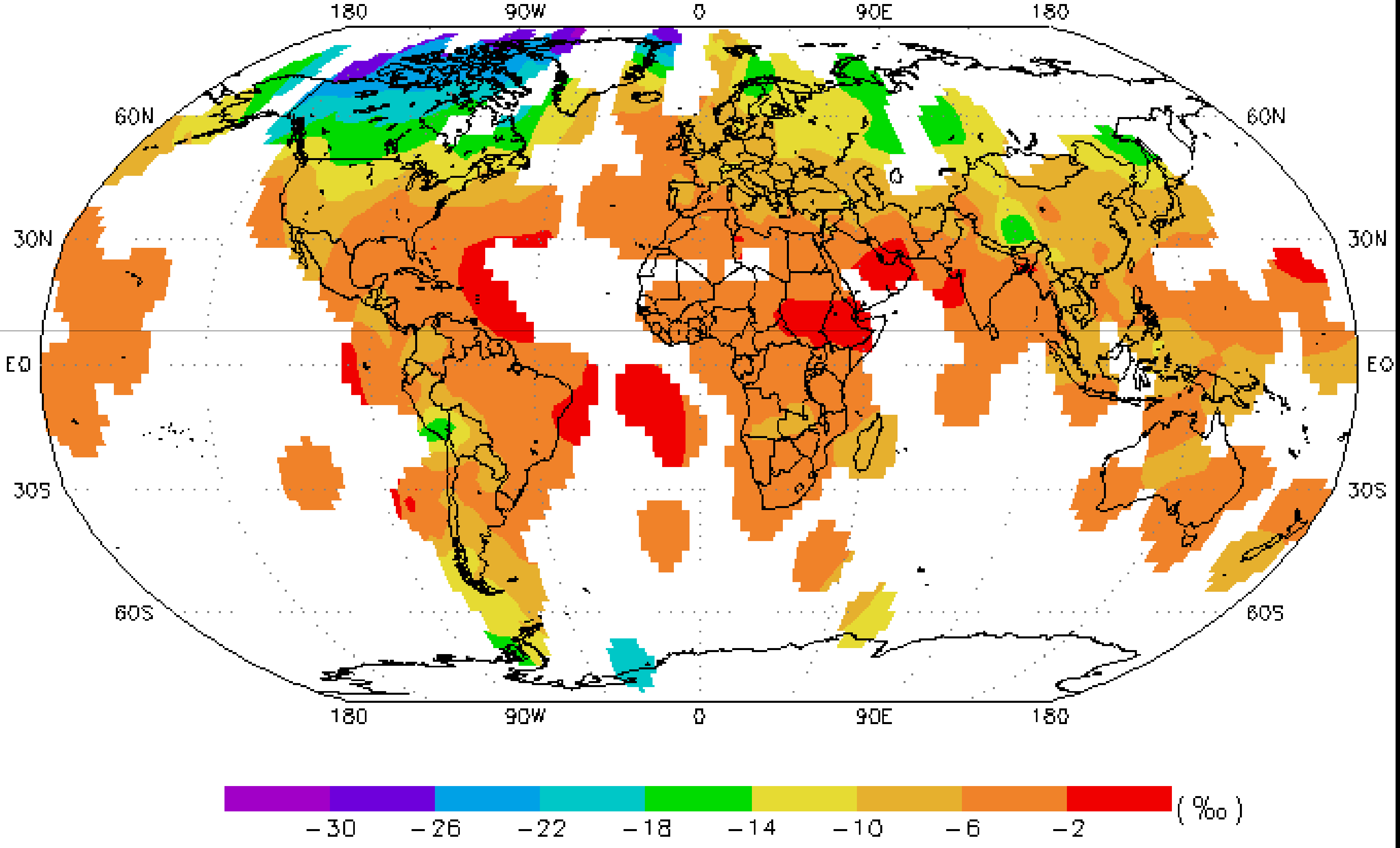


After Leng *et al.*, 2005

Stable-Isotopes



Weighted Annual $\delta^{18}O$



Stable-Isotopes

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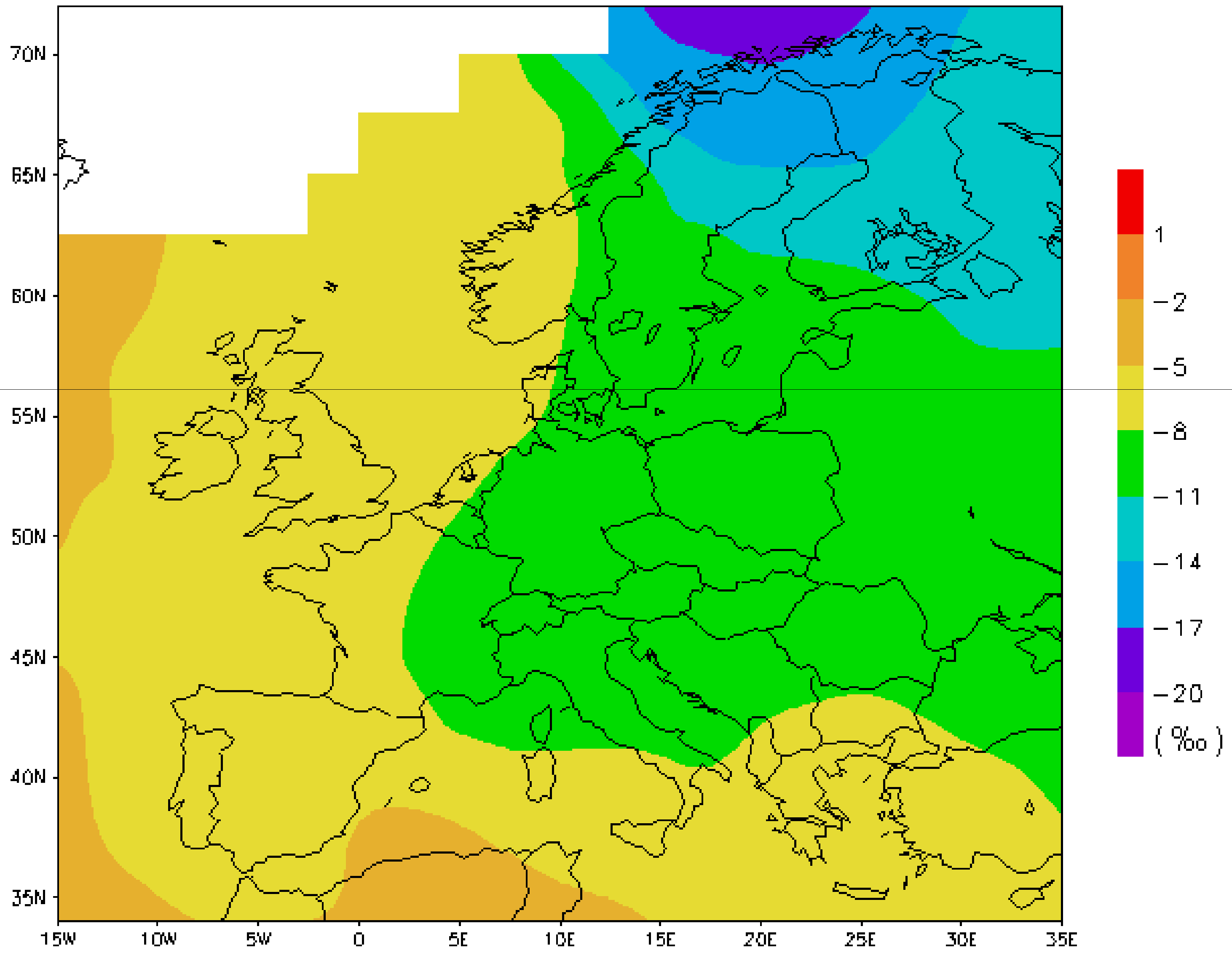


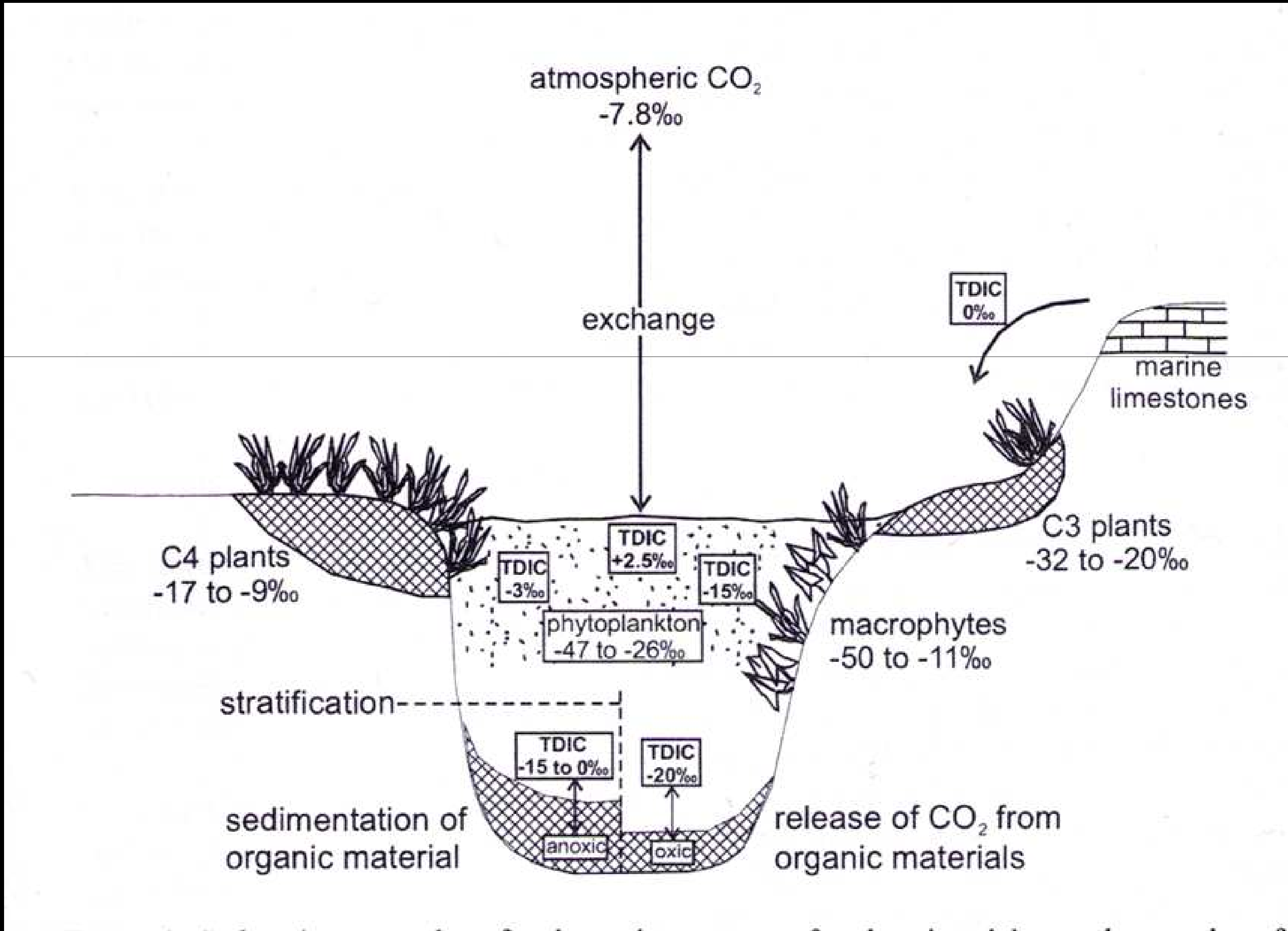
Stable-Isotopes

For CARBON, the isotopic composition of the water is affected by changes in carbon cycling within the lake

- Increased CO_2 respiration (plant and algal activity) linked to productivity and nutrient supply
- Methanogenesis (CH_4) due to anaerobic bacterial breakdown within the sediment will lead to the production of isotopically light carbon
- Over longer timescales, climate will have some effect

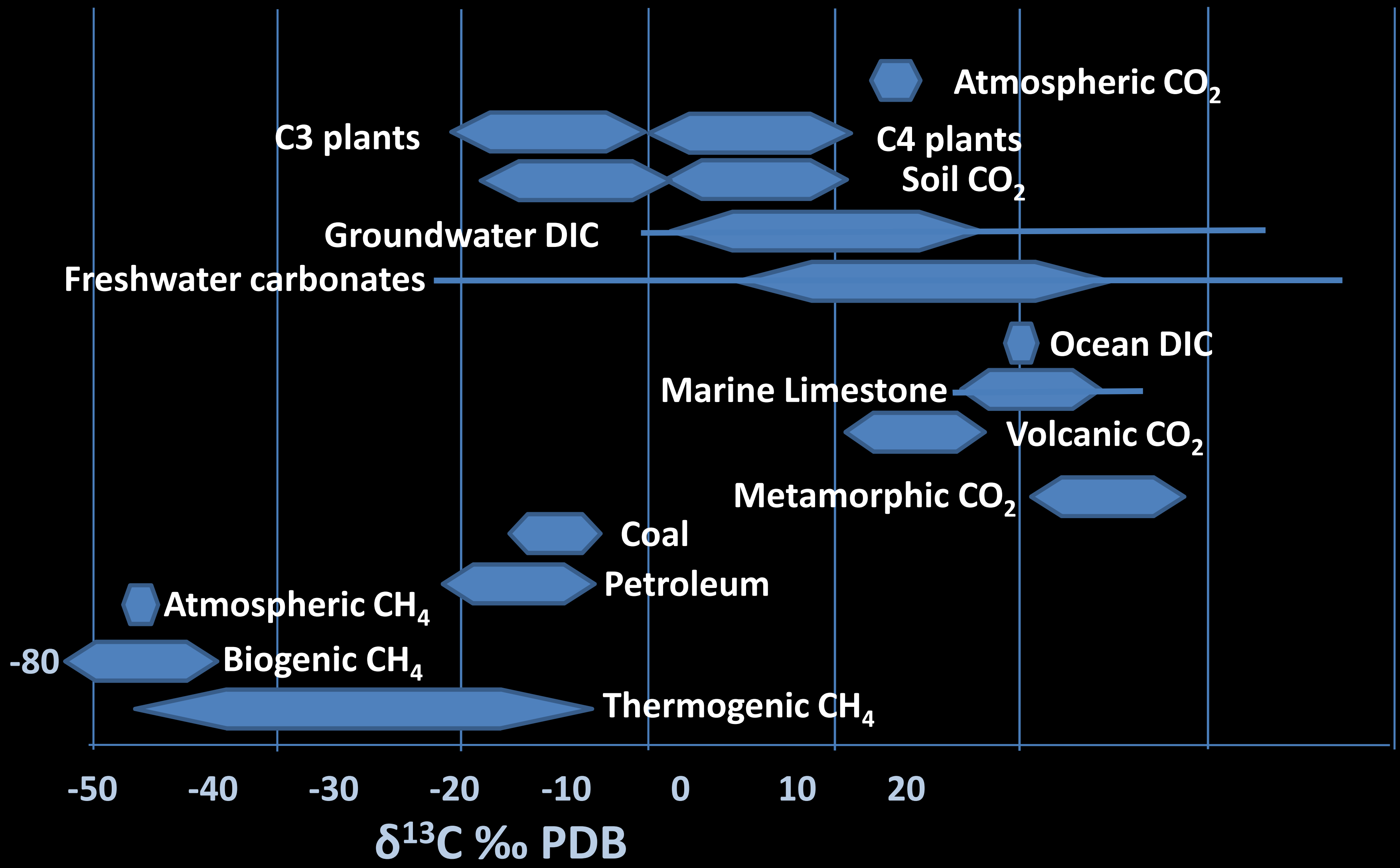
Stable-Isotopes

From Leng *et al.*, 2005. Carbon isotope budget in lakes.



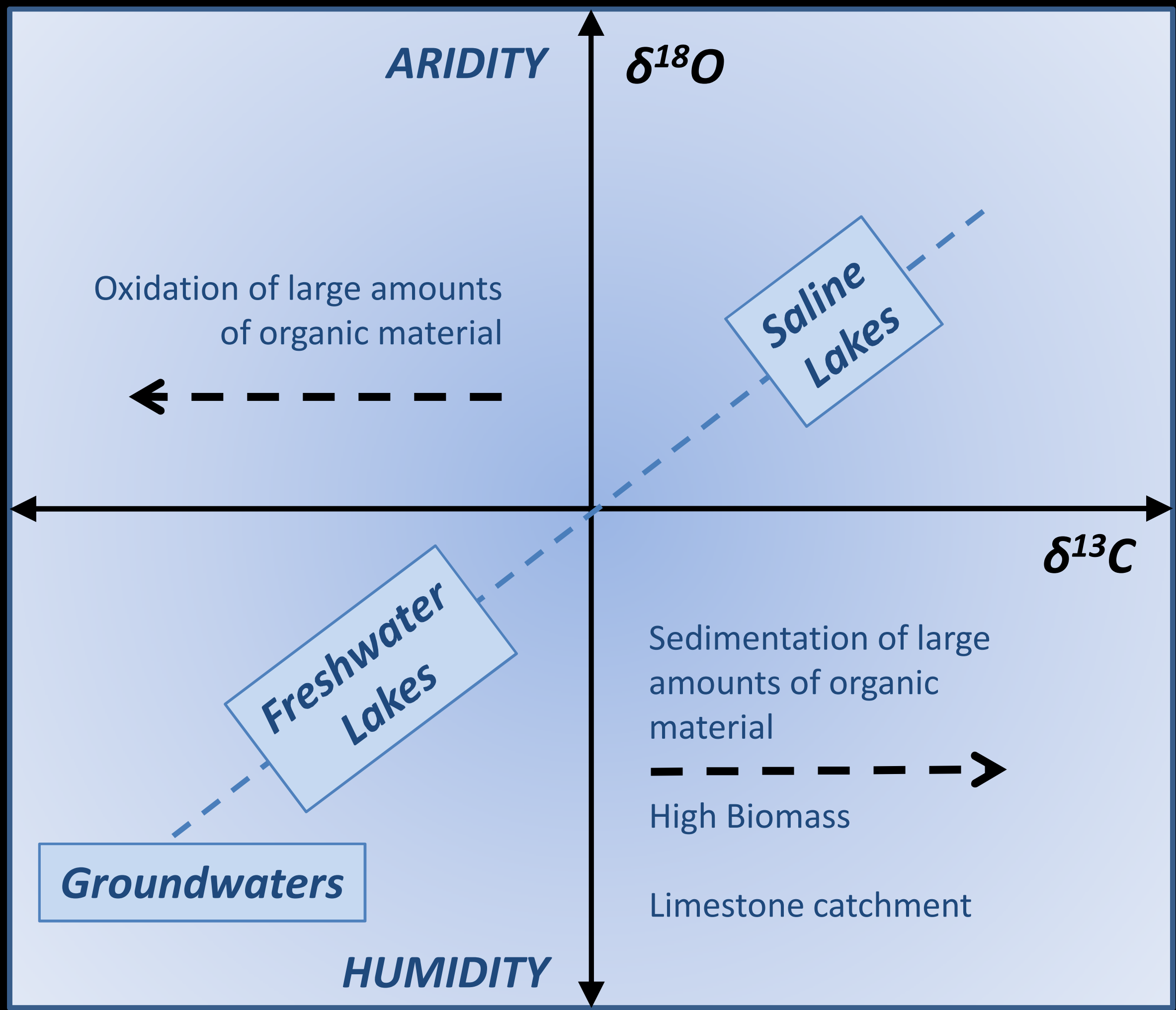
Stable-Isotopes

Graph showing $\delta^{13}C$ values for a range of different sources



Stable-Isotopes

Controls on carbon and oxygen isotopes in lakes



After Leng *et al.*, 2005.

Stable-Isotopes

Selecting carbonate material for analysis

Bulk sediment samples determine all primary calcite (authigenic and biogenic) as well as detrital

Fine-grained ‘bulk marl’/authigenic may be separated by size

Biogenic (ostracods, molluscs)

Many mineral carbonate minerals (calcite, aragonite, dolomite – need XRD, SEM etc.)

Stable-Isotopes

Water v Calcite

In general, authigenic and biogenic carbonates will have a carbon and oxygen isotope signature that is closely related to the temperature and isotopic composition of the waters in which they grew.

Additionally, organisms may present a habitat-controlled or a genetic, species-controlled influence on their isotopic composition (vital effect, especially $\delta^{18}O$).

Therefore, single-species analyses are essential.

Stable-Isotopes

Vital effects in Ostracoda

Most ostracods from calcite that is enriched in $\delta^{18}O$ relative to the equilibrium calcite from the host water

Values range up to as much as 2.5 ‰.

These are generally constant within a genus/family

Candoninae	+ 2.20 ‰	±0.15
Darwinula stevensoni	+ 0.73 ‰	±0.23
Cytherissa lacustris	+ 1.20 ‰	±0.23
Limnocythere inopinata	+ 0.78 ‰	±0.20

From von Grafenstein et al., 1999

Workshop Methods in Ostracodology

Understanding palaeoenvironmental records

Ultimately for any palaeo-study, you must first understand the modern lake hydrology (turnover, residence, stratification, P:E, etc)

As with shell chemistry studies, closed system lakes (no surface outflow) respond differently to open system lakes

Stable-Isotopes

Palaeotemperature equations

An empirical relationship between temperature , the stable-isotope composition of the water and the composition of carbonate minerals forming from that water

Craig (1965) established the first palaeotemperature equation

Several recent experiments have refined this for calcite.

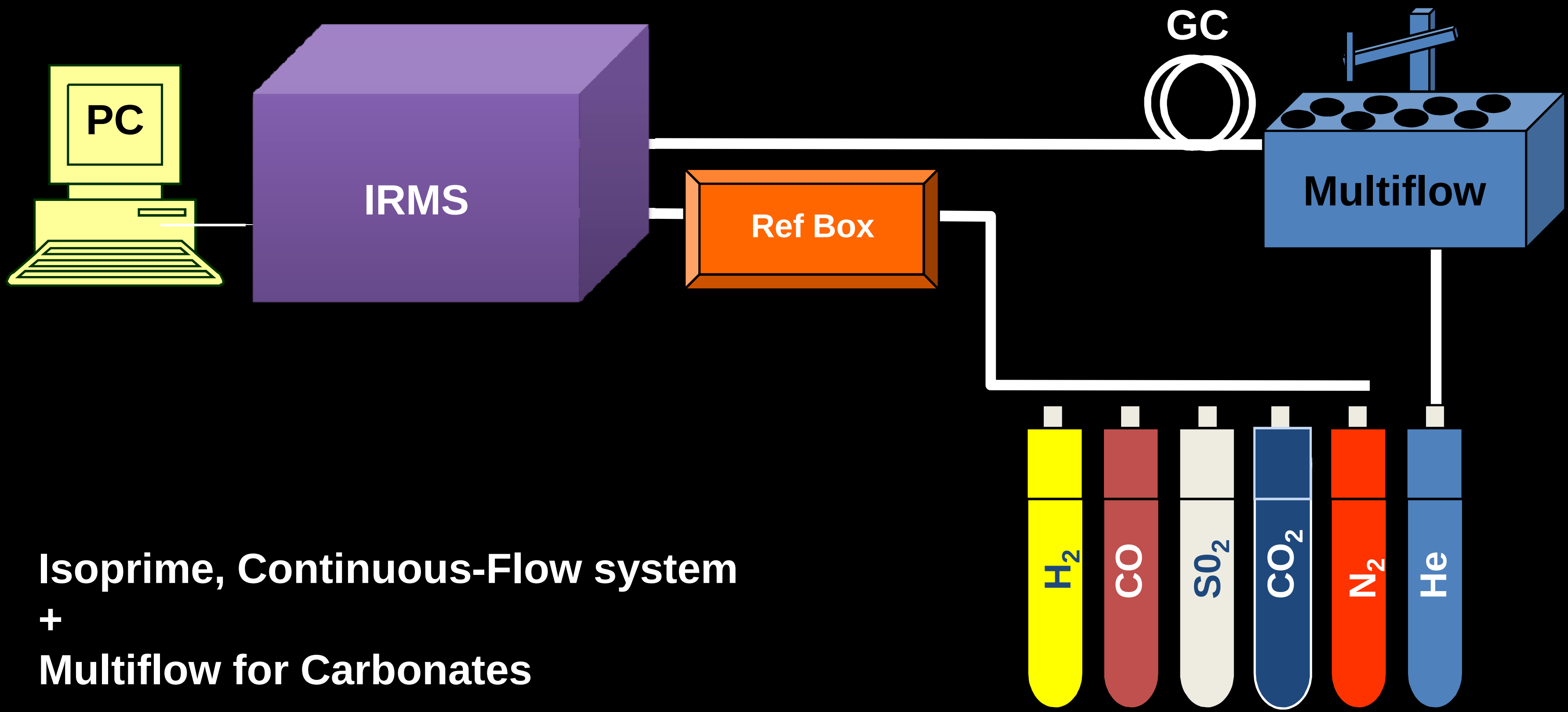
Kim & O'Neil (1997) and Leng & Marshall (2004) redefined it as

$$T\ ^\circ C = 13.8 - 4.58\ (\delta c - \delta w) + 0.08\ (\delta c - \delta w)^2$$

Measuring isotopes

Schematic setup, SILLA, Birmingham

CF-IRMS : Continuous flow – Isotope ratio mass spectrometry

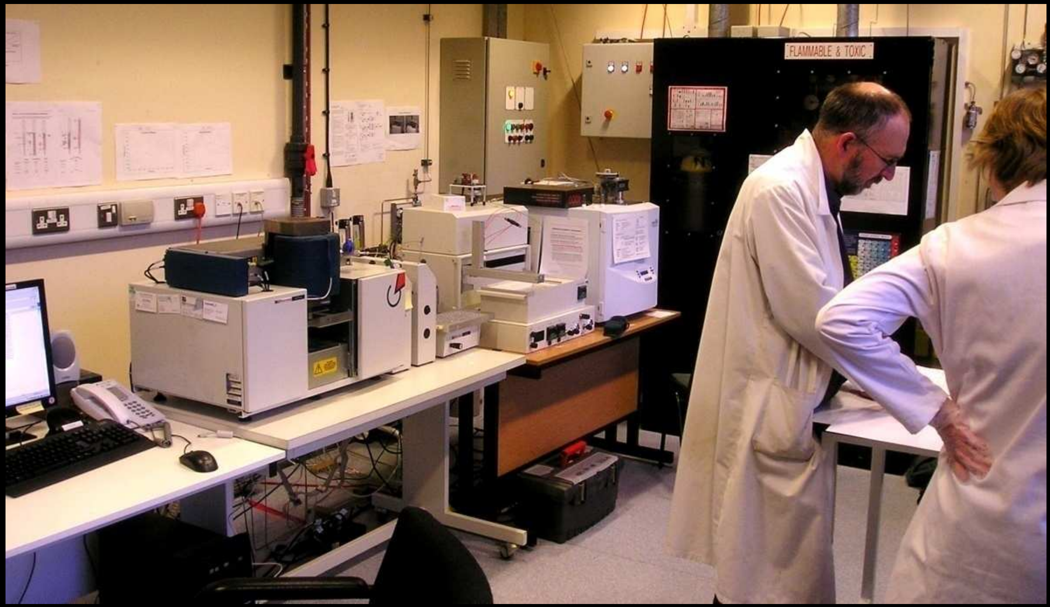


Reference Gases

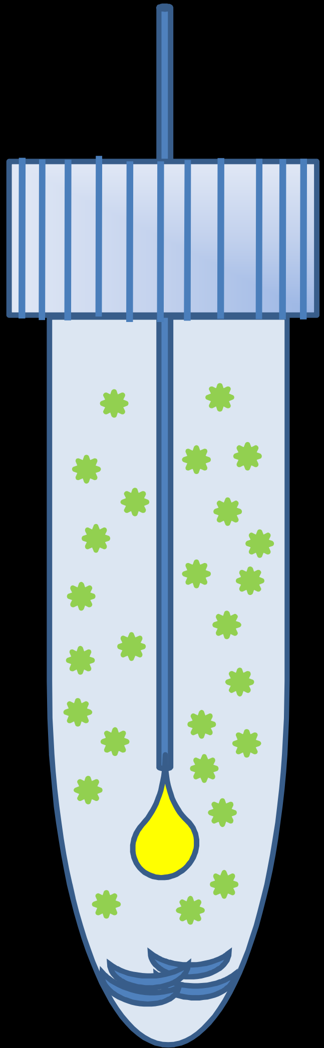
Isoprime, Continuous-Flow system
+
Multiflow for Carbonates

Continuous-flow mass-spectrometry

- 'Prepare' sample
- Introduce sample
- Convert to Gas
- Flow through GC to separate CO_2
- Inject reference gas to IRMS
- Inject sample to IRMS



IRMS Principles



Preparation 1

Weigh 50-200 ug ostracods (~2-10 adult *C. torosa)*

Place in exetainer (gas-tight)

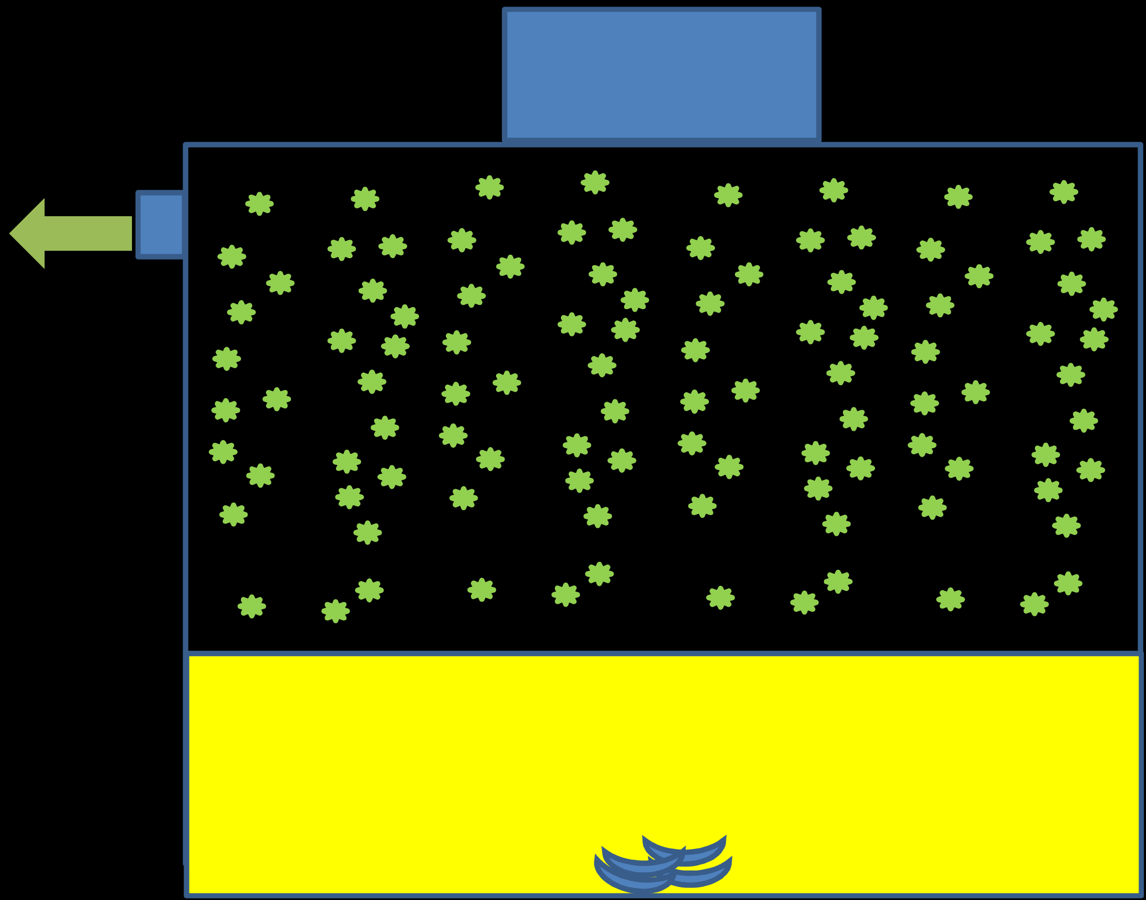
Flush with Helium to remove all other gases

Add a few drops (200-400 ul) H_3PO_4

Leave for one hour to react

Withdraw CO_2 for analysis

IRMS Principles



Common acid-bath
Sealed container under vacuum

Preparation 2

Weigh <50 ug ostracods

Evacuate acid-bath

Add ostracods

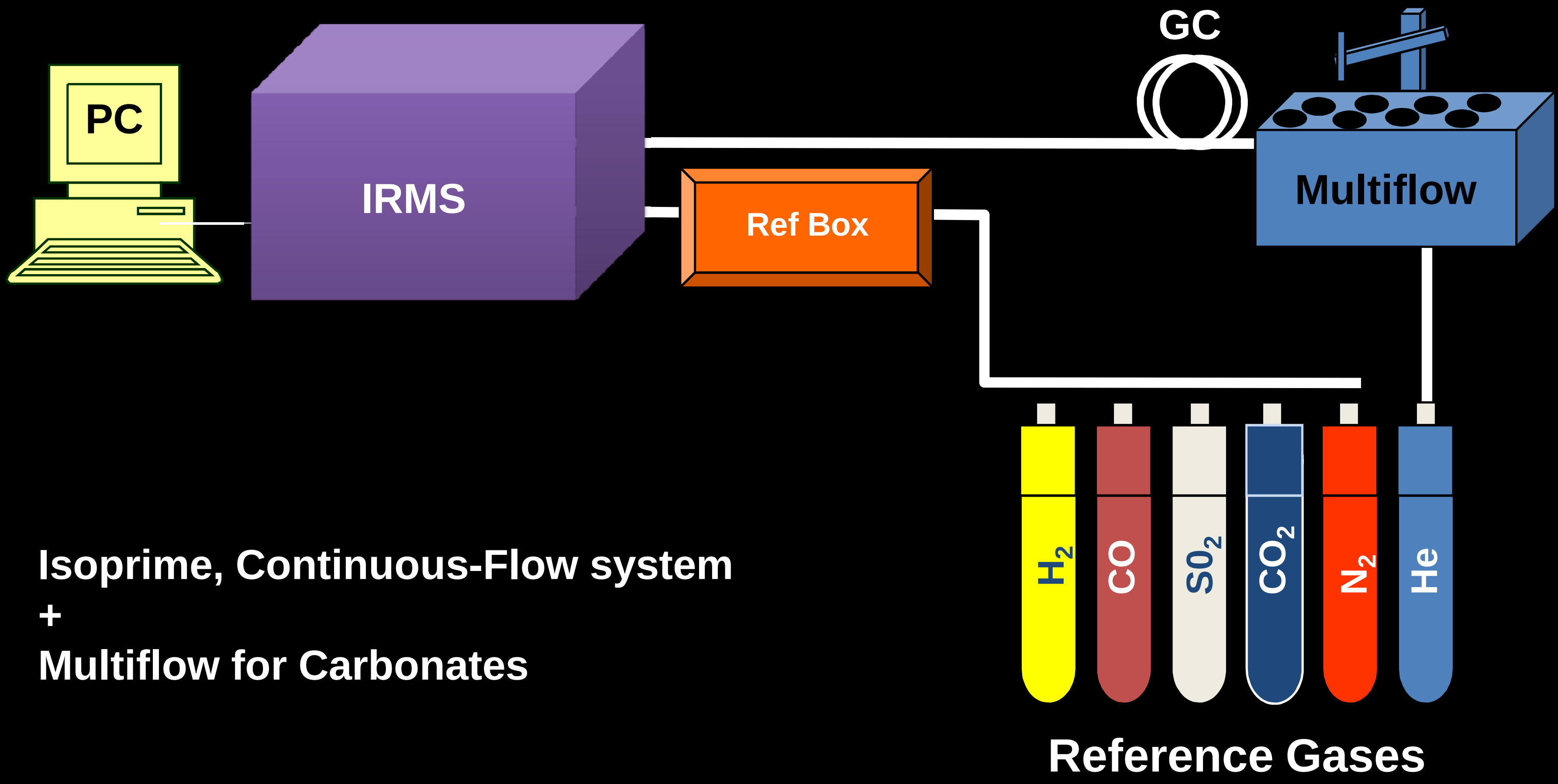
Leave to react totally

Withdraw CO_2 for analysis

CF-IRMS

Schematic setup, SILLA, Birmingham

CF-IRMS : Continuous flow – Isotope ratio mass spectrometry



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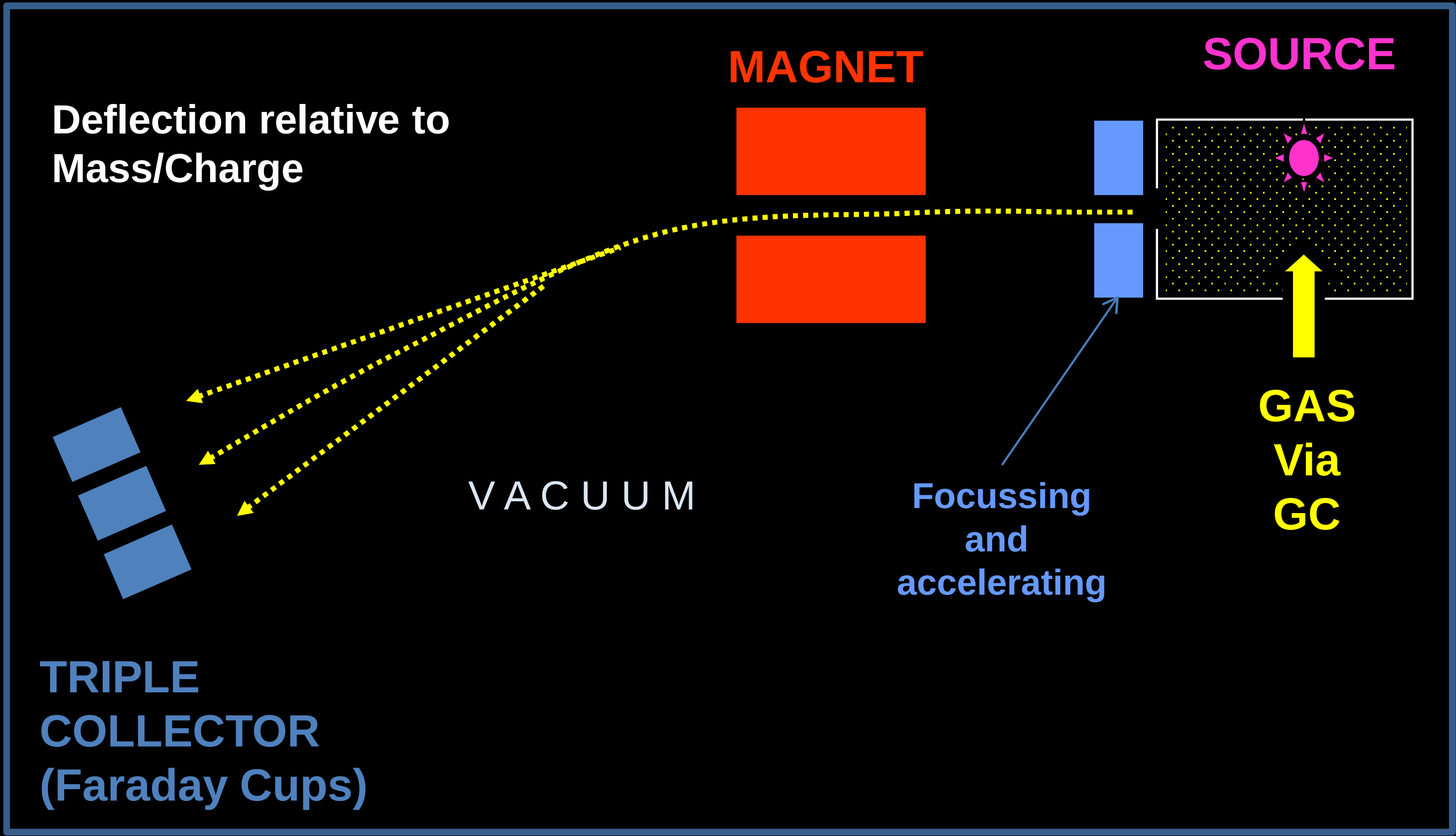
IRMS Principles



Continuous-flow mass-spectrometry

- ‘Prepare’ sample
- Introduce sample
- Convert to Gas species (CO_2)
- Flow through GC
- Inject reference gas to IRMS
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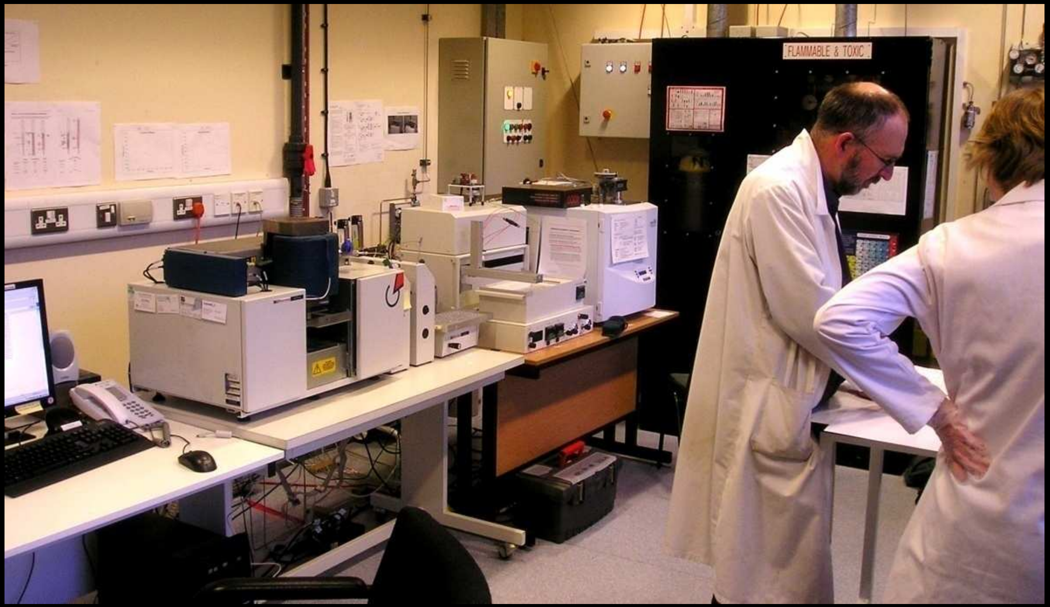
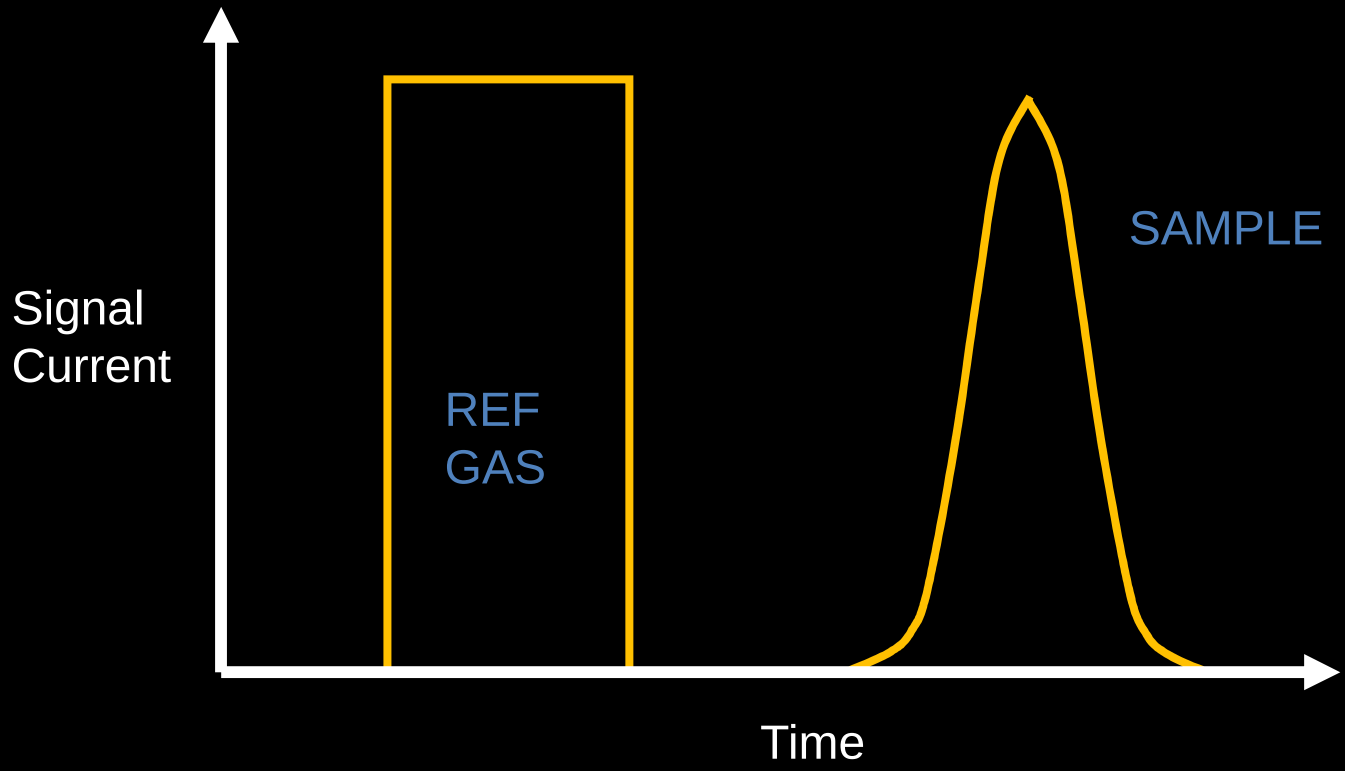


IRMS Principles

Typical output (Chromatogram)



Stable-Isotope measurement

Workshop Methods in Ostracodology

The collectors measure number of ionised *molecules* hitting for given mass, carbon and oxygen measured together

The IRMS reports ratios, not the abundance, of individual isotopes

For CO_2, three masses are reported 44, 45, 46

Composition	Mass	Abundance
$^{12}C\ ^{16}O\ ^{16}O$	44	>99 %
$^{13}C\ ^{16}O\ ^{16}O$	45	<1 %
$^{12}C\ ^{16}O\ ^{18}O$	46	<1 %

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Mass 44/45 ratio gives $\delta^{13}C$ - Mass 44/46 ratio gives $\delta^{18}O$

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