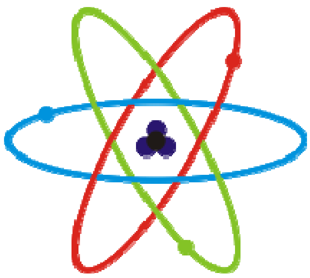
Methods in Ostracodology 2, Graz, 2011.

Isotopes: theory, principles and practicalities



Ian Boomer

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MIO 2
Methods in Ostracodology
Graz, 29. - 31. July, 2011

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Web Sites

Isotopes in Hydrology. Taken from Clark & Fritz, 1997. Environmental isotopes in Hydrogeology.

Water Isotopes: http://www.science.uottawa.ca/eih/ch2/ch2.htm

Many useful pages on Marine isotopes from Ellen Thomas's web pages

Oxygen Isotopes: http://ethomas.web.wesleyan.edu/ees123/paleoxiso.htm

Carbon Isotopes: http://ethomas.web.wesleyan.edu/ees123/caiso.htm

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MIO 2 Methods in Ostracodology Graz, 29. - 31. July, 2011

Isotopes: theory, principles and practicalities

Ian Boomer
University of Birmingham

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

Overview

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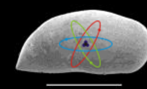

1. Understanding isotopes
2. What controls isotope composition of water & carbonates?
3. Selecting, preparing and analysing isotope samples
4. Interpreting isotope results & Case studies

1. Understanding isotopes

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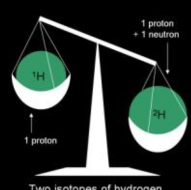
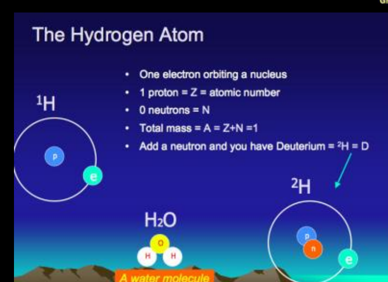
What are isotopes ?



1. Understanding isotopes

MIO 2 Methods in Ostracodology Graz, 29. - 31. July, 2011



All isotopes available for inclusion in environmental molecules
One very common, the other(s), very rare.
Importance of the Hydrological Cycle

1. Understanding isotopes

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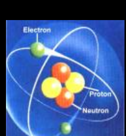
Most elements (e.g. Oxygen, Nitrogen, Carbon etc..) may exist as one of a number of isotopes

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 two stable isotopes ***1****, 2 (Deuterium)*

1. Understanding isotopes

MIO 2 Methods in Ostracodology Graz, 29. - 31. July, 2011

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

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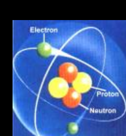

e.g. Hydrogen has two stable isotopes ***1****, 2 (Deuterium)*

Carbon has two stable isotopes ***12****, 13 (^{14}C unstable)*

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

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

1. Understanding isotopes

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Carbon & oxygen stable isotopes in ostracod carbonate

Q: Where does the carbonate come from?

From water to $CaCO_3$

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

Carbon – as DIC (dissolved inorganic carbon), HCO_3^- - Bicarbonate ions dissolved in water (formed by interaction between rocks, soils and ground/water in the catchment)

Water is the key

1. Understanding isotopes

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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 CO_2 respiration by plants in lake and catchment, nature of bedrock

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

Q: What is a delta value?

1. Understanding isotopes

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Delta values

Isotope are generally reported as 'delta' values (δ)

These are values that relate the isotopic ratio 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 to the standard

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

1. Understanding isotopes

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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' value, rather than being reported as, +0.0034, it would be +3.2 per mil.

1. Understanding isotopes

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Isotope standards

Carbonate Standard
PDB – Pee Dee Belemnite (from Cretaceous Pee Dee Formation). The original soon ran out and was replaced by artificial V-PDB (Vienna PDB, a marble of approx. same composition). ZERO for carbon & oxygen.

Water Standard
SMOW – Standard Mean Ocean Water, used for all fresh, brackish and marine water now as V-SMOW. ZERO for 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

1. Understanding isotopes

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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' between phases)

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

1. Understanding isotopes

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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 evaporation or 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.

1. Understanding isotopes

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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, Mutual temperature methods, etc) then it is possible to reconstruct the changing $\delta^{18}O$ of the source water.

Therefore, stable isotope analysis on carbonates cannot directly give you both palaeotemperature & a record of ^{18}O composition of the host water.

2. Isotopes in water & carbonates

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How do we arrive at particular isotope compositions in carbonates ?

First, think about the water…….

2. Isotopes in water & carbonates

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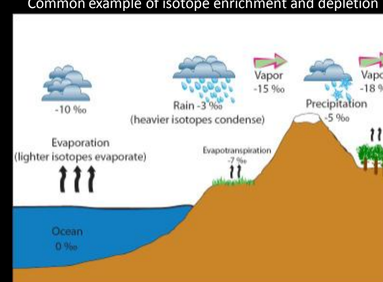
Common example of isotope enrichment and depletion



http://serc.carleton.edu/microbelife/research_methods/environ_sampling/stableisotopes.html

Evaporation is a physical process, it's easier to evaporate $H_2{}^{16}O$ than it is $H_2{}^{18}O$

2. Isotopes in water & carbonates

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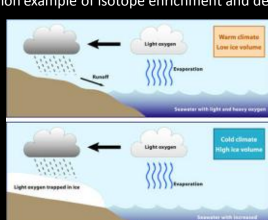
Common example of isotope enrichment and depletion



http://www.noc.soton.ac.uk/gg/IPY/background.html

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

2. Isotopes in water & carbonates

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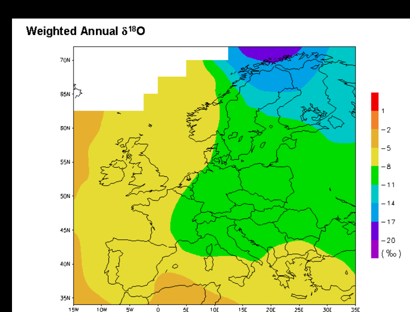

2. Isotopes in water & carbonates

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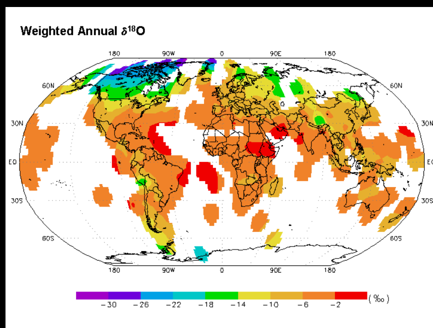

2. Isotopes in water & carbonates

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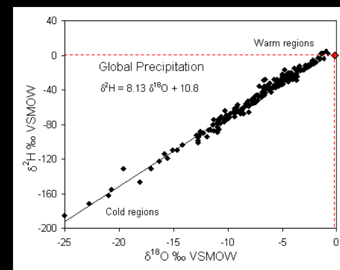
GMWL – Global Meteoric Water Line



2. Isotopes in water & carbonates

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Not a simple story…

Difficult to link any observed changes in oxygen isotopic composition of calcite with just one particular environmental variable

- A change in lake water temperature and/or depth
- 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

2. Isotopes in water & carbonates

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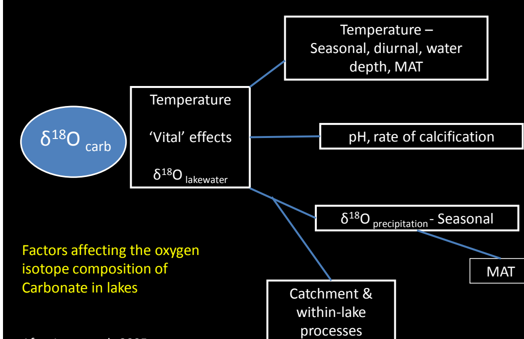

Factors affecting the oxygen isotope composition of Carbonate in lakes

After Leng *et al.*, 2005

2. Isotopes in water & carbonates

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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

2. Isotopes in water & carbonates

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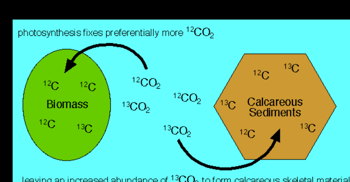
Elevated Photosynthesis (higher productivity) results in isotopically 'heavier' carbon reservoir



http://myweb.cwpost.liu.edu/vdivener/notes/stable_isotopes.htm

2. Isotopes in water & carbonates

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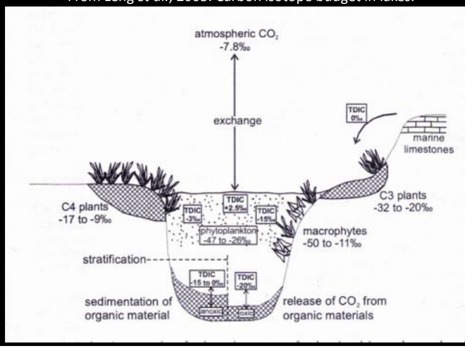
From Leng *et al.*, 2005. Carbon isotope budget in lakes.



2. Isotopes in water & carbonates

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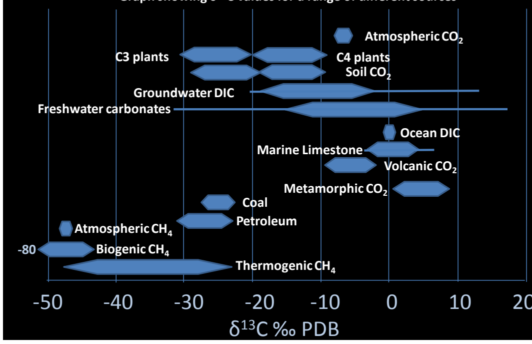
Graph showing $\delta^{13}C$ values for a range of different sources



2. Isotopes in water & carbonates

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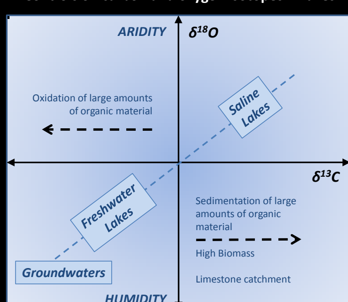
Controls on carbon and oxygen isotopes in lakes



After Leng *et al.*, 2005.

3. Preparing isotope samples

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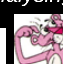
Selecting, preparing and analysing isotope samples



Stable isotope analyses can be both expensive and time consuming. Do I really need stable isotopes?

3. Preparing isotope samples

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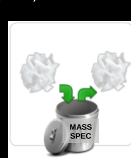
Selecting carbonate material for analysis – Take Care !

Bulk sediment samples determine all primary calcite (authigenic and biogenic) as well as secondary cements and detrital grains.

Fine-grained authigenic carbonate may be separated by filtration

Biogenic (ostracods, molluscs)

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



Warning: "Rubbish in – Rubbish out" !

3. Preparing isotope samples

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KEATINGS *et al.*, 2006.

Tested the effects on shell composition of a number of methods for the pre-treatment of ostracod valves, including roasting in a vacuum, plasma ashing, & soaking in reagents such as hydrogen peroxide, sodium hypochlorite, hydroxylamine hydrochloride solution and sodium dithionite.

Large differences in the geochemical effects of these methods, all have the potential to alter the trace element and stable isotope composition of ostracod valves.

Recommended that valves ***only be cleaned manually***, with fine brushes, needles & deionised water whenever possible. However, it was recognised that manual cleaning will be insufficient to remove inorganic or organic contamination.

In such cases, hydrogen peroxide and plasma ashing recommended as good methods for oxygen isotope analysis, if no other analyses are to be performed. For carbon isotope analysis, only plasma ashing should be used.

Hydroxylamine hydrochloride is suitable for the removal of aluminosilicate material, and sodium hypochlorite is a suitably non-invasive method for the removal of organic material, if subsequent trace element analysis is to be carried out.

3. Preparing isotope samples

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Preparation 1 (washing & Drying)

Standard micropalaeontological processing techniques are fine. But it is important to avoid contamination from carbonates precipitating from rinse water.

Excessive exposure to hydrogen peroxide and deionised water can both be harmful to calcium carbonate and may preferentially remove distinct isotopic components (use manual cleaning, see Keatings *et al.*, 2006).

Do not leave samples to dry in tap water – ethanol preferred (see von Grafenstein *et al.*, 1999 and Mischke *et al.,* 2007 for details).

3. Preparing isotope samples

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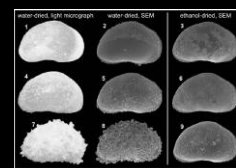
Mischke *et al.*, compared isotopic values of shells dried in tap water with those dried in ethanol

Greater variability in $\delta^{13}C$ and $\delta^{18}O$ in water-dried to precipitation of inorganic calcite on the shells (seen in SEM – not visible to naked eye)



3. Preparing isotope samples

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Preparation 2 (selecting material)

Sample size based on weight of calcium carbonate, weight required depends on lab and technique employed (50-200 ug; *Cyprideis* ~20 ug, *Limnocythere* ~5 ug).

Generally, samples should be mono-specific or, at worst, mono-generic

Traditionally, adults and juveniles can be mixed (but see caveats in Keatings *et al.,* 2002).

3. Preparing isotope samples

MIO 2
Methods in Ostracodology
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KEATINGS *et al.*, 2002 (see also von Grafenstein *et al.*, 1999)

Investigated carbon and oxygen isotopes in ostracods living in the near-constant conditions of spring-fed ponds in southern England

This allowed accurate determination of the ostracod's calcite-water $^{13}C/^{12}C$ and $^{18}O/^{16}O$ fractionations.

The $^{13}C/^{12}C$ fractionations of two species, *Candona candida* and *Pseudocandona rostrata*, correspond to values expected for isotopic equilibrium with the pond's dissolved inorganic carbon at the measured temperature (11°C) and pH (6.9), whilst those of *Herpetocypris reptans*, would represent equilibrium at a slightly higher pH (7.1).

The $^{18}O/^{16}O$ fractionations confirm previous studies in being greater, by up to 3‰, than 'traditionally' regarded as representing equilibrium.

The observations can be explained in terms of equilibrium if the process of calcite formation at the ostracod lamella occurs at a relatively low pH (≤7) irrespective of the pH of the surrounding water.

The pH of calcite formation, and therefore the calcite-water $^{18}O/^{16}O$ fractionation, may be species and stage (adult versus juvenile) specific, and related to the rate of calcification. *GET TO KNOW YOUR OSTRACODS !!*

3. Preparing isotope samples

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Graz, 29. - 31. July, 2011

We are 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.)

3. Preparing isotope samples

MIO 2
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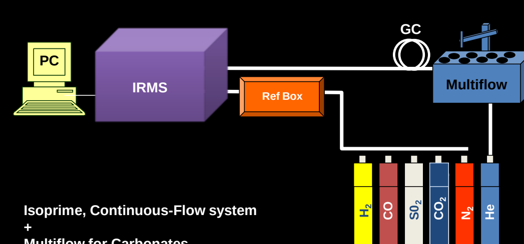
Graz, 29. - 31. July, 2011

Schematic setup

CF-IRMS : Continuous flow – Isotope ratio mass spectrometry



Isoprime, Continuous-Flow system
+
Multiflow for Carbonates

Reference Gases

3. Preparing isotope samples

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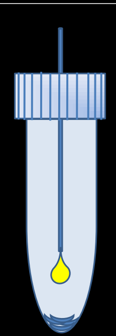


Preparation 1

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

Place in exetainer (gas-tight) , at 90°C

Flush with Helium to remove all other gases

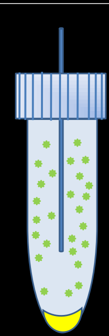
Add a few drops (50-100 ul) H_3PO_4

Leave for ~1 hr to react

Withdraw CO_2 for analysis

3. Preparing isotope samples

MIO 2 Methods in Ostracodology Graz, 29. - 31. July, 2011



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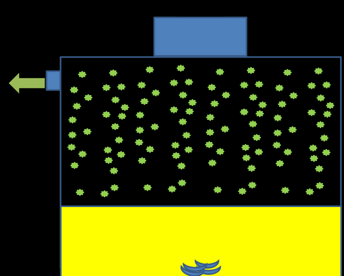


Common acid-bath
Sealed container under vacuum

Preparation 2

Weigh <50 ug ostracods

Evacuate acid-bath "headspace"

Add ostracods

Leave to react totally

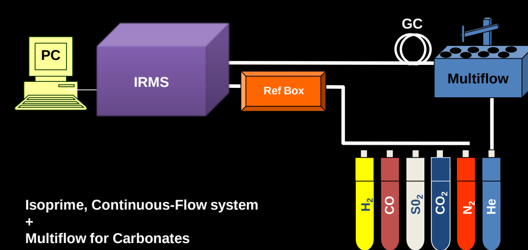
Withdraw CO_2 for analysis

3. Preparing isotope samples

MIO 2 Methods in Ostracodology Graz, 29. - 31. July, 2011

Schematic setup

CF-IRMS : Continuous flow – Isotope ratio mass spectrometry



3. Preparing isotope samples

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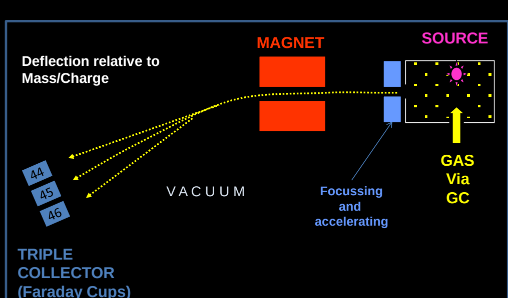

3. Preparing isotope samples

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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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Graz, 29. - 31. July, 2011

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

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MIO 2
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4. Interpreting isotope results

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What do my results mean?

(Well, What was the original question?)

4. Interpreting isotope results

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Water v Calcite

In general, authigenic and biogenic carbonates will have a carbon and oxygen isotope signature that is closely related to the temperature (for O) and isotopic composition (for C and O) 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. Usually this means that you can combine taxonomically related 'within a genus'.

4. Interpreting isotope results

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Vital effects in Ostracoda

Most ostracods form calcite that is enriched in $\delta^{18}O$ relative to the equilibrium calcite from the host water (little effect for $\delta^{13}C$)

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

4. Interpreting isotope results

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Understanding palaeoenvironmental records

Ultimately for any palaeo-study, you must , where possible, 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

Don't 'over-interpret'. How does variability relate to instrumental error (typically 0.1 per mil for both $\delta^{13}C$ & $\delta^{18}O$)

Plots of $\delta^{13}C$ v $\delta^{18}O$ (cross-plots) can be useful

4. Interpreting isotope results

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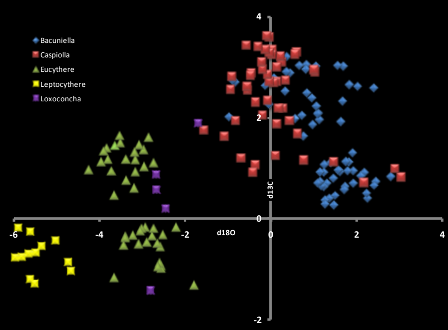

4. Interpreting isotope results

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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

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

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Case studies

Classic paper by von Grafenstein *et al*., 1999 (*Science*, 284)

High-resolution study (decadal) of palaeo-precipitation from a central European lake based on ostracods. ~15-5 ka BP.

1. Modern hydrology well-understood. Oxygen-isotopic composition of the lake water simply linked to isotopic composition of precipitation (a 50% change in output or input would only result in a change of about 0.4 per mil).
2. Vital offsets for the main species are well-known
3. Correlation established between instrumental record and oxygen-isotope record of ostracods from shallow cores
4. Fixed water temperature <50 m of about +4˚C

Stable-Isotopes

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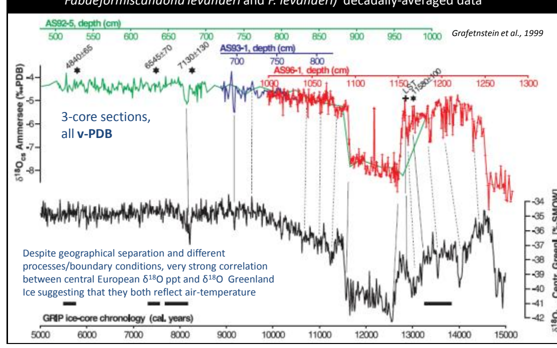
Graz, 29. - 31. July, 2011

Isotope analyses based on Candonids (juveniles of *Fabaeformiscandona levanderi* and *F. levanderi)* decadally-averaged data



Stable-Isotopes

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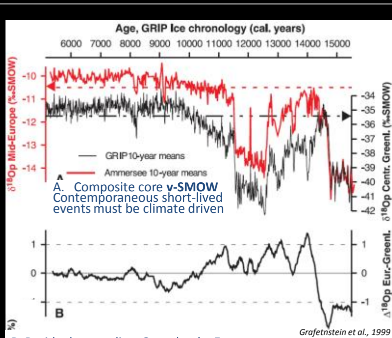
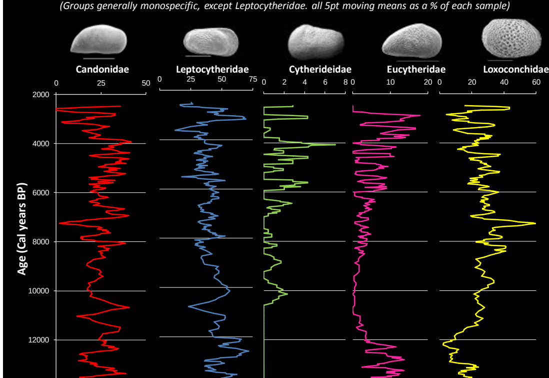
Methods in Ostracodology
Graz, 29. - 31. July, 2011

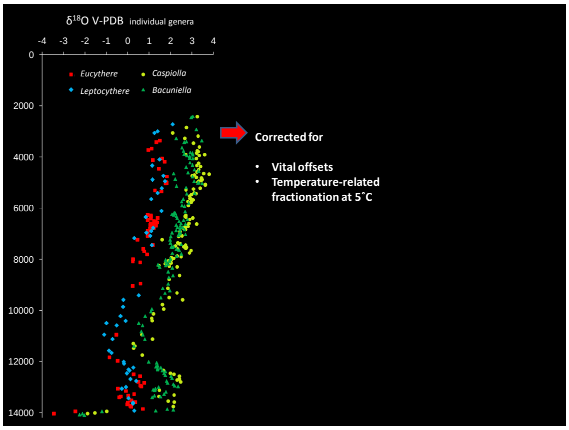


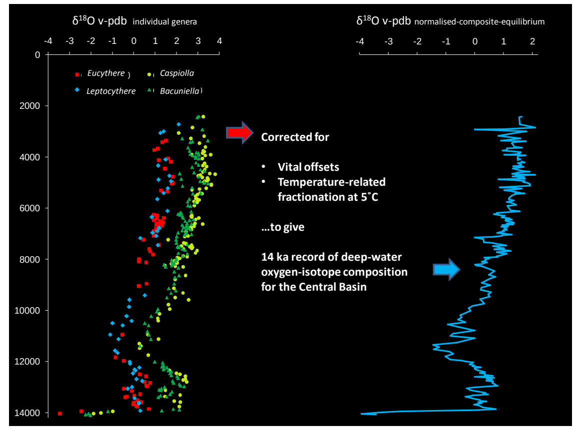
$$\delta^{18}O_{SMOW} = 1.03091*(\delta\ ^{18}O_{PDB}) + 30.91$$

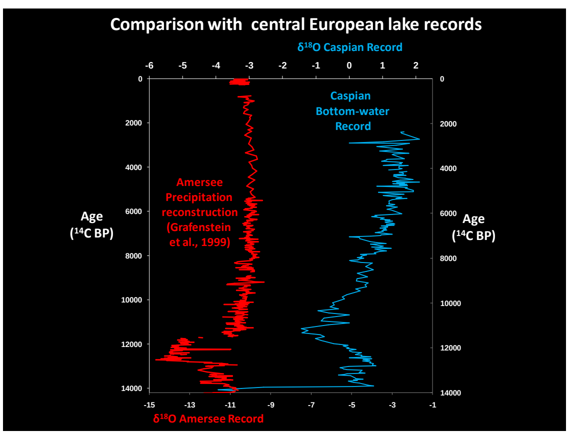
Main groups of Ostracods recovered from core GS20

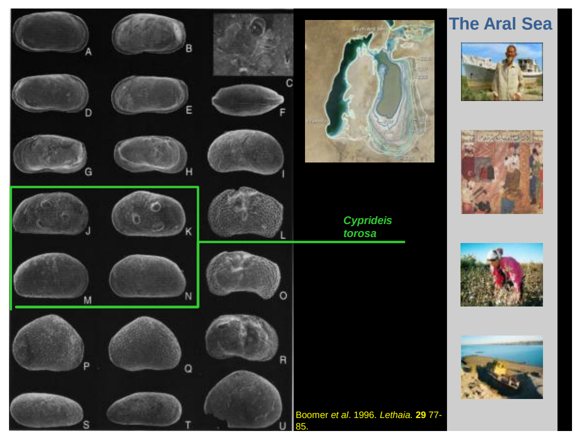
(Groups generally monospecific, except Leptocytheridae. all 5pt moving means as a % of each sample)

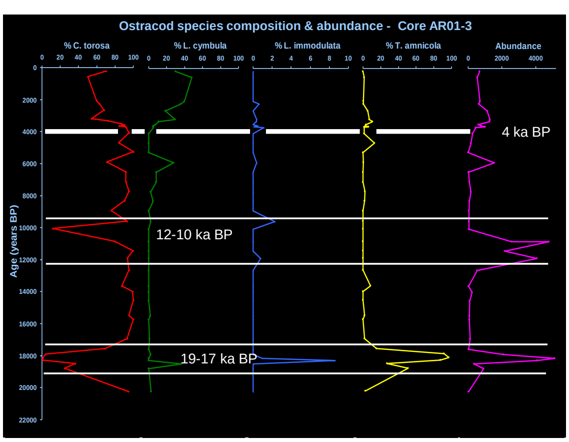


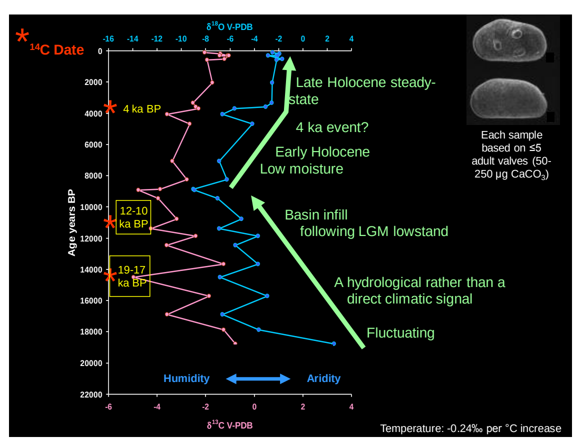

δ18O V-PDB individual genera
Eucythere
Caspiolla
Leptocythere
Bacuniella
Corrected for
• Vital offsets
• Temperature-related fractionation at 5˚C


δ18O v-pdb individual genera
δ18O v-pdb normalised-composite-equilibrium
Eucythere
Caspiolla
Leptocythere
Bacuniella
Corrected for
• Vital offsets
• Temperature-related fractionation at 5˚C
…to give
14 ka record of deep-water oxygen-isotope composition for the Central Basin


Comparison with central European lake records
δ18O Caspian Record
Caspian Bottom-water Record
Amersee Precipitation reconstruction (Grafenstein et al., 1999)
Age (14C BP)
Age (14C BP)
δ18O Amersee Record


The Aral Sea
Cyprideis torosa
Boomer et al. 1996. Lethaia. 29 77-85.


Ostracod species composition & abundance - Core AR01-3
% C. torosa
% L. cymbula
% L. immodulata
% T. amnicola
Abundance
Age (years BP)
4 ka BP
12-10 ka BP
19-17 ka BP


14C Date
δ18O V-PDB
Age years BP
4 ka BP
12-10 ka BP
19-17 ka BP
Late Holocene steady-state
4 ka event?
Early Holocene Low moisture
Basin infill following LGM lowstand
A hydrological rather than a direct climatic signal
Fluctuating
Humidity
Aridity
δ13C V-PDB
Each sample based on ≤5 adult valves (50-250 µg CaCO3)
Temperature: -0.24‰ per °C increase

Stable-Isotopes

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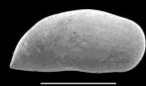
Overview



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

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

Stable-Isotopes

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Questions, Problems and Some solutions

It is important to understand as much as possible about the modern hydrology (where possible) of the lake system you are studying. If this is a 'Palaeo'-setting, then its important to use other proxies to understand environmental variability so as to interpret isotope data correctly.

Oxygen isotopes are one of the most widely used proxies but problems remain in isolating the "signal" from the results. Ostracods might *not* be the answer!

One solution may be to analyse oxygen-isotopes from organic matter in the same lake. Aquatic cellulose is thought to be independent of temperature and plant type/species. Similarly oxygen in silica (e.g. diatoms) may provide an independent story.

DH ratios in similar organic compounds (including chironomids) may also relate closely to lake hydrology and be independent of temperature.