Online isotope ratio monitoring using a RGA

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Talk outline

- Motivation
- Rationale - Carbon isotope measurement with portable QMS
- The challenge
- Results
  - Live reaction monitoring experiments
  - Stability optimisation
  - On-site system
- Conclusions and next steps
- Acknowledgements

Motivation

HISTORY NOW

Was the skeleton in the car park *really* Richard III?

The discovery of the king's remains in Leicester in 2012 made worldwide headlines, but now experts have raised doubts about whether we can truly say the bones are his. **Emma McFarnon** reports

Archaeologists "cannot say with any confidence" that bones found in Leicester are those of Richard III, leading experts have claimed.

Speaking exclusively to *BBC History Magazine*, Michael Hicks, head of history at the University of Winchester, and Martin Biddle, archaeologist and director of the Winchester Research Unit, raised concerns about the DNA testing, radiocarbon dating and damage to the skeleton. Biddle also

Hicks said he is not convinced that the remains are those of the king. Instead, he argues, they could belong to a victim of any of the battles fought during the Wars of the Roses, of which the 1485 battle of Bosworth – at which Richard was killed – was the last significant example. While the location of the grave in the former site of the Grey Friars priory matches information provided by John Rous, an associate of Richard's, Hicks notes that "lots of other people who suffered

Motivation

- Halton Castle (Runcorn)
- Medieval, care of **Norton Priory**
- Seat of the Barons of Halton from the C.11th to C.14th
- Bodies found in the bailey 2015
  - Unusual (unhallowed ground?)
  - Why? Who were they?
  - Local or from elsewhere?
  - What was their social status?

http://www.webbaviation.co.uk/gallery/v/cheshire/runcorn/Halton_Castle_Runcorn_jd28060.jpg.html

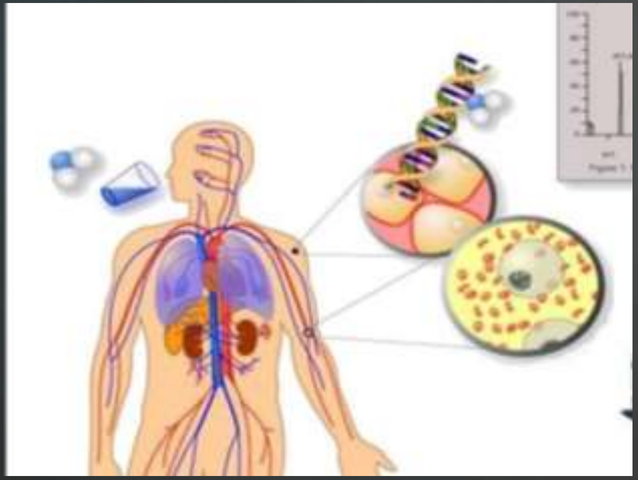
http://www.ecastles.co.uk/haltonch.html

Why portable Carbon isotope analysis?

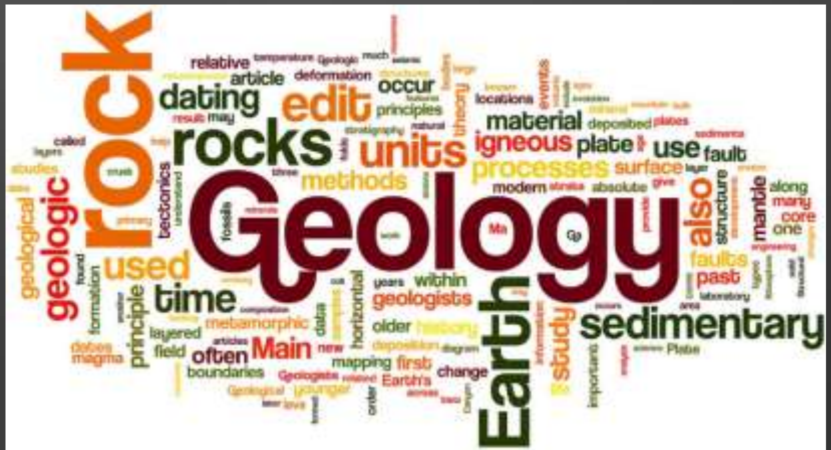
- Carbon isotope analysis is relevant to multiple disciplines
- Which need affordable, field-applicable analytical tools

Environmental monitoring
(isotopes from fossil fuels)

Archaeology
(Dating, diet, migration)

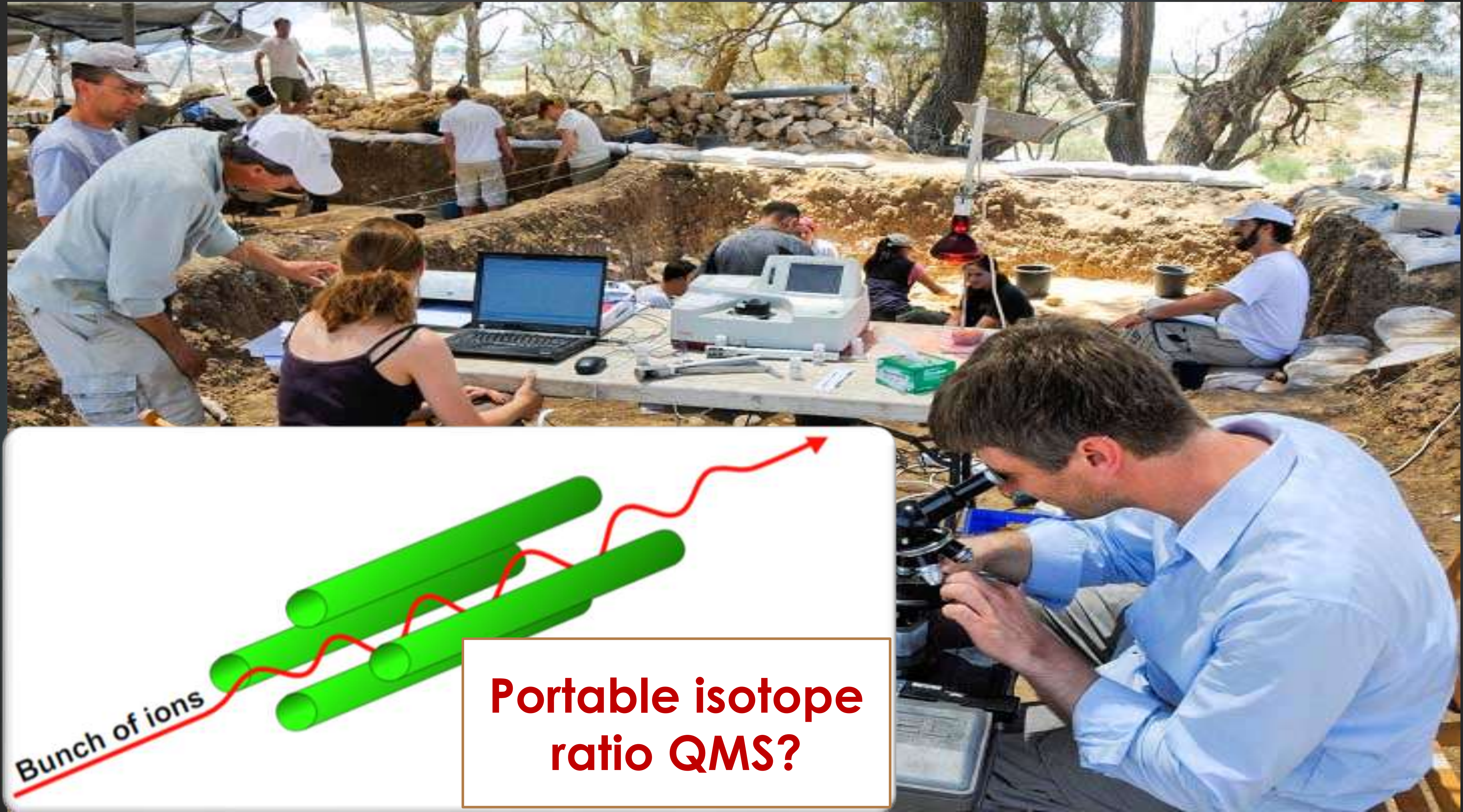


Medicine
(Isotopes as metabolic tracers)



Geology
(Dating, diet, metabolism)

Why portable Carbon Isotope analysis?



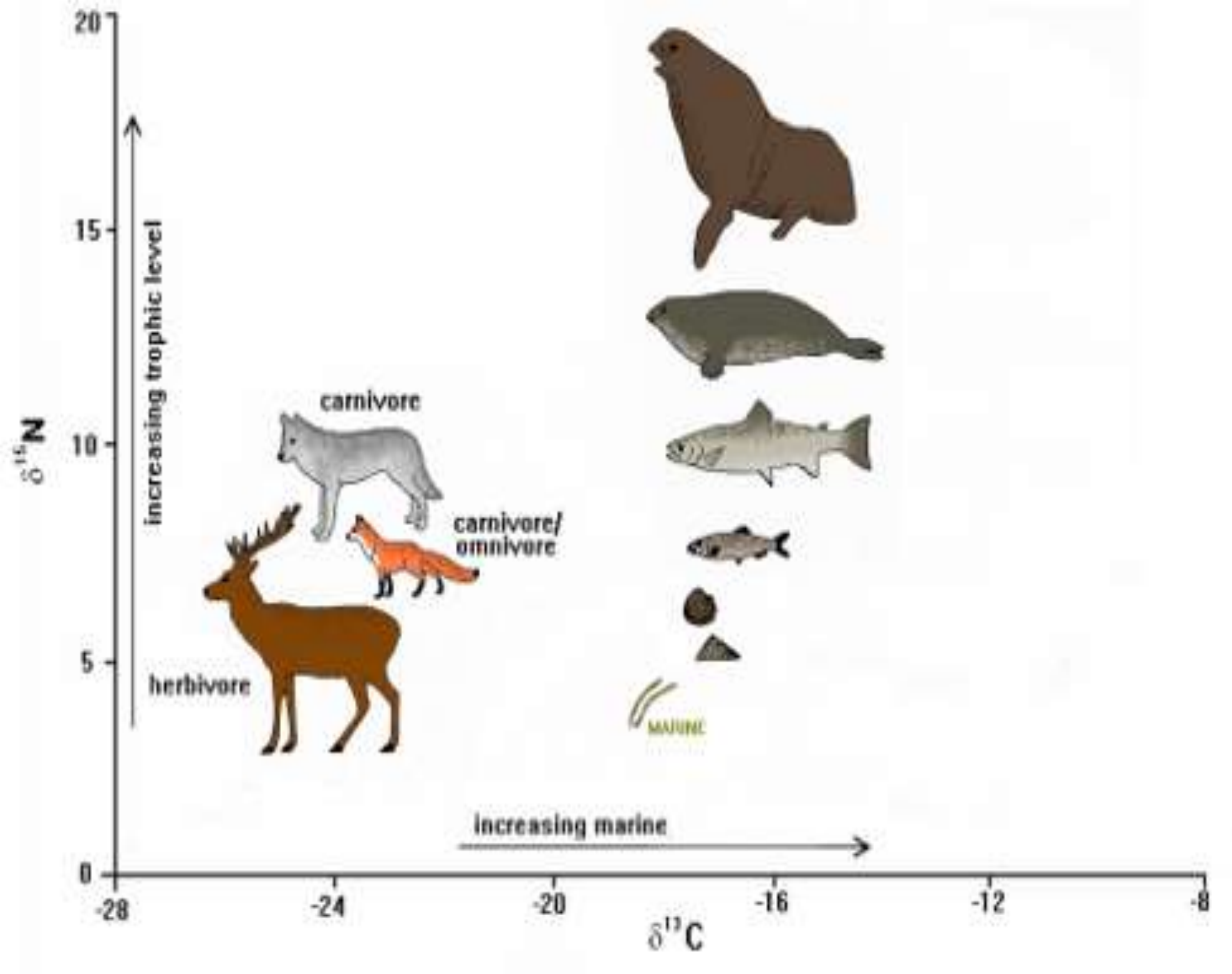
Portable isotope ratio QMS?

https://gath.files.wordpress.com/2008/11/fig_1.jpg

Why IR-**QMS**?

- Portable and miniaturisable
- Affordable, robust, versatile
- Programmable → multiple isotopic ratios with little reconfiguration:
  - **$^{12}C/^{13}C$** (metabolism; environment)
    - e.g. marine reservoir effect → diet
    - e.g. C3 or C4 plants
  - **$^{14}N/^{15}N$** (trophic level → diet)
  - **$^{16}O/^{18}O$** (ancient temperature)
  - **$^{87}Sr/^{86}Sr$** (food origins → migration)
  - **$^{40}Ar/^{39}Ar$** (geochronology)
- Archaeological example:

$\delta^{13}C$ and $\delta^{15}N$ → combine for detailed info about diet and so social status; also (indirectly) migration

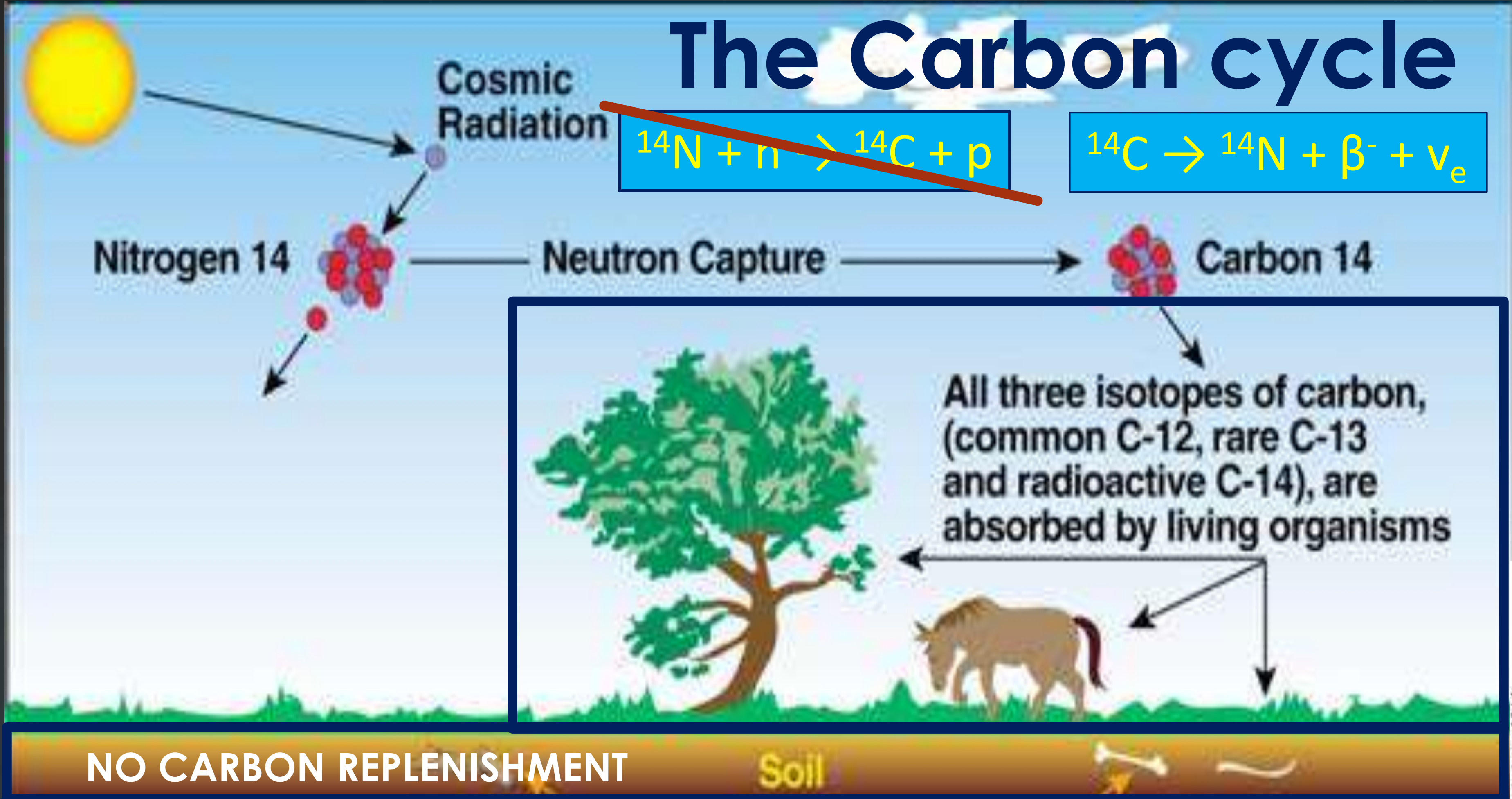


http://www.schoolscience.co.uk/zooarchpage6

The Carbon cycle

$\cancel{{}^{14}N + n \rightarrow {}^{14}C + p}$

${}^{14}C \rightarrow {}^{14}N + \beta^{-} + \nu_e$

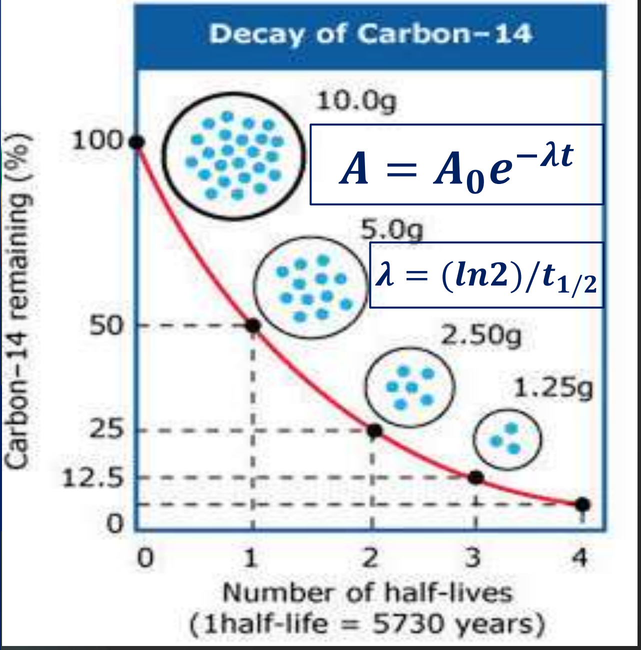


${}^{12}C \rightarrow\rightarrow \rightarrow$ control

$\boxed{{}^{13}C \rightarrow\rightarrow\rightarrow \delta^{13}C}$

${}^{14}C$ $\cancel{\uparrow}$ $\downarrow$ dating

$$t = 5568 \frac{\ln\left(\frac{A_0}{A}\right)}{0.693}$$



$$A = A_0 e^{-\lambda t}$$

$$\lambda = (\ln 2)/t_{1/2}$$

Carbon 12 does not decay in its proportion – acts as a control for overall C content

Carbon 13 does not decay in its proportion (~1.1% of ${}^{12}C$)
Precise proportion informs about organism's diet, metabolism & environment

Carbon 14: beta decay dominates (to 14N) … exact rate calibrated (historical dates),
Ambient concentration: 1 ppt of atmospheric carbon

https://allyouneedisbiology.wordpress.com/2016/01/25/dating-fossils/

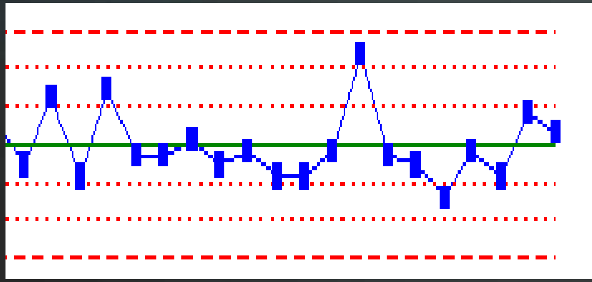
https://www.sciencelearn.org.nz/resources/1686-carbon-14-dating-artefacts

Physicists must feel very popular……

Archaeologists keep asking them for DATES!

I must go on a **diet** and **migrate** to somewhere with a high concentration of **stable** archaeologists

δ^{13}C with portable QMS?



Dynamic range (inc. variable gain) √

10^5

L.O.D. √

$\sim 10^{-2}$

Abund. Sensitivity √

$\sim 10^{-5}$

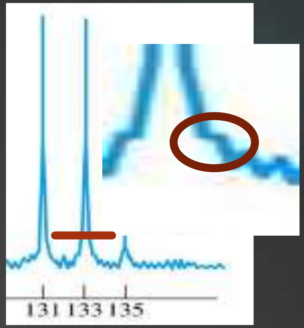
CO_2

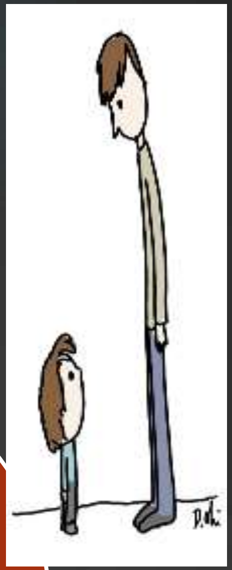
Precision

$\frac{^{13}C}{^{12}C}\ \sigma \sim 10^{-5}$

(~1‰)

~Half-unit resolution √ (math. correction)

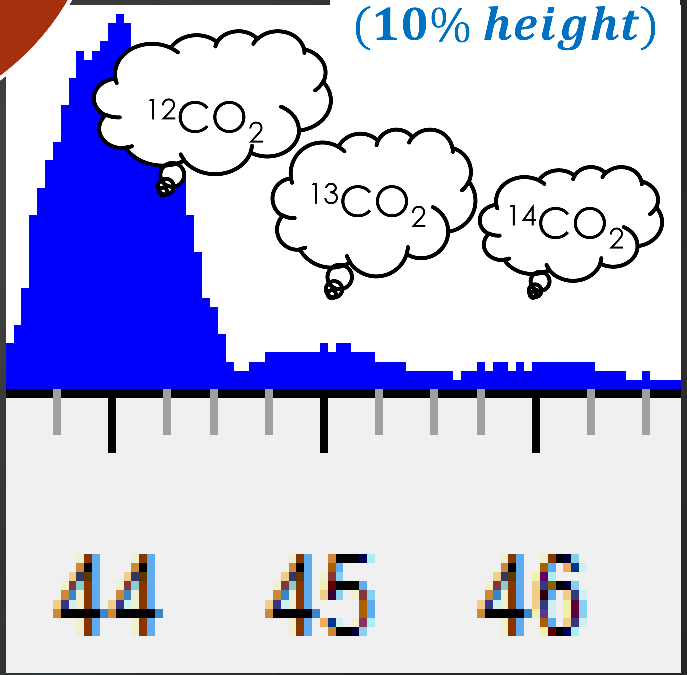




$*A = \frac{I_{M\pm1}}{I_M}$

$R = \frac{M}{\Delta M}$

(10% height)



$\delta^{13}C$ with portable QMS? - stability

- $\delta^{13}C\ (‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$
  - *Biological*: -14‰ to -28‰ → bone samples *(e.g. archaeological)*: 10‰ or << variations significant
  - *Ecological / geological* (soils etc.): much smaller variations may be significant
  - *Medical* – isotopes as metabolic tracers: less precision required
- QMF not classically known for stable quantitative work – why?
  - A) Voltage (in)stability… RF in particular
  - B) Not typically flat top – possible but more challenging in a small instrument
  - C) Fringing field effects? (altering angle and position of QMF entry)
- QMS must collect alternately – peak-jumping
- Ratio linearity – ratio varies significantly with sample pressure

Results

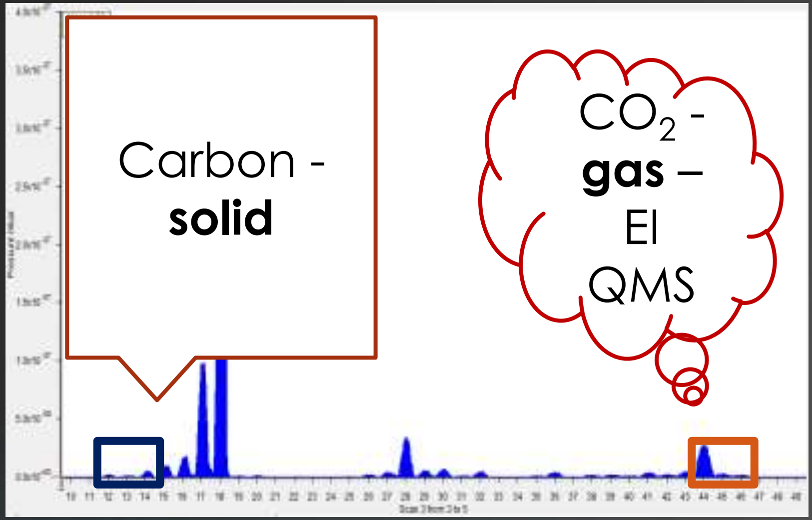
- Initial experimentation
- Measurement stability optimisation
- Discussion / conclusions

Instruments

- HySEM-80
- Single filter
- Hyperbolic electrodes, 250 mm
- Detector: multiplier only
- 85 x 60 x 50 cm
- ~30-40 kg (ECU 1.25 kg)
- Transport: wheeled cabinet
- Pfeiffer HiPace-300 & ACP-15 or MVP-015 diaphragm pump
- Custom chamber / CF seals
- 0-80 Da mass range

- VapourSense-500
- Dual-filter
- Round electrodes, 100 mm
- Detector: Dual Faraday / Multiplier
- 62 x 49 x 23 cm
- 20 kg (ECU 1.25 kg)
- Transport: Peli case
- Pfeiffer HiPace-80 & MVP-020 diaphragm pump
- Custom chamber, CF seals
- 0-500 Da mass range
- QMF and prefilter – UoL design
- Both ECUs - Cyionics Ltd

Evolving CO_2 gas from bone bone



Bone apatite (bioapatite) - like hydroxylapatite:

$$Ca_{10}(PO_4)_6(OH)_2$$

with carbonate substituted in phosphate position [11-12]:

$$Ca_{10-x}[(PO_4)_{6-x}(CO_3)_x](OH)_{2-x}$$

Chloride or phosphate ion can displace CO_3 → $\mathbf{CO_2}$

Acid + bone → $CO_2 + H_2O +$ … [6-10]

Calcium carbonate: useful standard

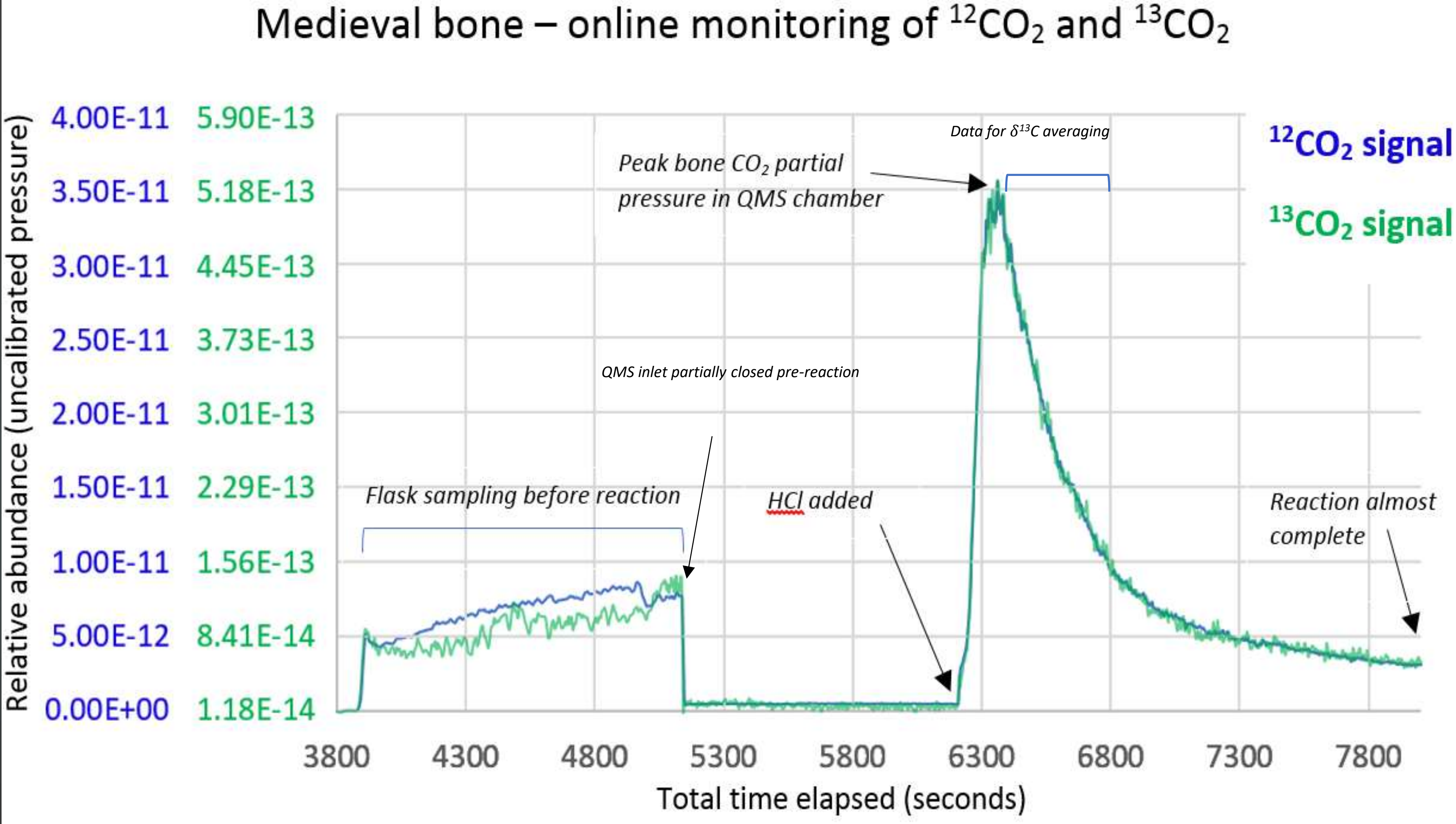
$CaCO_3 + 2HCl = CO_2 + CaCl_2 + H_2O$

$3CaCO_3 + 2H_3PO_4 = 3CO_2 + Ca_3(PO_4)_2 + 3H_2O$

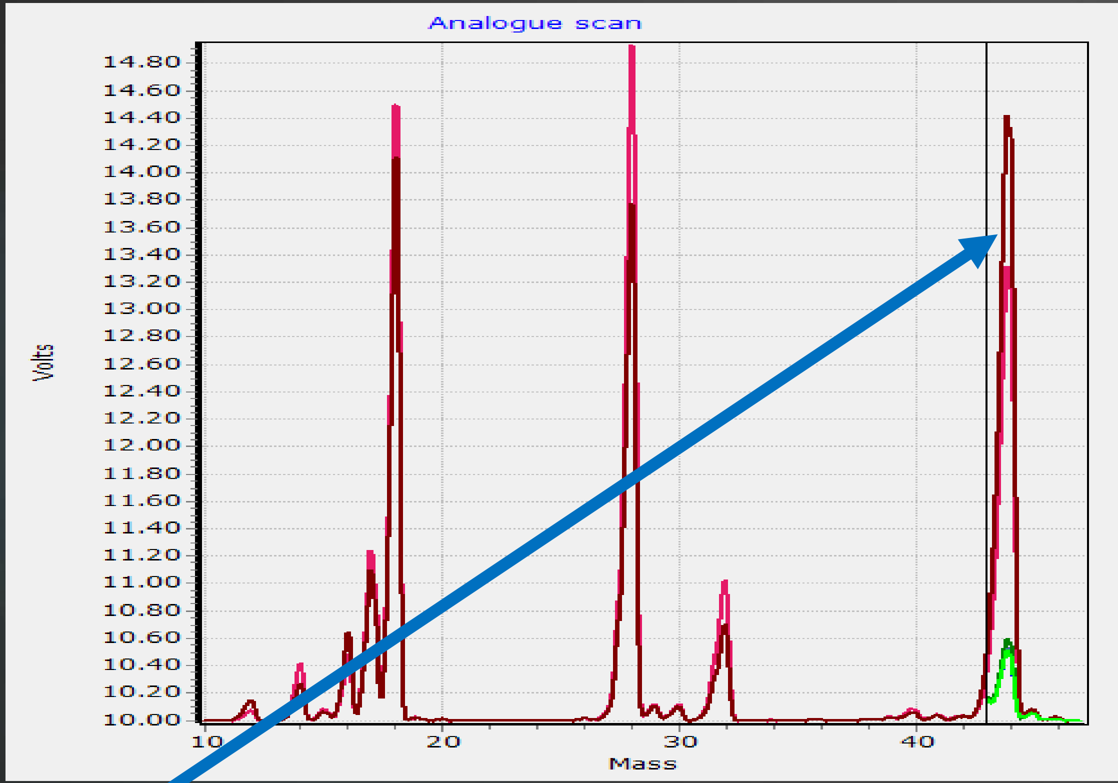
Norton Priory Medieval Cattle bone photographed by Carla Burrell (LJMU)

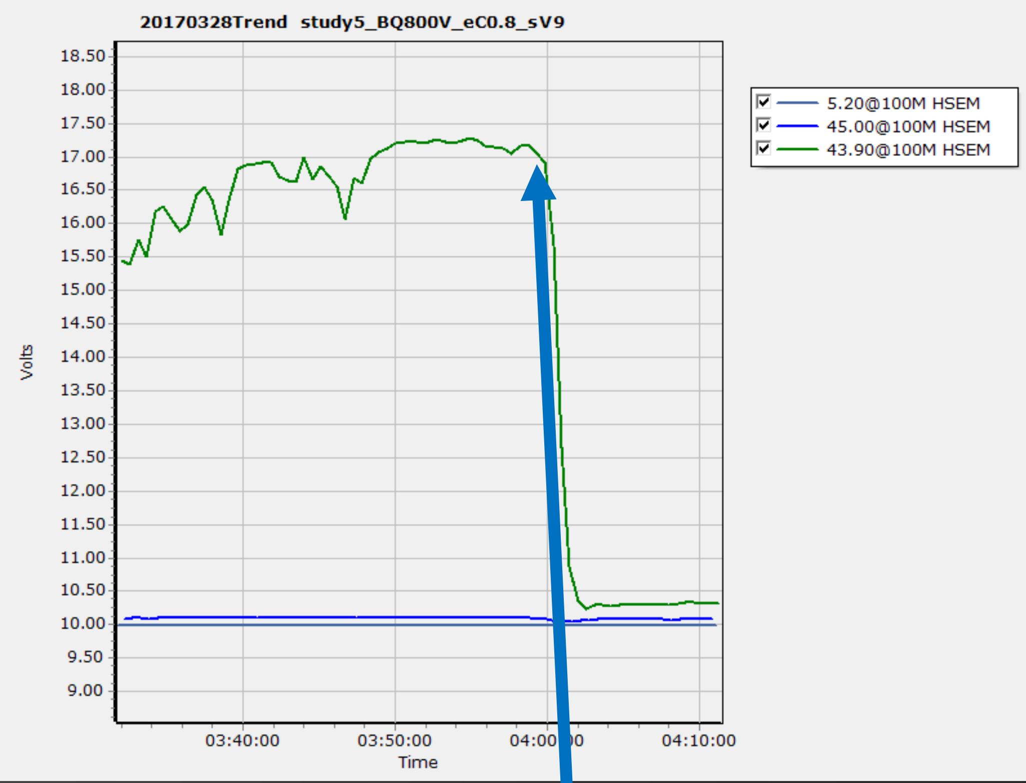
Experimental: live reaction monitoring
(i) Medieval bone (HCl) HySEM-80

- Good 'tracking' between the two signals – positive sign
- By stable isotope standards this is still poor ratio precision (during reaction): σ = 60‰
- Need:
  - Stable sample CO_2 pressure at the inlet
  - Capillaries for turbulent flow
  - Concurrently evacuating flask may cause isotopic fractionation



Live reaction monitoring
(ii) $CaCO_3 + H_3PO_4$ HySEM-80; capillary inlet



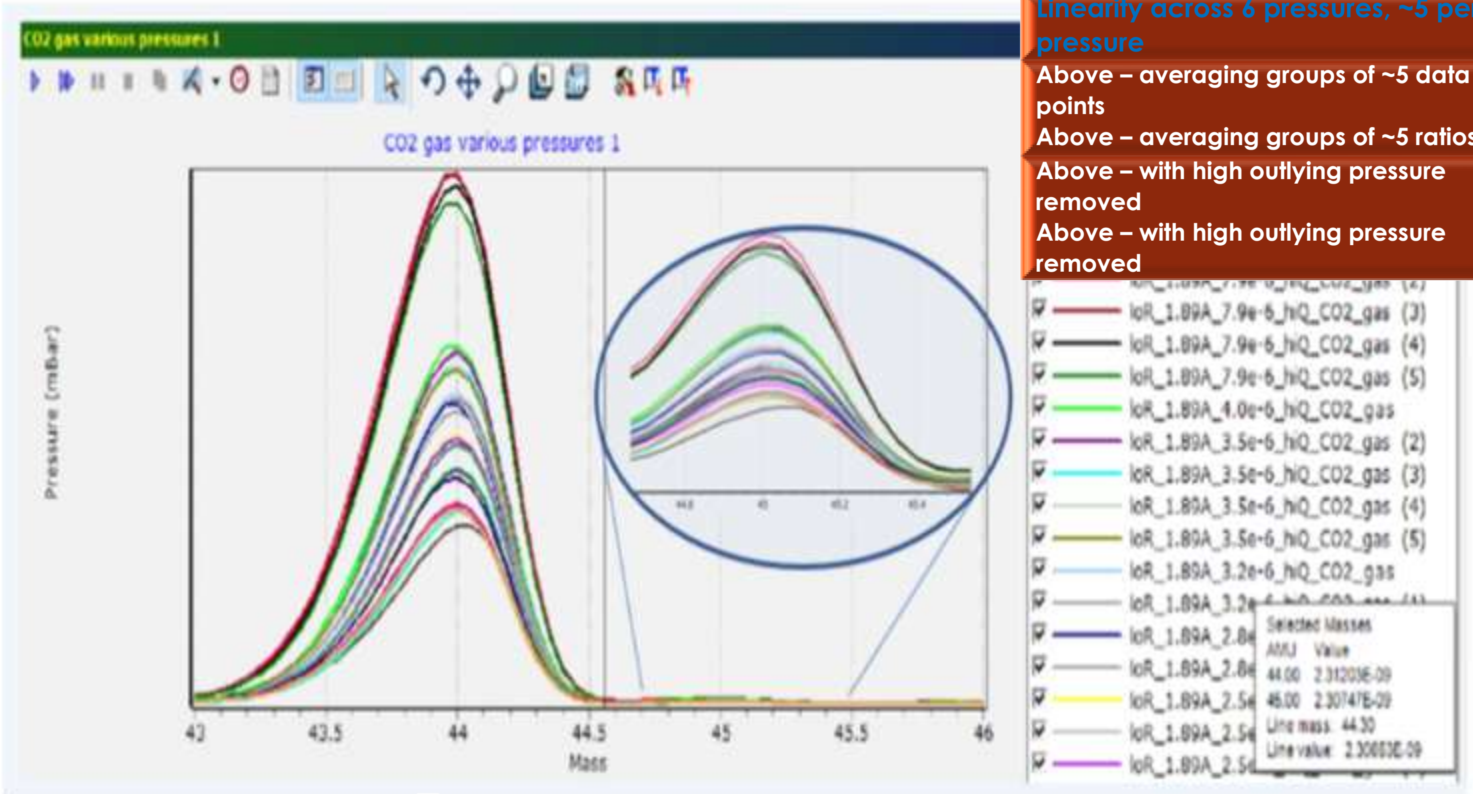


CO_2 detected from reaction

CIM: reaction complete

Stability and linearity – early results (*HySEM*)

CO_2 cylinder gas	Pressure range (Torr)	Mass 45/44 standard deviation	Predicted $\delta^{13}C$ standard deviation
Linearity across 6 pressures, ~5 per pressure	$7.9 \times 10^{-6} – 1.6 \times 10^{-6}$	0.00025	22.4‰
Above – averaging groups of ~5 data points	$7.9 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000159	14.1‰
Above – averaging groups of ~5 ratios	$7.9 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000122	10.9‰
Above – with high outlying pressure removed	$3.6 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000089	7.84‰
Above – with high outlying pressure removed	$3.6 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000090	7.99‰

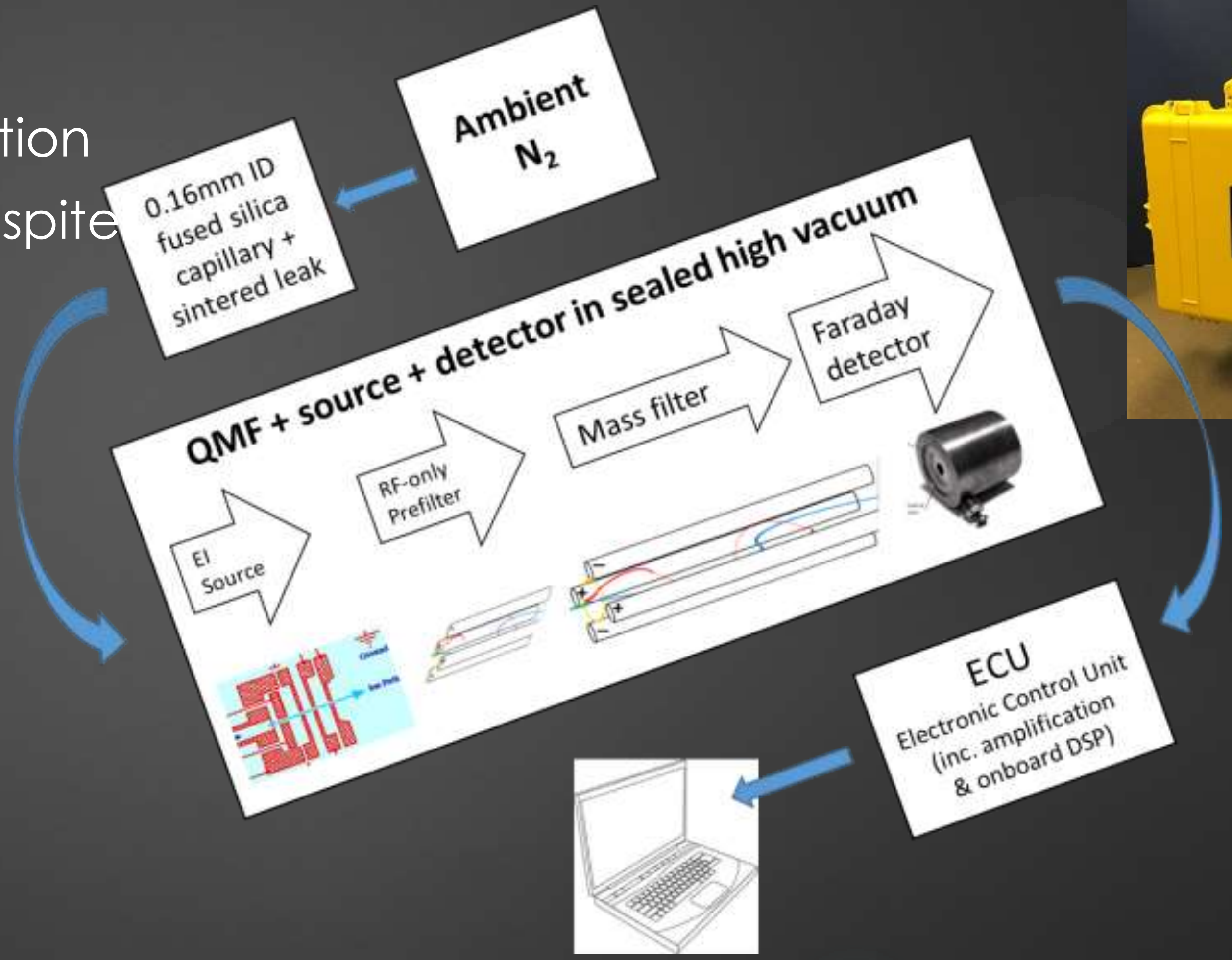


Measurements from line 1 of Table . Six clear groups can be discerned in the mass 44 peak (= mostly $^{12}CO_2$) corresponding to 6 reducing pressure bands of introduction of cylinder CO_2 gas to the needle valve inlet of the portable QMS. The first four of these can be clearly discerned on the inset (mass 45 = ~93% $^{13}CO_2$).

- Need stable sample pressure

Stability – VapourSense (N_2)

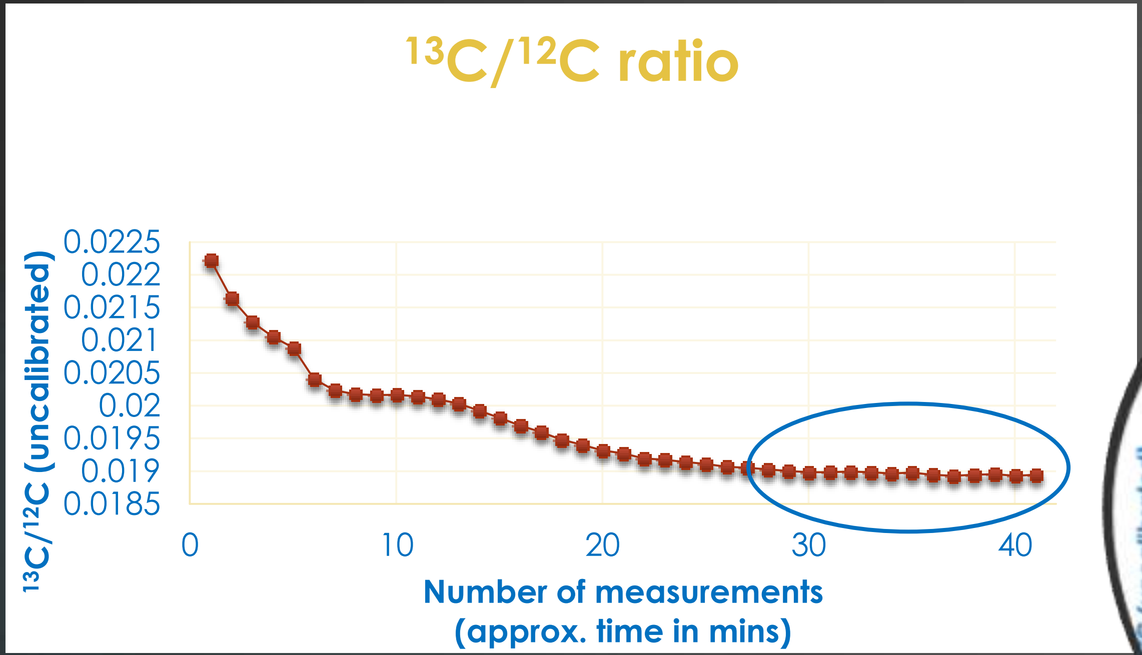
- Peak-jumping mode (MIM)
- Sample not pressurised
- Capillary not standard
- Sintered leak may cause fractionation
- 29/28 signal is surprisingly stable despite non-ideal setup

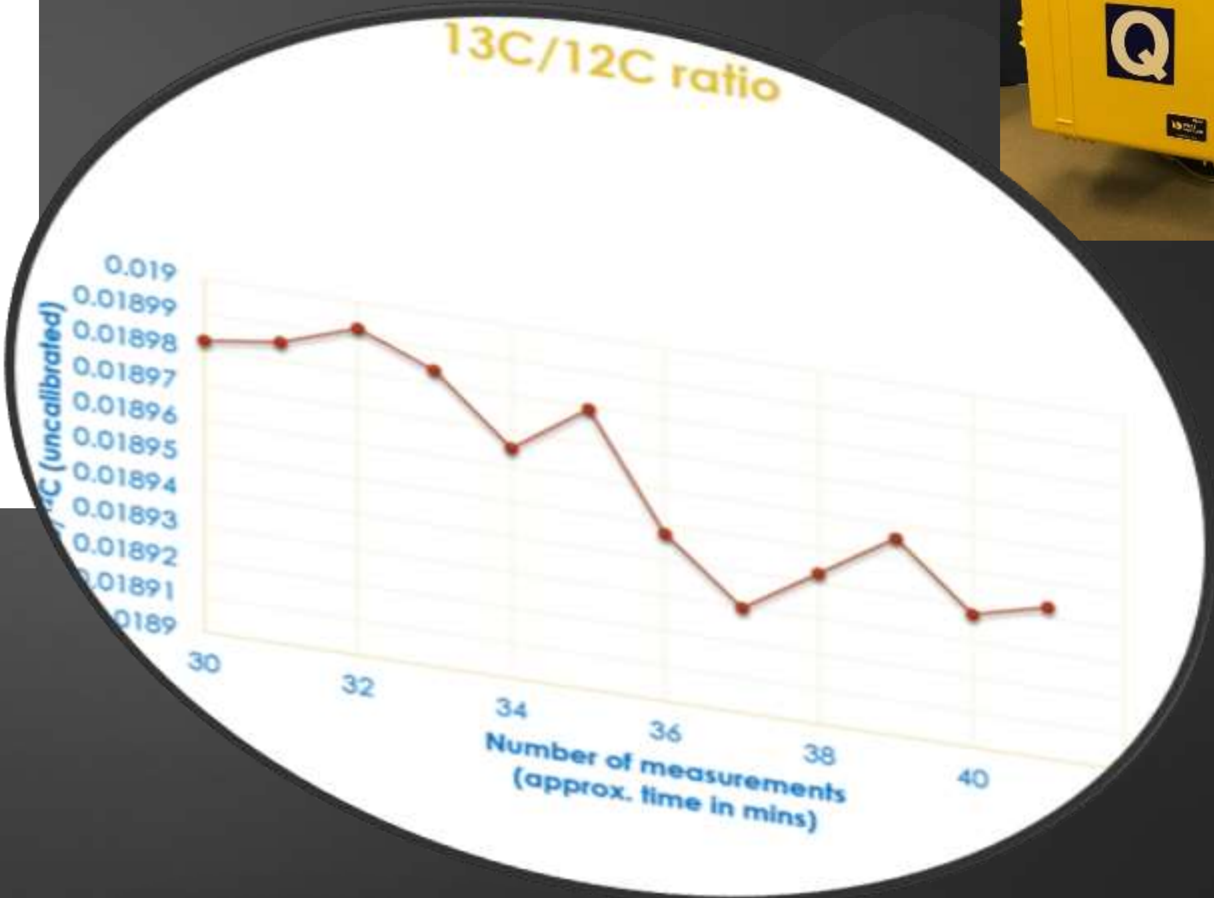


VapourSense-500, ambient N_2 MIM mode (peak jumping)	m/z 29/28 stand. dev. (1σ)
Stability across 247 measurements (34-minute period)	0.0000501
Above – final 37 measurements only (5-minute period)	0.0000275

Stability – VapourSense (CO_2)

- Sample @ 30psi; 0.15mm ID stainless-steel crimped capillary
- Optimised onboard signal averaging and decimation



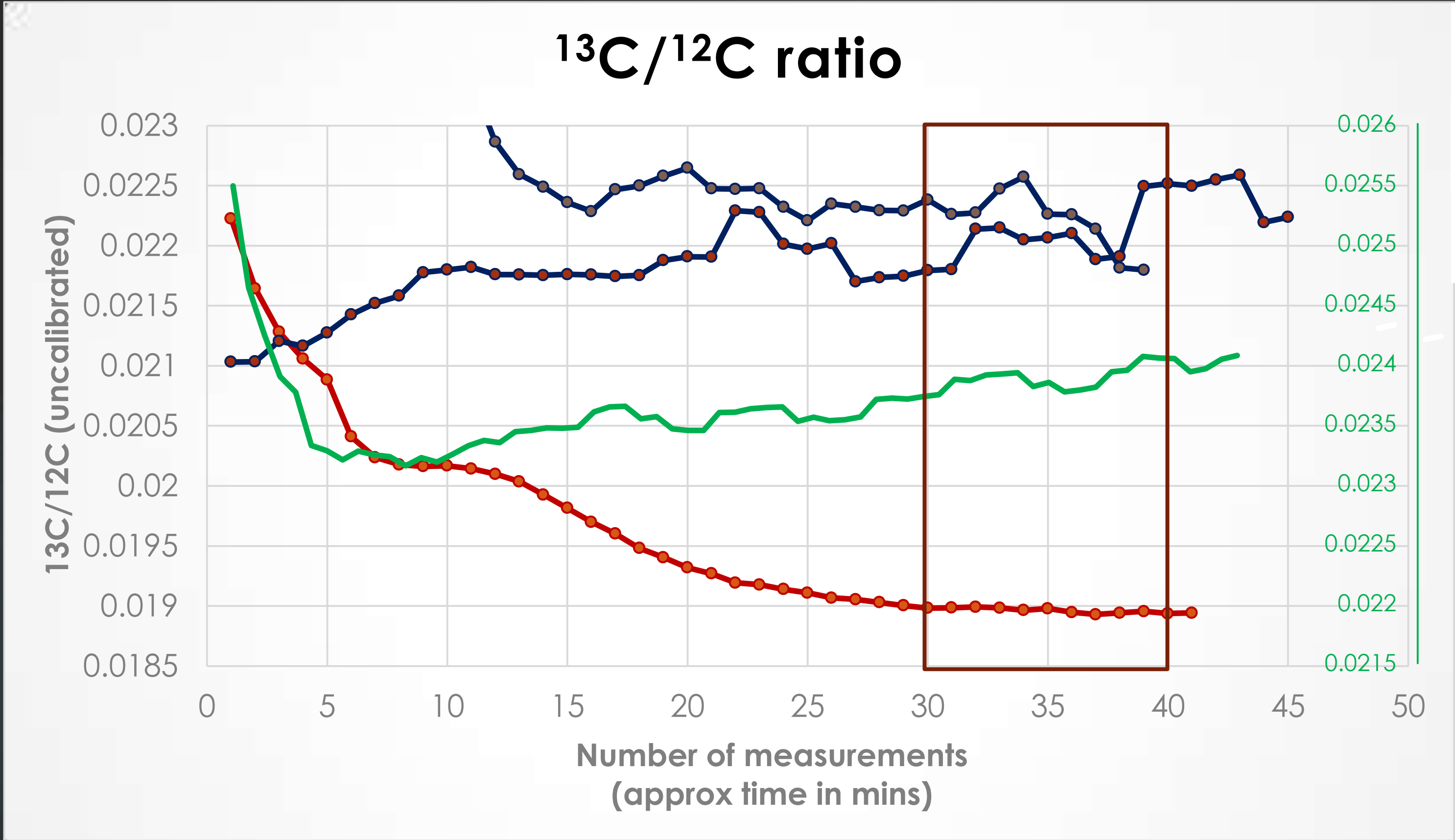


$$1\sigma \frac{^{13}C}{^{12}C} = 2.15 \times 10^{-5}$$

$$RSD = 0.113\%$$

$$\delta^{13}C \rightarrow 1 - 2‰$$

Heuristic comparisons with earlier results



Averaging: 500
Reservoir pressure: $\leq 15\ psi$

Averaging: 250
Reservoir pressure: $25\ psi$

Averaging: 200
Reservoir pressure: $31\ psi$

$$1\sigma\frac{^{13}C}{^{12}C} = 1 - 2\times 10^{-4}$$
$$RSD = 0.5 - 1\ \%$$
$$\delta^{13}C \rightarrow 5 - 20\ ‰$$

$$1\sigma\frac{^{13}C}{^{12}C} = 1.0\times 10^{-4}$$
$$RSD = 0.44\ \%$$
$$\delta^{13}C \rightarrow 4 - 9\ ‰$$

$$1\sigma\frac{^{13}C}{^{12}C} = 2.40\times 10^{-5}$$
$$RSD = 0.13\ \%$$
$$\delta^{13}C \rightarrow 1 - 2\ ‰$$

- Averaging period is critical
- Balance – neither too high nor low
- ~200 readings per point optimal
- Reynolds number: $Re = \frac{\bar{v}D\rho}{\mu}$

  $v = mean\ velocity$ $\quad \rho = gas\ density$
  $D = vessel\ diameter$ $\quad \mu = gas\ viscosity$
- Re should exceed critical value > ~2000 for 0.15mm I.D. capillary, crimped, ~15 psi
- Higher Re → meta-turbulent flow

Onsite reaction monitoring – Halton Castle

Stainless steel capillary inlet

Reaction flask: H_3PO_4 + medieval bone

Live on-screen monitoring

Portable QMS enclosure

Portable HySEM-80 QMS operational in Halton Castle grounds, 2017

Conclusions and next steps

- ***A portable QMS for onsite isotopic analysis is realistic***
  - On the basis of observed results, we believe sufficient precision and local stability are attainable, for useful application; aim to validate results more systematically

- **Measurement stability (local):**
  - Observed 0.1% RSD → ~1‰ standard deviation in the $\delta^{13}C$ figure may be possible
  - Next step: dual changeover valve – continually subtract readings from a standard gas
    - Precision: prospect of local ('medium-term') stability enhancement
    - Precision: prospect of local ('short-term') stability enhancement OR deterioration?
    - Accuracy: offset longer-term instrumental drift

- **Experimental / application**
  - Concept demonstrated
  - Refine method using well-established IRMS sample collection / introduction approaches
    - Traps (cryogenic, nitrogen) + bellows: stable, high-pressure introduction of purified CO_2

Acknowledgements

- *Norton Priory Museum & Gardens (Runcorn) – access to archaeological collection / dig*
  - ***Frank Hargrave (Director), Lynn Smith (Senior Keeper), Tom Fildes (Business Officer)***
- *Q-Technologies (Liverpool) – instrumentation, technical support*
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- *PhD studentship funded by **EPSRC;** archaeological experiments / selected instrumentation funded by **Arts Council England** in collaboration with Q. Technologies and Norton Priory*

References & Bibliography

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[1] Table (slide 5) was jointly produced by D. McIntosh & S. Maher; SIMION simulations and graphs (slide 11) produced by N. France
[2] J. Gibson, S. Taylor, and J. Leck, "Detailed simulation of mass spectra for quadrupole mass spectrometer systems," *Journal of Vacuum Science & Technology A,* vol. 18, pp. 237-243, 2000.
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P. H. Dawson, *Quadrupole Mass Spectrometry and its applications*. Woodbury (NY): American Institute of Physics, 1995 *Note: image of Mathieu stability diagram on slide 8 also taken from here*
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Slide 3: Image of QMF based on cartoon image: Wiki user 'Angelus'. "Quadrupole mass analyzer". Internet: https://commons.wikimedia.org/wiki/File:Quadrupole_mass_analyzer.svg , Sep. 4, 2011 [Oct. 2015]. From Wikipedia article "Quadrupole mass analyzer". Internet: https://en.wikipedia.org/wiki/Quadrupole_mass_analyzer . Above image based on original image by Wiki user 'Mkotl', "Quadrupole mass analyzer used in mass spectrometers". Internet: https://commons.wikimedia.org/wiki/File:Quadrupole_en.gif , Jun. 28, 2009.
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Slide 4: image from http://www.schoolscience.co.uk/zooarchpage6
Slide 5: isotopologues table jointly produced by S. Maher & D. McIntosh
Slide 6-7: Infographic of 4 trillion dollar bills from the Earth to the Moon: information and background image from: Author unknown (The Endowment for Human Development, Inc.). "Grasping Large Numbers". Internet: http://www.ehd.org/science_technology_largenumbers.php , © 2001-2017 [Oct. 2015]. Dollar bills image from (or similar to, and from same website): Milosh Kojadinovic (hosted at 123rf Limited, image ID: 19776446. "Stock Photo – stack of dollars". Internet: https://www.123rf.com/stock-photo/stack_money.html , website © Sep. 2017 [Oct. 2015]
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Photograph of wall from: https://marketplace.secondlife.com/p/Huuuuge-High-Resolution-Distressed-White-Brick-and-Concrete-Wall-with-2-Full-Perm-Textures-Included-8612-8611/636264?id=636264&slug=Huuuuge-High-Resolution-Distressed-White-Brick-and-Concrete-Wall-with-2-Full-Perm-Textures-Included-8612-8611 [Sep. 18, 2017]
Slide 9: Schematic of a QMS: Author's illustration after P. Gates (University of Bristol). "A schematic of a quadrupole mass analyser", from article "Gas Chromatography Mass Spectrometry (GC/MS)". Internet: http://www.bris.ac.uk/nerclsmsf/techniques/gcms.html . © 2002-2017 [June 3 2016].
Rod set and adapted equipotential diagram from: P. H. Dawson, *Quadrupole Mass Spectrometry and its applications*. Woodbury (NY): American Institute of Physics, 1995
Slide 11: SIMION simulations and graphs by N. France
Slide 13: Photograph of Norton Priory medieval cattle bone, taken by Carla Burrell (Liverpool John Moores University)
Slide 16: Halton Castle skeletons photographed by (and courtesy of) Norton Priory 2017 Halton Castle Excavation. Halton Castle photographs from: http://www.ecastles.co.uk/haltonch.html and (aerial view): http://www.webbaviation.co.uk/gallery/v/cheshire/runcorn/Halton_Castle_Runcorn_jd28060.jpg.html
Slide 17: HySEM-80 photographed by D. McIntosh; set up and operated onsite by D. McIntosh & T. Fildes
Slides 20-21: Photograph of Q-Technologies VapourSense-500 courtesy of Q-Technologies; information available at https://www.q-technologies.co.uk/vapoursense/
Within the infographics of the experimental process, schematic of an ion source taken from image: "Cross Section of an Electron Impact Source" within: R.P.W. Scott, "Analytical Spectroscopy" (chapter 'Electron Impact Ionization'). Internet: http://www.analyticalspectroscopy.net/ap8-3.htm [Sep. 5, 2017]
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