Stable isotope characterisation - how it works, why it works & how good is it?

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Plan

1. Intro & Welcome
2. Objectives of FIRMS 2002
3. Why bother?
4. Basics/definitions
5. Elements commonly measured
6. Criteria for characterisation
7. Intro to analytical methods

Before we start properly

- Welcome
- Thanks
- Mixed ability class
- NOT Chatham House Rules
  - all open, potentially publishable

Why are we here?

EPSRC
Engineering and Physical Sciences Research Council

Network to Develop Applications of Stable Isotope Mass Spectrometry in Forensic Science & Crime Detection

The Network Developing Forensic Applications of Stable Isotope Mass Spectrometry

FIRMS 2002

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Objectives (inter alia)

- Exchange info
  - »Spectrum of views: researchers ↔ users
  - »Res/Tech: tech. transfer to Pointy Hats
  - »End users: problem trans. to Pointy Heads
- Expand the Network
- Understand the *State of the Art*
- Start to formulate strategy for dev.
- Determine interest in a workshop to define research priorities

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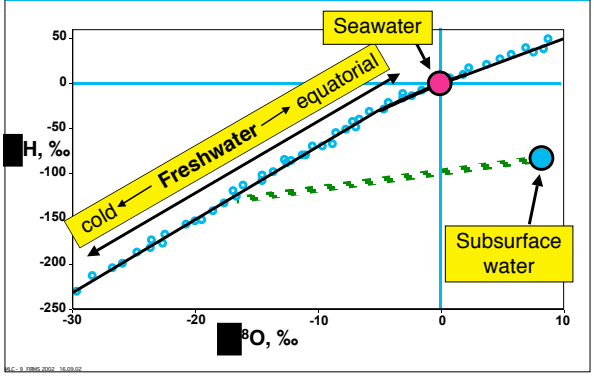
Origin of water

- **Bottle of Highland Spring water - but where does the water come from?**
- **Water consists of H & O mainly**

H & O isotopes in water



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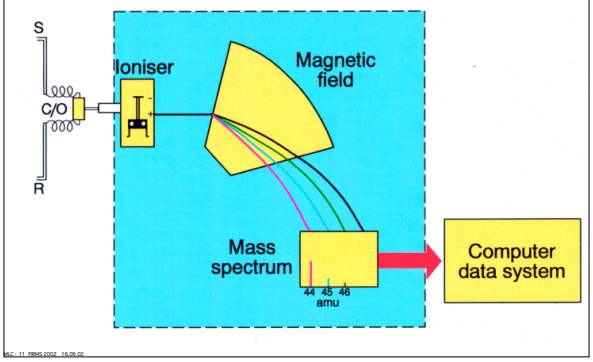
Dual inlet stable isotope mass-spectrometer



Abundances of trace isotopes

Major isotope	Largest trace iso.	p.p.m. rel largest iso
^{1}H	^{2}D	158
^{12}C	^{13}C	11,000
^{14}N	^{15}N	3,700
^{16}O	^{18}O	2,000
^{32}S	^{34}S	42,000
^{35}Cl	^{37}Cl	244,700

Stable Isotope Notation

$$\delta^{13}C\ (‰) = \frac{(R^{13}_{samp} - R^{13}_{std})}{R^{13}_{std}} \times 10^3$$

where $R^{13} = {}^{13}C/{}^{12}C$

$$\delta_{a-b} = \delta_a - \delta_b$$

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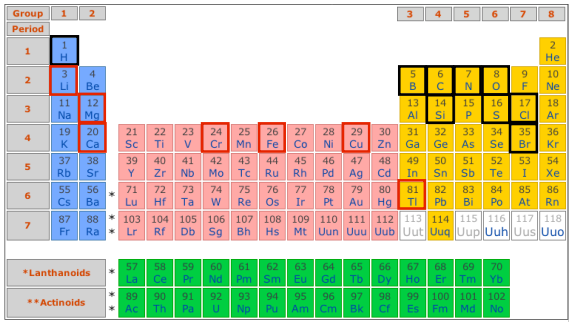
3. Elements (commonly) measured

- **H** - most materials
- **Li** - most materials
- **B** - most materials
- **C** - all materials
- **N** - most materials
- **O** - all materials - silicates need F
- **Si** - all materials - needs fluorine
- **S** - all materials

STABLE isotope variations measured



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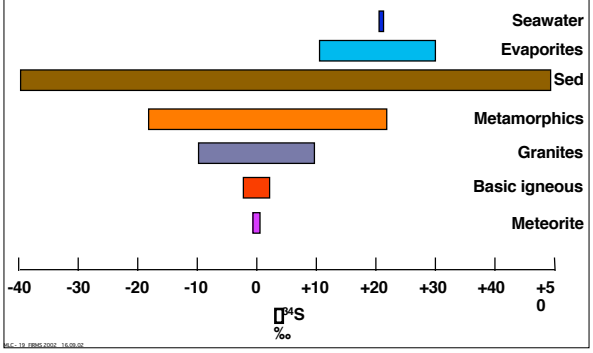
Criteria for characterisation

- **Natural ranges of values**
- **Man-made improvements on nature**
- **Uniqueness of values**
- **Homogeneity**
- **Sample integrity**

Natural ranges of values - S



Sulphate S isotope variation with geological time

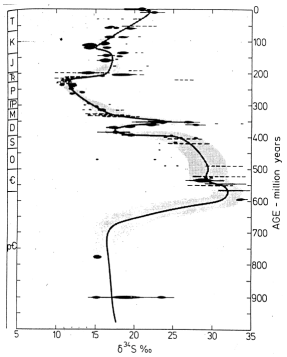


Fig 9. Summary sulfur isotope evolution curve for sulfate.

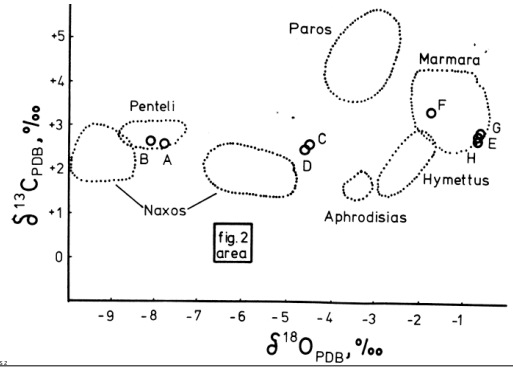
Ancient forensic problem

Roman period sarcophagus

"Roman, third quarter of 3rd century A.D. - Pentelic marble"

BUT - is it genuine?

Uniqueness of values



Homogeneity

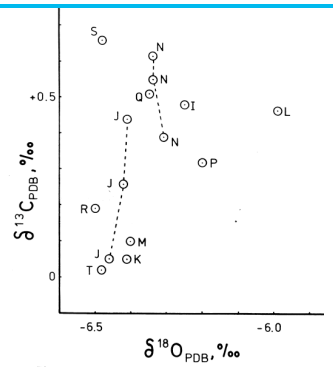
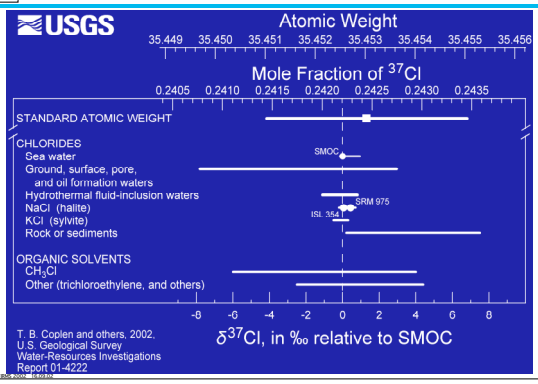


Figure 2 *Isotopic data from fragments of Sidamara sarcophagi*

Range of values of Cl isotopes



WARNING

THE FOLLOWING MESSAGE IS AN UN-PAID-FOR ADVERTISEMENT FOR THE US GEOLOGICAL SURVEY

Isotope range info - your own copy?

Date: Sat, 07 Sep 2002 11:25:35 -0400
From: **Tyler B Coplen <tbcoplen@usgs.gov>**
Subject: Re: Min/Max Isos Report
To: Max Coleman <Max.Coleman@jpl.nasa.gov>

Hi Max,
. . . . . .
url is **http://pubs.water.usgs.gov/wri014222**

This takes you to the website from which you can download the figures. If people just email me with their address, I will happily send them a copy of the report. The bound copy is so much nicer than a pdf that we prefer to use the old fashioned printed report method over pdfs.

I do not know how many participants you have at the forensic meeting, but if given addresses of those interested, I could send them copies of the report. If you could make a list for me and email or fax (703-648-5274) it to me, that would be great.
. . . . . .
Ty

WARNING
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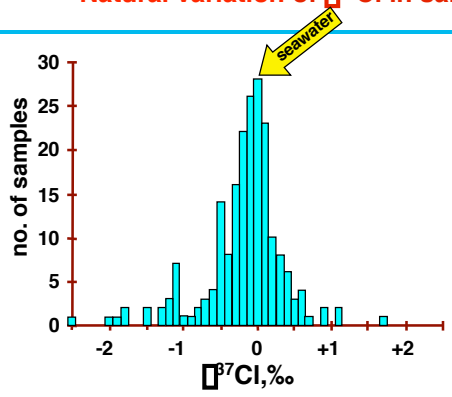
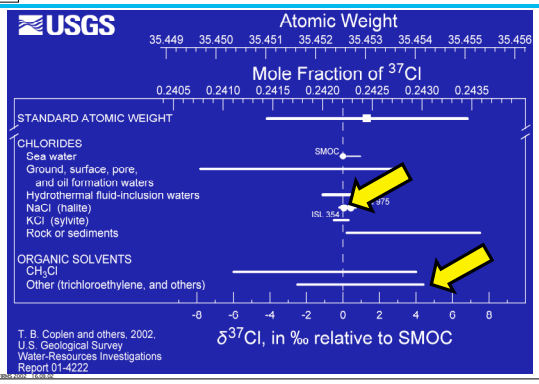
END OF ADVERT

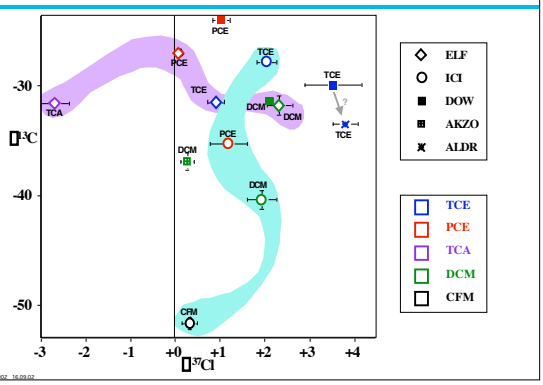
Natural variation of $\delta^{37}Cl$ in salt



Manuf. subs are not natural



Cl solvents - two isotopes

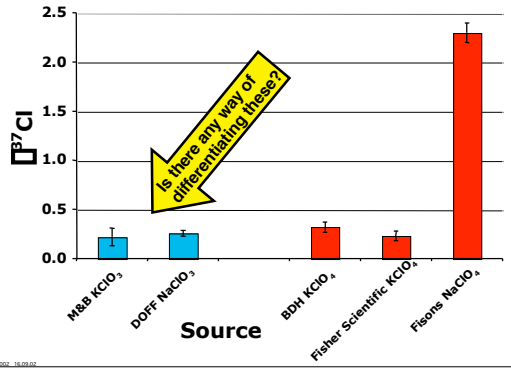


The moral

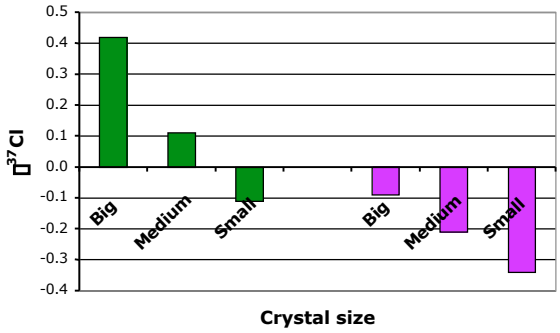
One isotope GOOD

Two isotopes BETTER

(Per)chlorate Cl iso characterisation



Two BDH sodium chlorate samples



Characterisation possibility

- Intrinsic heterogeneity may work
- For chorate, chloride impurity may be of use too

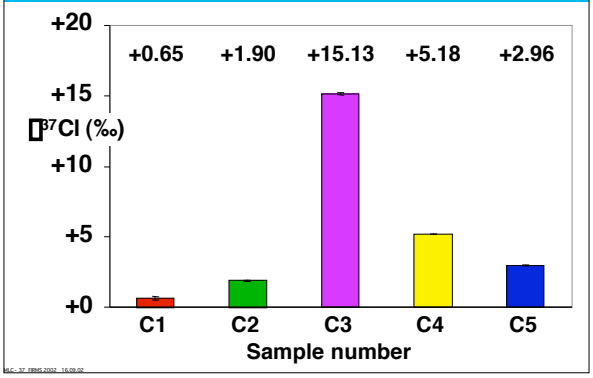
Sample integrity

Do materials retain their isotopic values?

Audience participation time

You too can be an intrepid isotopist

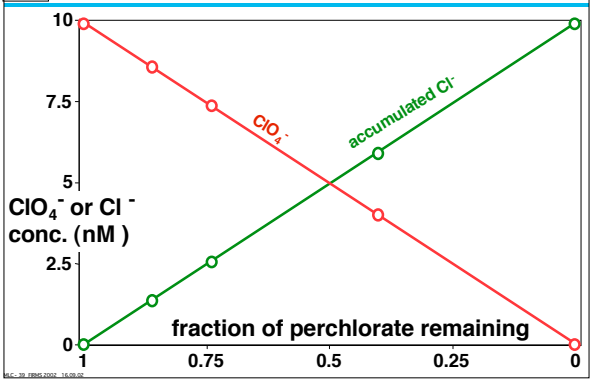
Cl iso. analyses of Cl-compounds



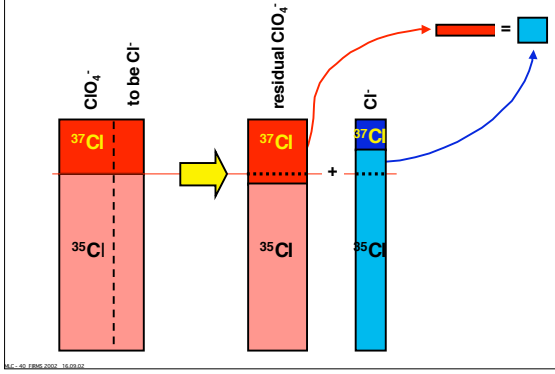
Cl isotope characterisation of samples?

- distinctive range of sample values
- small analytical errors
- can the data identify different sources? No Why?
- can the data identify manufacturers? No

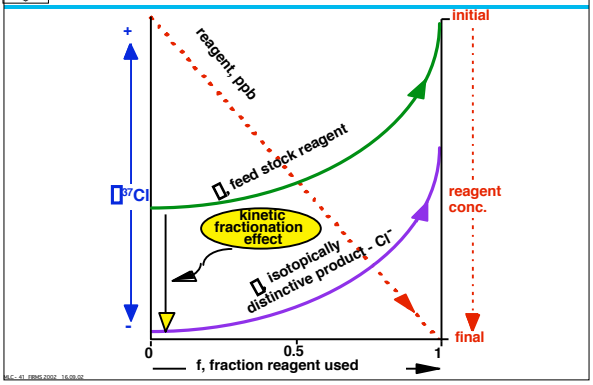
Microbial perchlorate reduction (unpub.)



Rayleigh fractionation - basis



Rayleigh fractionation - quantitative



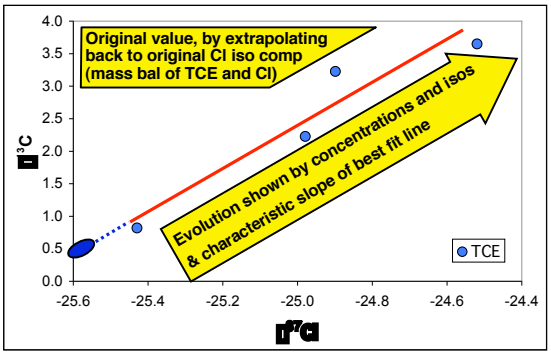
Microbial perchlorate reduction

- Effective microbial reduction process
- Very large change in redox state
- Very large isotopic fractionation, as expected
- Preliminary, unpublished data but looks like a consistent process
- Therefore recognisable

Death knell for iso. char?

- NO!
- Effect is small for solids
- Effects are recognisable - mass bal
  - chloride + residual chlorate
- Characteristic effects for two isotopes

Cl solvent - two isotopes



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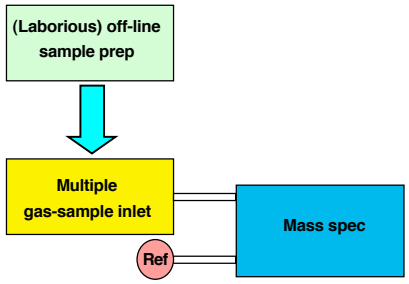
Review of analytical methods

a) Sample prep
b) Gas source mass-spectrometry
c) SIRMS - dual inlet - most precise and "accurate"
d) Analytical uncertainty and stats
e) Continuous flow inlet - more sensitive
f) GC-IRMS- individual compounds
g) LA (SIRMS usually) - spatially resolved

Sample prep

1. Sample must finish up as a gas
2. Any chemical process (understood, not understood, misunderstood) will do to give
   PRECISE and **ACCURATE** answers
3. Sample preparation methods
   a) reaction
   b) purification
   c) measure yield
   d) analyse on mass-spec

Dual inlet



This is the primary calibration method

"the primary calibration method"

- Just how good is it?
- Get the statistics from the computer (integral part of mass spec)

$$\delta^{13}C\ (‰) = \left(\frac{R^{13}_{samp} - R^{13}_{std}}{R^{13}_{std}}\right) \times 10^3$$

$$\frac{R^{13}_{samp}}{R^{13}_{std}} - 1$$

Lies, damn lies and statistics - and then?

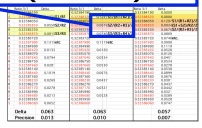
	Ratio 3/1	Delta		Ratio 3/1	Delta		Ratio 3/1	Delta	
R	0.32384190			0.32384190			0.32384190	0.0000	
S	0.32388320	0.1275	S1/R1	0.32388320	0.1297	S1/(R1+R2)/2	0.32388320	0.0000	
R	0.32384050			0.32384050			0.32384050	0.1297	S1/(R1+R2)/2
S	0.32385830	0.0550	S2/R2	0.32385830	0.0676	S2/(R2+R3)/2	0.32385830	0.0934	(S1+S2)/R2/2
R	0.32383230			0.32383230			0.32383230	0.0676	S2/(R2+R3)/2
S	0.32385870	0.0815	S3/R3	0.32385870	0.0740	S3/(R3+R4)/2	0.32385870	0.0805	
R	0.32383720			0.32383720			0.32383720	0.0746	etc.
S	0.32387980	0.1315	etc	0.32387980	0.1119	etc	0.32387980	0.0990	
R	0.32384990			0.32384990			0.32384990	0.1119	
S	0.32385420	0.0133		0.32385420	0.0120		0.32385420	0.0528	
R	0.32385070			0.32385070			0.32385070	0.0120	
S	0.32387640	0.0794		0.32387640	0.0534		0.32387640	0.0451	
R	0.32386750			0.32386750			0.32386750	0.0534	
S	0.32387660	0.0281		0.32387660	0.0530		0.32387660	0.0278	
R	0.32385140			0.32385140			0.32385140	0.0530	
S	0.32388440	0.1019		0.32388440	0.0676		0.32388440	0.0899	
R	0.32387360			0.32387360			0.32387360	0.0676	
S	0.32388230	0.0269		0.32388230	0.0437		0.32388230	0.0301	
R	0.32386270			0.32386270			0.32386270	0.0437	
S	0.32387170	0.0278		0.32387170	0.0321		0.32387170	0.0442	
R	0.32385990			0.32385990			0.32385990	0.0321	
S	0.32386680	0.0213		0.32386680	0.0528		0.32386680	0.0289	
R	0.32383950			0.32383950			0.32383950	0.0528	
S	0.32386060	0.0652		0.32386060			0.32386060	0.0747	
	Delta	0.063			0.063			0.057	
	Precision	0.013			0.010			0.007	

How to calculate δ via S/R

R	0.32384190	
S	0.32388320	0.1275 S1/R1
R	0.32384050	
S	0.32385830	0.0550 S2/R2
R	0.32383230	
S	0.32385870	0.0815 S3/R3

How to calculate δ via S/R

0.32384190	
0.32388320	0.1297 S/(R1+R2)/2
0.32384050	
0.32385830	0.0676 S/(R2+R3)/2
0.32383230	
0.32385870	0.0740 S/(R3+R4)/2

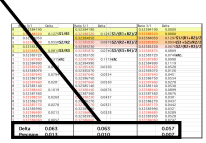


How to calculate δ via S/R

0.32384190	0.0000
0.32388320	0.0000
0.32384050	0.1297 S1/(R1+R2)/2
0.32385830	0.0934 (S1+S2)/R2/2
0.32383230	0.0676 S2/(R2+R3)/2

How to calculate δ via S/R

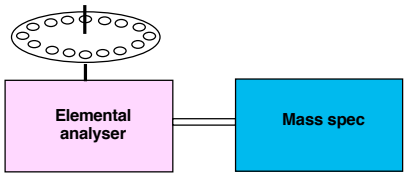
Delta	0.063	0.063	0.057
Precision	0.013	0.010	0.007



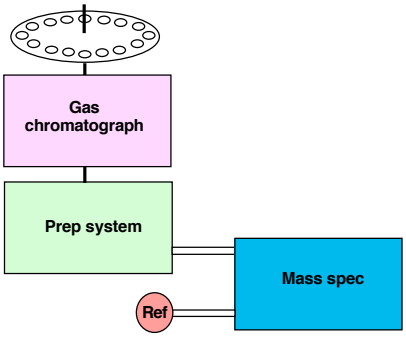
The moral

- Precision and reproducibility are important
- The parameters you think you are measuring may not be exactly what you think

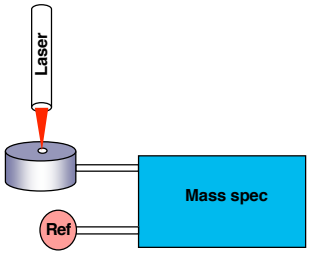
Continuous flow inlet



GC-IRMS



LA (SIRMS usually, but not only)



Future direction(s)

MC-ICP-MS

- High sensitivity
- Many more elements - e.g. Mg, Ca, Fe
- LA, GC, LC front ends

Main points

- Stable isotope characterisation works
- One isotope good, two isotopes better, etc.
- Heterogeneity is a characteristic too
- Stable isotopes just one of many tools to be used in unison

Summary

Stab. Iso. Analysis

(like other techniques)

is only as good as

your care in using it