University of Glasgow | College of Science & Engineering

Quality Assurance in Environmental Geochemistry: Delivering Fit For Purpose Data

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ENSURING INTEGRITY OF SAMPLE MATERIALS

An example from my "previous life" as a mantle geochemist.....

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Individual lava flows can be surprisingly uniform in composition, so a 1 kg sample can be representative.

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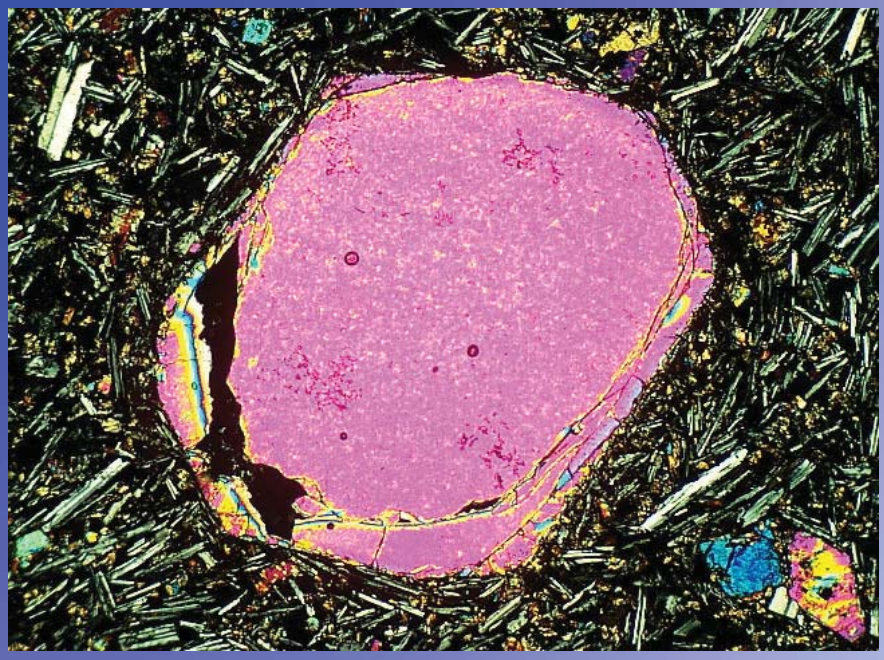

But very heterogeneous if we look closely, so still need careful preparation of "whole rock" powders.

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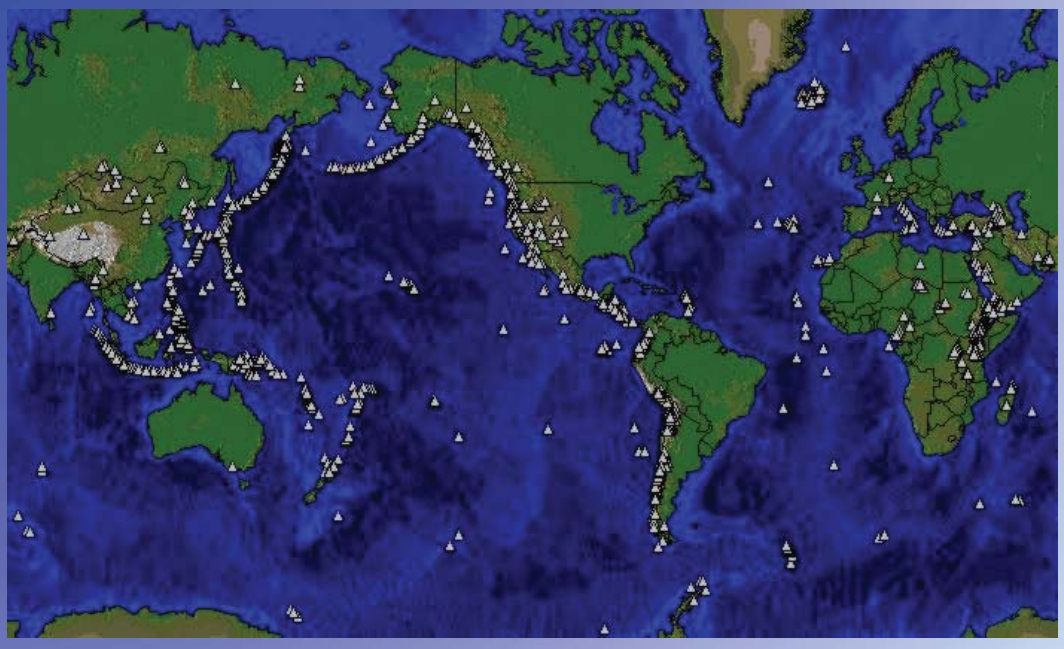
Only c. 500 volcanoes worldwide, so easy to sample…



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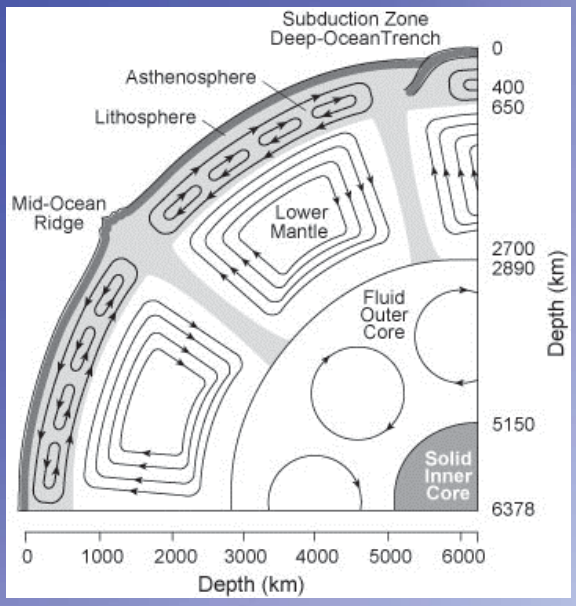
…but we are trying to sample 1 x10^{12} Km^3 of Earth's mantle.



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Environmental Science has the inverse problem – infinite samples but representative of what?

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And marine geochemistry is even harder!

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Ensuring integrity of sample materials

- What are we hoping to sample?
- Does sampling method work? e.g. core tops sampled?
- Does sampling change sample? e.g. compression of a soil sample.
- Is sample representative? e.g. heterogeneous intra- and inter-site.
- How is sample preserved? e.g. acidification of water samples.

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Nielsen et al. (1993) J. Radioanal. Nucl. Chem. 171. 303-317

Two Cumbrian sites near Sellafield – Ennerdale & Corney Fell. Upland, acid grassland sites, grazed by sheep, apart from manipulation of grazing pressure, minimal agricultural management.

5 laboratories using different sampling procedures.

Corney Fell

Ennerdale

LAB A: i. 10 x 10 cm or 15 x 15 cm blocks cut with a knife as deep as possible, 5 cm depth sectioned with scissors.
ii. 5.6 cm diameter x 10 cm deep cylindrical metal corer, no vertical information. Samples 1-2

LAB B: i. 30 x 30 quadrat extracted by trenching around quadrat, 0-5 cm, 5-10 cm, 10-15 cm and further 10 cm sections to base. Samples 3-7

LAB C: i. 25 cm x 25 cm soil pit, "where possible" 5 cm slices – issues with rocks. Samples 8-10

LAB D: i. 6.5 cm diameter metal corer, 13 locations cored to each 5 cm depth segment. Soil compression compromised depth segmentation. Sample 11

LAB E: i. 5.6 cm diameter x 25 cm length plastic cylinders, where possible removed in field, where necessary frozen in lab and 5 cm sectioned. Composited into 0-5 cm, 5-10 cm and 10-20 cm slices. Sample 12

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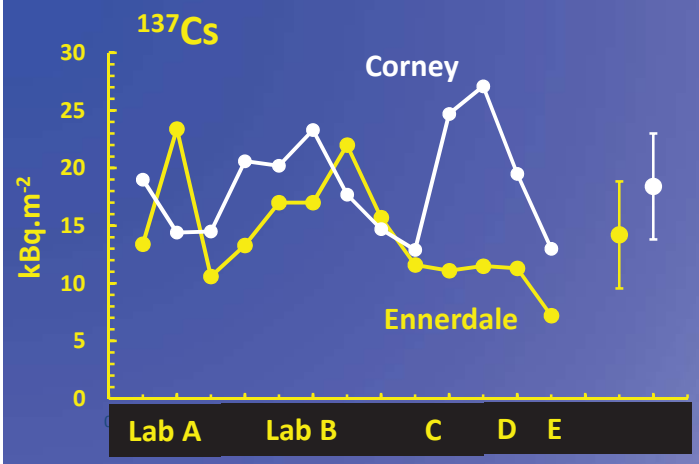
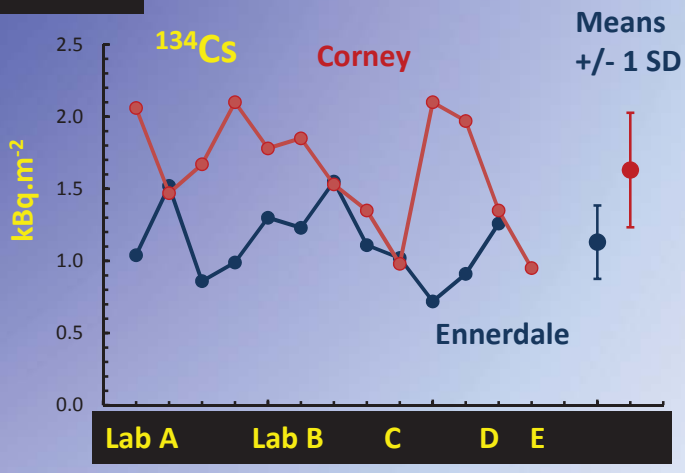
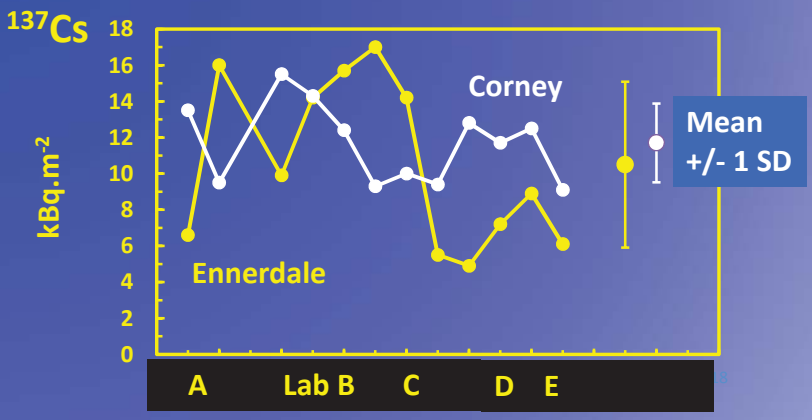
Total Radiocaesium





0-5 cm depth slice



- Different sampling protocols yield different results.
- Need to understand what is being sampled and whether sampling changes sample.
- Standard protocols and trained samplers.

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Coupling sampling to analytical strategy

- Sampling needs to be informed by requirements of methods – e.g. no point collecting 10 ml if measurement needs 1 l.
- Where possible should archive material e.g. common practice to halve core samples.
- Difficult, but should attempt to anticipate future analytical capability and motivation.
- Dynamic sample localities, future work depends on getting it right now.

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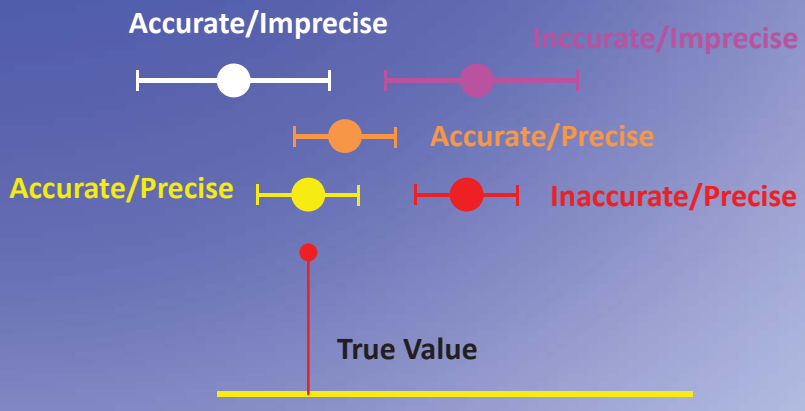
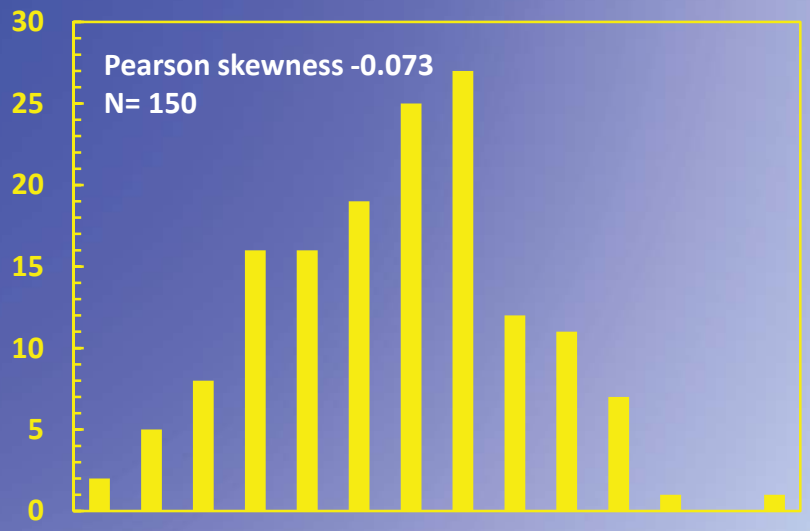
Maintaining analytical integrity: Precision & Accuracy

Accuracy: How close is the analysed data to the "true" composition of the sample?

Precision: How reproducible is the analysis?



Precision & Accuracy – an example from TIMS analysis of $^{87}Sr/^{86}Sr$



NIST SRM987 $^{87}Sr/^{86}Sr$ = 0.710247 – community consensus

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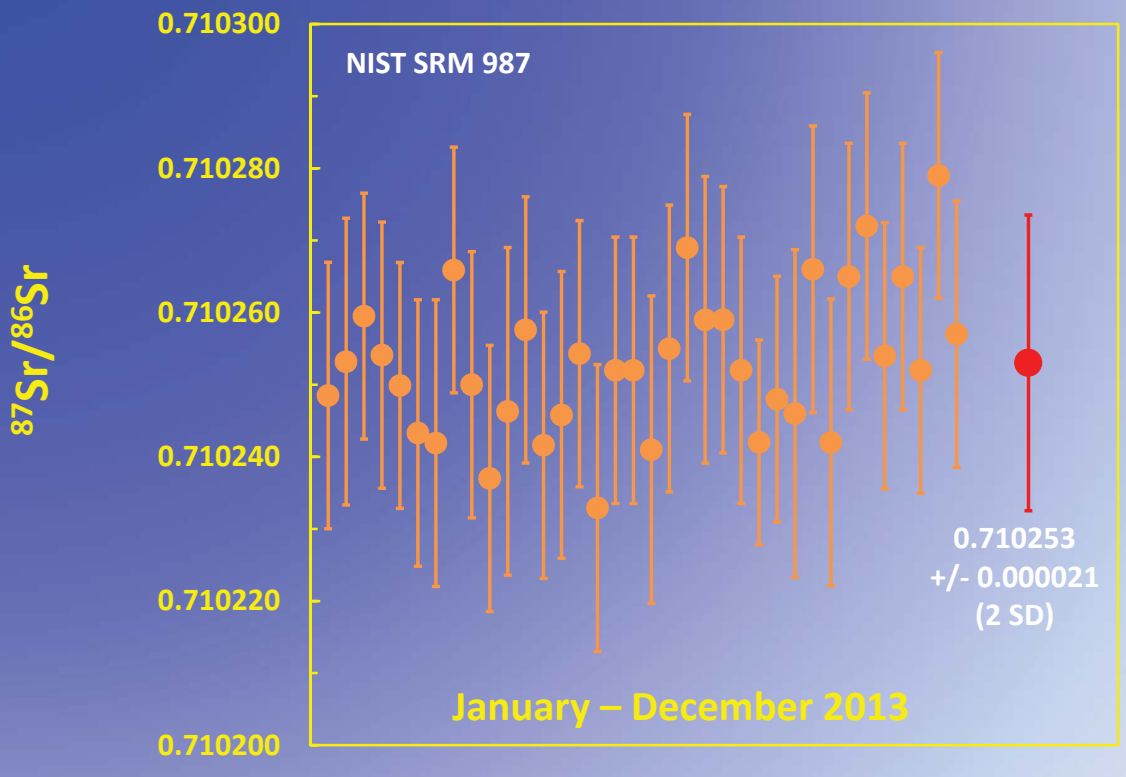
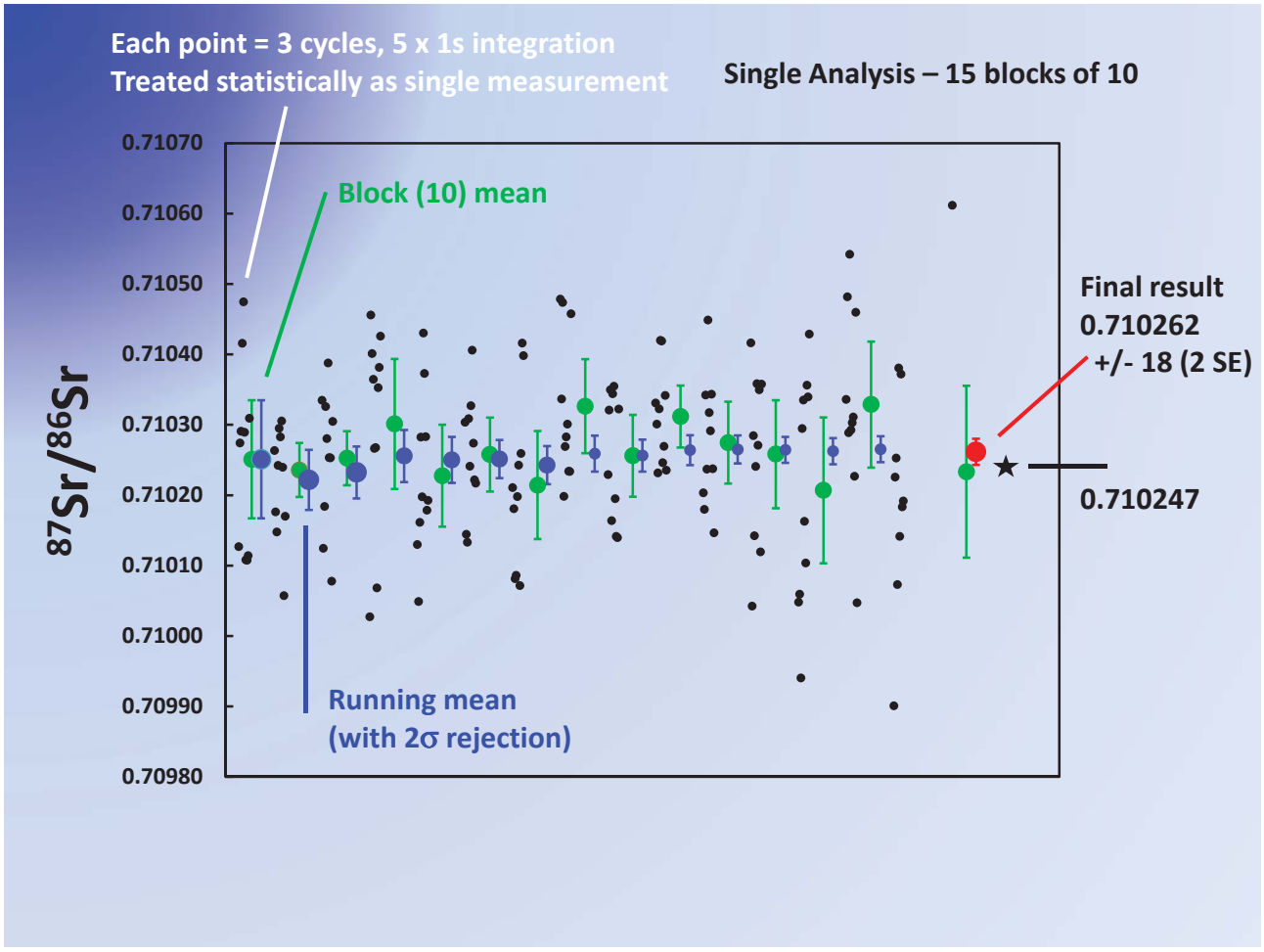
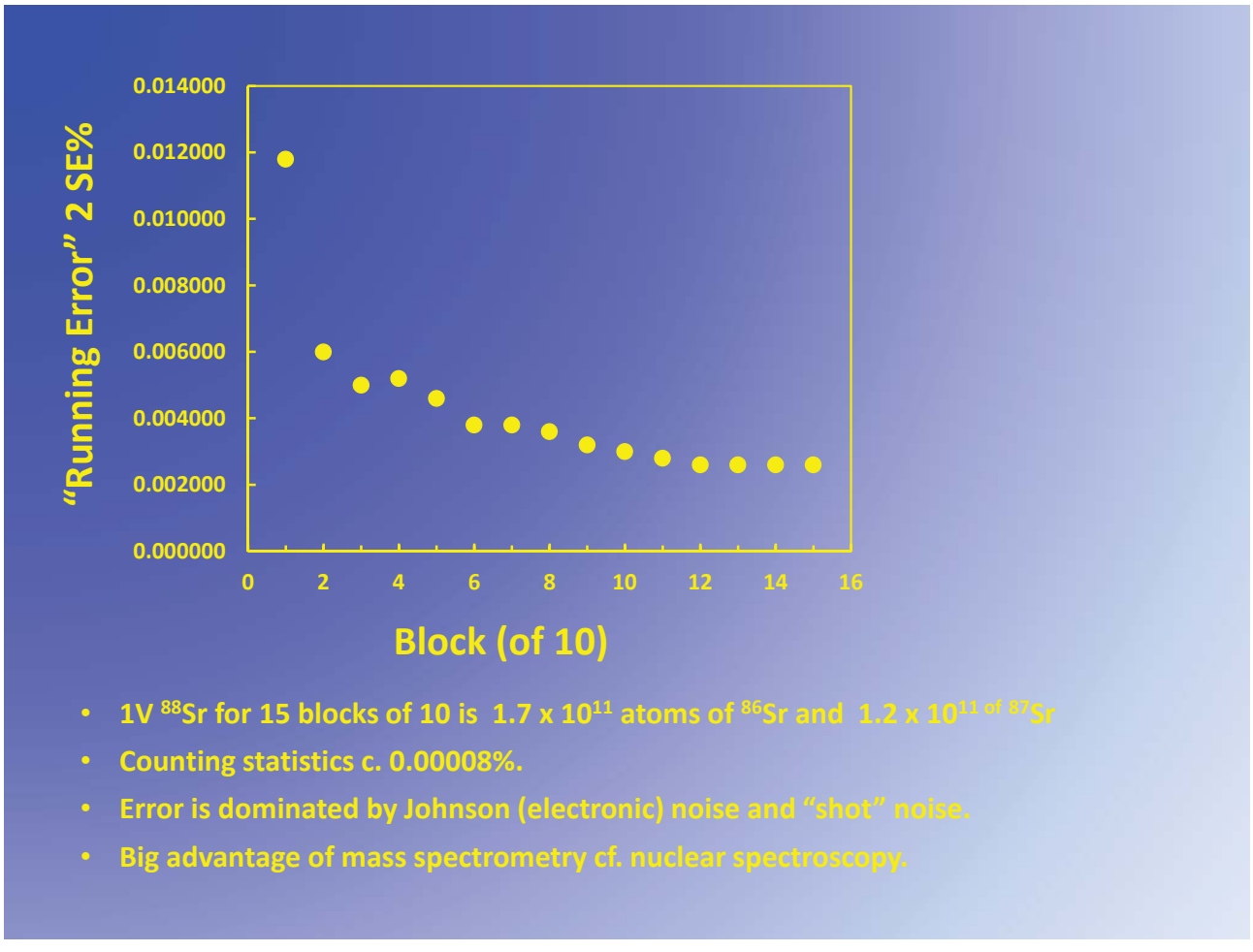
"External" Precision – replicate measurements over extended period







- 1V ^{88}Sr for 15 blocks of 10 is 1.7 x 10^{11} atoms of ^{86}Sr and 1.2 x 10^{11} of ^{87}Sr
- Counting statistics c. 0.00008%.
- Error is dominated by Johnson (electronic) noise and "shot" noise.
- Big advantage of mass spectrometry cf. nuclear spectroscopy.

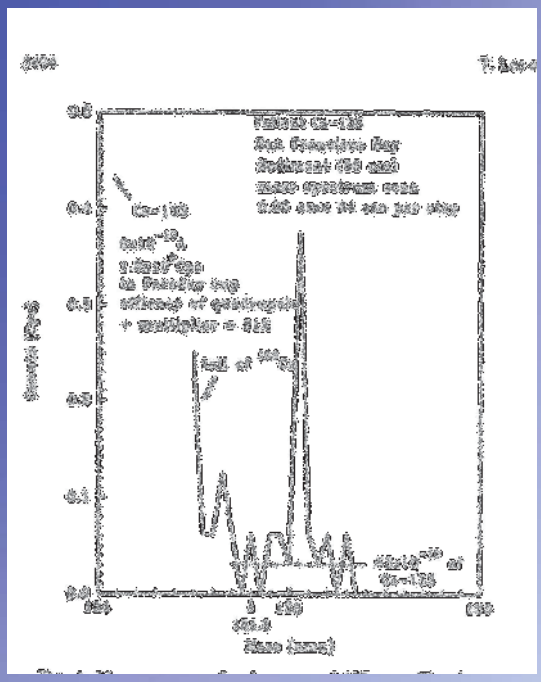
TIMS for Cs - Lee et al. Geochim. Cosmochim. Acta 57, 3493-3497, 1993

^{133}Tail onto ^{135}Cs

&

^{135}Cs < 1 cps

Fukushima samples would be much higher.



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Shibahara et al. – J. Nucl. Sci. Tech. 51, 575-579, 2014

^{134}Cs/^{137}Cs will soon "disappear" as a tracer of FDNPP.

^{135}Cs shielded by neutron capture of precursor ^{135}Xe to form ^{136}Xe, ^{137}Cs is unaffected.

^{135}Cs/ ^{137}Cs characteristic of reactor operation and shutdown: source identification, dispersion modeling, long-term Cs behaviour, sediment geochronology.

Shibahara et al determined ^{134}Cs/ ^{137}Cs to 0.5% and ^{135}Cs/ ^{137}Cs to 0.1% on 5Bq of ^{137}Cs i.e. c. 1 pg.

Issues: Fractionation control with no known ratio.
Isotope dilution (concentration) would normally choose ^{135}Cs.
Blanks?
Multiplier noise from decay.

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Zheng et al. Anal. Chem. 86, 7103-7110, 2014

$^{134}Cs/^{137}Cs$ will soon "disappear" as a tracer of FDNPP.

^{135}Cs ($t_{1/2}$ = 2 x 10^6 a) difficult by radiometric methods – long $t_{1/2}$ and low-energy (76 keV) β decay.

ICP-MS – high environmental Ba interference (134, 135, 137) isobaric $^{95}Mo^{40}Ar$ & $^{97}Mo^{40}Ar$, $^{119}Sn^{16}O$, $^{119}Sn^{16}O$

ICP-MS/MS – Agilent 8800 triple quadrupole

Detection limts - ^{135}Cs – 9 x 10^{-4} mBq/g
^{137}Cs – 40 mBq/g cf 1 mBq/g for γ-spec

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Standardization, Certification & Metadata

- Typical approach would be to matrix match an "old" sample, ensure ^{134}Cs and ^{137}Cs free, then spike with ^{134}Cs and ^{137}Cs as calibration standard.
- Approach not suitable for ^{135}Cs.
- A "geostandard" approach to ^{134}Cs isn't feasible because it would likely take longer to establish a consensus than the effective life-time of ^{134}Cs.
- However, for ^{137}Cs and ^{135}Cs a "geostandard" could be useful
- E.g. IAEA - 375

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IAEA – 375

Origin and preparation of the material

The material (top soil to a depth of 20 cm) was obtained from the "Staryi Viskov" collective farm in Novozybkov, Brjansk, Russia in July 1990. The material was air dried and milled to give a grain size less than 0.3 mm by the Brjansk Centre for Agricultural Radiology and Chemistry. The material was packed into 25 polythene sacks (containing approximately 20 kg of soil each) and dispatched to the Agency's Laboratories at Seibersdorf in November 1990.

The bulk material was recombined and homogenized at the Agency's Laboratories at Seibersdorf by mixing the powder in a 3000 L drum for 24 hours and then dispensed into plastic bottles in 250 g units. Subsequently, the samples were irradiated to a dose of 2.5 x 10^4 Gy using a ^{60}Co source to ensure long-term stability of the material by inhibiting microbial action.

Homogeneity

The homogeneity of the bottled material was assessed using marker analytes for trace elements (U), β-emitters (^{90}Sr) and γ-emitters (^{134}Cs and ^{137}Cs) for intake masses of 0.2 g (trace elements) and 6g (radionuclides) respectively. For this study, seven bottles were chosen at random and three determinations were made from each bottle. Taking into account the statistical uncertainties on the observed results, this material can be considered sufficiently homogeneous for it's intended purposes at or above the specified intake masses.

Note: Some evidence has been presented to suggest that this material may be contaminated with "hot particles" resulting from the Chernobyl accident. The frequency of the occurrence of these "hot particles" is unknown and consequently, it is possible that significantly elevated activities may be observed for anthropogenic radionuclides in some sub-samples.

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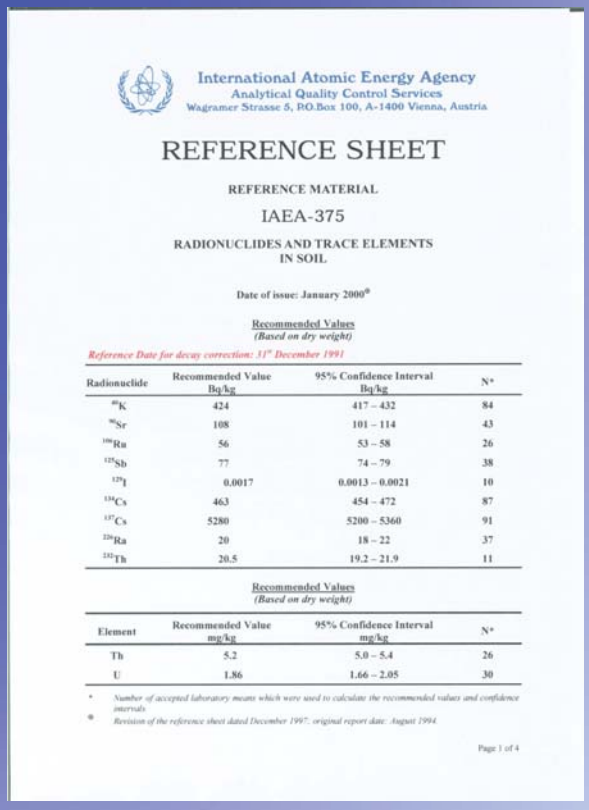

International Atomic Energy Agency
Analytical Quality Control Services
Wagramer Strasse 5, P.O.Box 100, A-1400 Vienna, Austria

REFERENCE SHEET

REFERENCE MATERIAL

IAEA-375

RADIONUCLIDES AND TRACE ELEMENTS IN SOIL

Date of issue: January 2000*

Recommended Values
(Based on dry weight)

Reference Date for decay correction: 31st December 1991

Radionuclide	Recommended Value Bq/kg	95% Confidence Interval Bq/kg	N*
^{40}K	424	417 – 432	84
^{90}Sr	108	101 – 114	43
^{106}Ru	56	53 – 58	26
^{125}Sb	77	74 – 79	38
^{129}I	0.0017	0.0013 – 0.0021	10
^{134}Cs	463	454 – 472	87
^{137}Cs	5280	5200 – 5360	91
^{226}Ra	20	18 – 22	37
^{232}Th	20.5	19.2 – 21.9	11

Recommended Values
(Based on dry weight)

Element	Recommended Value mg/kg	95% Confidence Interval mg/kg	N*
Th	5.2	5.0 – 5.4	26
U	1.86	1.66 – 2.05	30

* *Number of accepted laboratory means which were used to calculate the recommended values and confidence intervals*

* *Revision of the reference sheet dated December 1997; original report date: August 1994*

Page 1 of 4

Is anyone preparing similar materials from Fukushima Prefecture?

The best way to ensure the international credibility of the F-TRACE programme is to publish in the best international journals.

Also, establishes long-term visibility of results and data sets.

Nowadays, comes with significant QA and metadata expectations.

2009 Policy Statement: Chemical Geology, Earth & Planetary Science Letters, Biogeochemical Cycles, Science, Geology, Contributions to Mineralogy and Petrology, AGU Publications, Lithos, Nature, Nature Geoscience, GSA Publications, Geochimica Cosmochimica Acta, Geochemistry, Geophysics, Geosystems, Journal of Petrology.

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Data Accessibility and Format

All NEW geochemical data used in a publication must be made available for future use by:

1. Submission to an accessible persistent source suchas a public database or data archive (personal web sites are NOT persistent data archives, or by
2. Listing the data explicitly in a data table associated with the publication.

The data must in any case be available in downloadable format.

Data Quality Information

Authors must provide sufficient information (metadata) about the analytical process and reproducibility of measurements in order that the data can be properly evaluated.

Basic metadata such as analytical technique, lab and values measured on reference materials need to accompany the data … in standardized tabular format.

Sample Information

Essential information about the samples must be provided in order to allow proper identification of their origin and type, and to trace their analytical history.

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Data Accessibility and Format

- Data should be reported in a tabular format.
- Data must be available as a downloadable file.
- Data file must be easily converted into spreadsheet format (e.g. .csv, .txt).
- The file should include units for the listed measured values.

If a publication contains a data table in the main text or a pdf or image version of the data table as an electronic supplement, the data in the tables must also be available in a form that can easily be converted to a spreadsheet format.

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Data Quality Information

General Analytical Metadata:

- Analytical technique e.g. ICP, XRF, EMP
- Laboratory – name of department/lab & institution
- Analytical accuracy and reproducibility
  - Name(s) and measured value(s) of (internationally recognized) reference standard(s) measured as unknown standards.
  - Estimated uncertainty of reference standard measurement and, if applicable, number of measurements.
- **Method Specific Metadata**
  - Fractionation correction
  - Standardization (normalization)
  - Total procedure blank
  - Detection limit
  - Calibration

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Sample Information

Metadata

- Sample location, if possible latitude and longitude (if not approximate coordinates from Google Earth.
- Marine samples require a depth.
- Position within a stratigraphic section.
- Position within a core.
- Lithological classification and age.
- Cruise or field programme.

Unique Identification

- SESAR System for Earth Sample Registration – www.geosamples.org.
- 9-digit alphanumeric International Geo Sample Number (IGSN) used together with personal or institutional sample name to ensure unambiguous identification of sample.

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Legacy big data, maximising technological advantage

In 1986, I typed my PhD thesis on a MacPlus with a massive 1 Mb RAM and a lightening fast 8 MHz processor. I stored it a 1.44 Mb 3.5” HD disk that I no longer have the capability to read.

Today, I use a laptop PC with 4 Gb RAM and a 2.6 GHz chip, carry at least 25 Gb in my brief case and store my e-mails on the cloud; and I used a telephone to take the picture!

Compared to previous accidents we are going to be able to store infinite amounts of information.

How do we future-proof this legacy?

Massive opportunity but also a massive challenge.