Accelerator mass spectrometry analyses of ultra-trace radionuclides in the environment - application to geosciences studies -

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Measurement of Environmental Radionuclides

Radiation Spectrometry

***γ*-ray, *x*-ray**

Ge Semiconductor

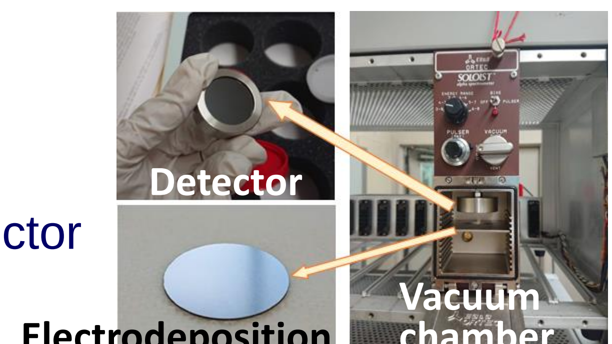
***β*-ray**

Gas Flow Counter

Liquid Scintillation Counter

***α*-ray**

Si Semiconductor



Short～Long Half-life

Mass Spectrometry

ICP-MS

TIMS

thermofisher.com/order/catalog/product/IQLAAEGAASFAFYMAMV#/IQLAAEGAASFAFYMAMV

SIMS

https://www.cameca.jp/product/sims/ims1300-hr3/

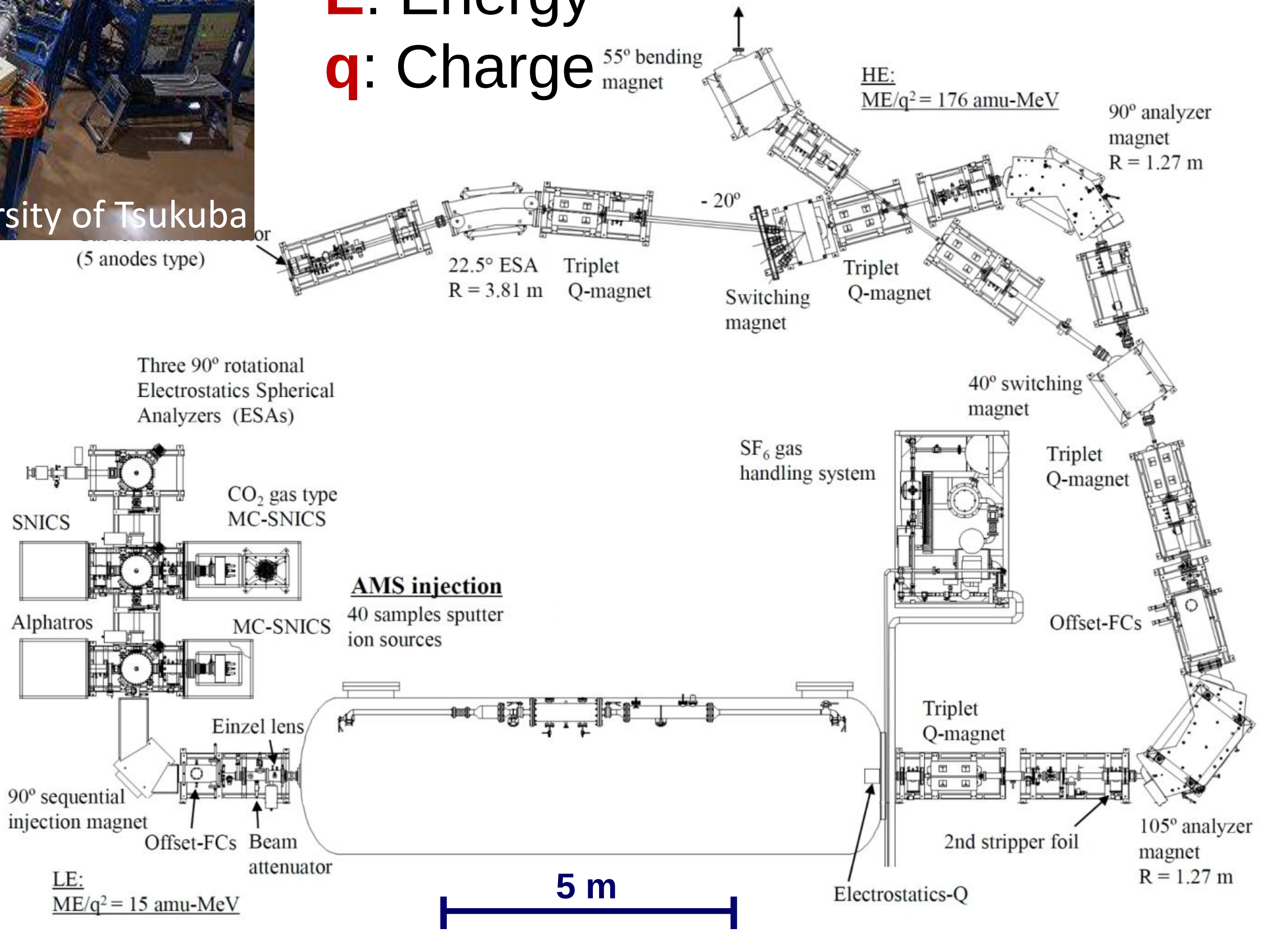
Long/Medium Half-life

Accelerator Mass Spectrometer

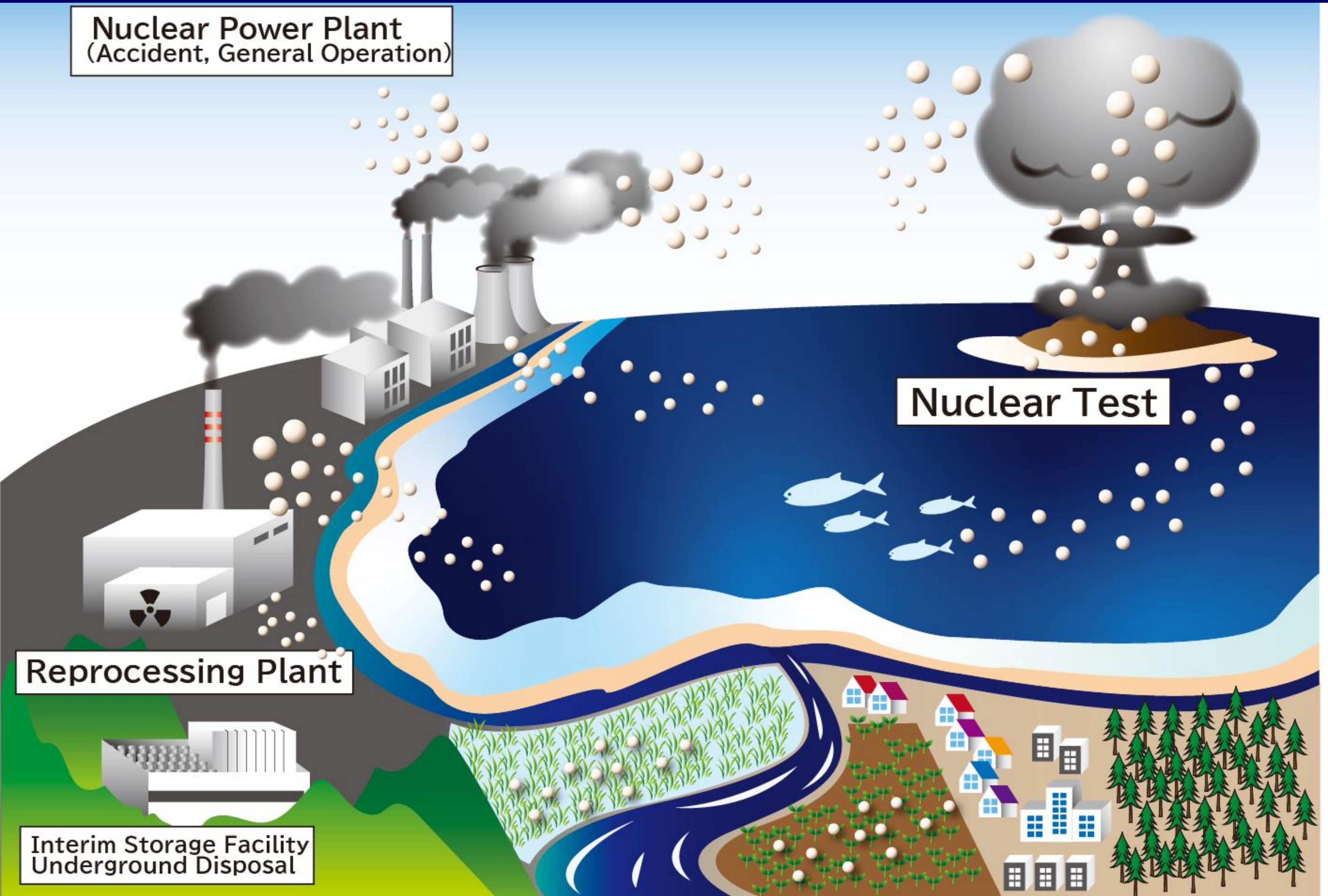
Discriminate the target isotope (ion) by specific combination of

M: Mass number
E: Energy
q: Charge

Analysing Magnet
Electrostatic Analyser
Tandem Accelerator
Ionisation Chamber



Long Half-life Anthropogenic Radionuclides



Classical way, but still higher potential

Applications to Environmental dynamics tracers

＊Material cycles in ocean, atmosphere, land

Availability of 'classical' method to modern environmental science

＊Behavior and metabolisms of plants and animals

High feasibility usage

＊Monitoring

Concentration, distribution and dynamics of nuclides are important around reprocessing plants, Fukushima and Chernobyl

＊Development of analytical method

Chemical separations and mass spectrometry of ^{233}U, ^{182}Hf, ^{79}Se, ^{135}Cs, Actinides, etc.

＊Imaging techniques and state analyses

Existence state, together with concentration analysis, reveals a different aspect from that of stable isotopes.

Usage of medium half-life nuclides

Possible to measure ultra-low levels of environmental nuclides

Non-destructive analysis for analogous research

Nuclear chemistry

＊Analog use of short half-life nuclides

Applications of difficult to trace elements (Zr, Hf, Nb, Ta, Ge, Si) in the environment

＊Spike production

Essential to mass spectrometry

＊ Break out from 'Earth' Science

Application to cosmic chemistry/physics

Application to meteorites, SK-Gd samples, etc.

Environmental Radionuclides

- **Many kinds of nuclides (elements)**
- **Specific half-lives**
- **Wide range of concentrations**
- **Chain nuclides**
- **Different isotopic compositions**
- **Introduction histories/amounts are clear in each system**

＊Unlimited possibility for γ analysis using destructive samples

The initial samples from Fukushima should have also been subjected to 'destructive' γ-ray analysis.

＊Avoid extinction of environmental α analysis

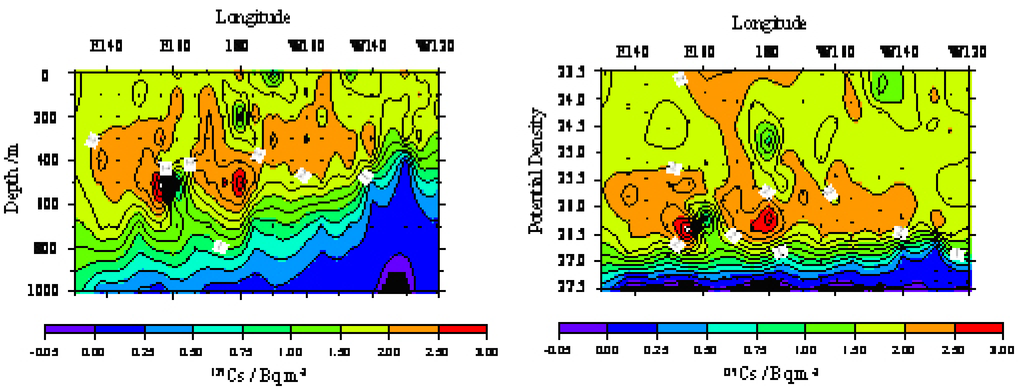
Nobody will be able to conduct α analysis

Radiation measurements

Real 'ultra-trace'!

Study of Application of Anthropogenic Radionuclides to Geoscience

Oceanic Circulation Tracers



Cs-137 concentration depth and density distributions at N24°

^{137}Cs **($T_{1/2}$=30.2 y)**

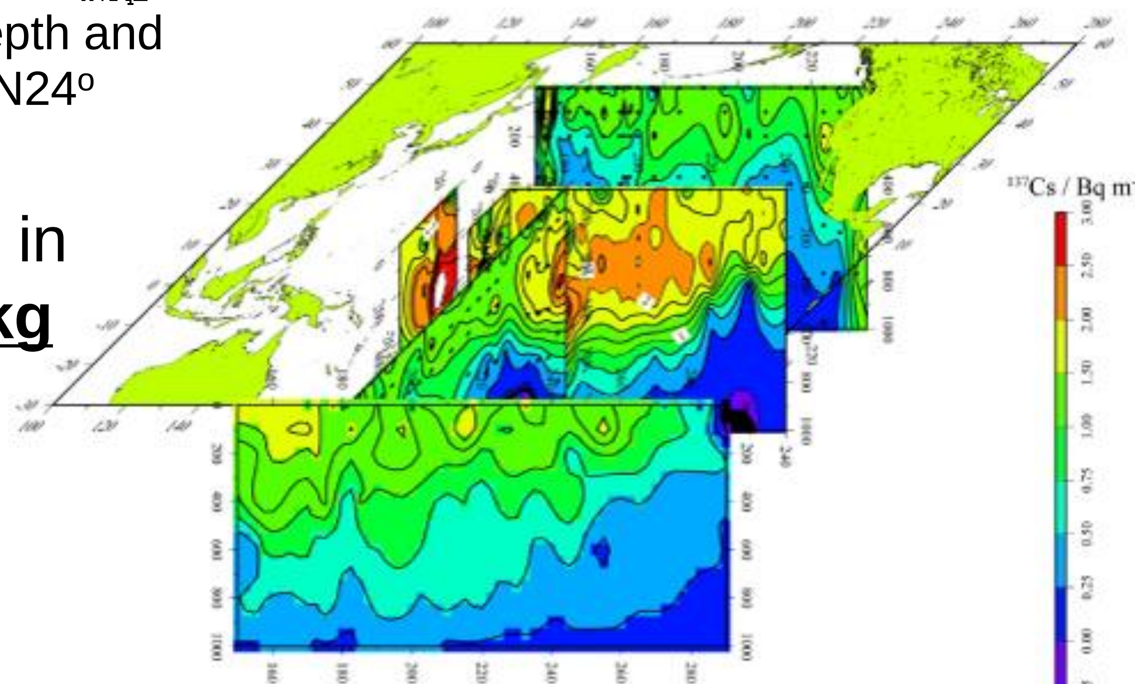
・dissolved metal （alkali metal）

・well known origin

⇒Global-fallout

Ultra-low level of ^{137}Cs in deep water: **<u>0.2 mBq/kg</u>**

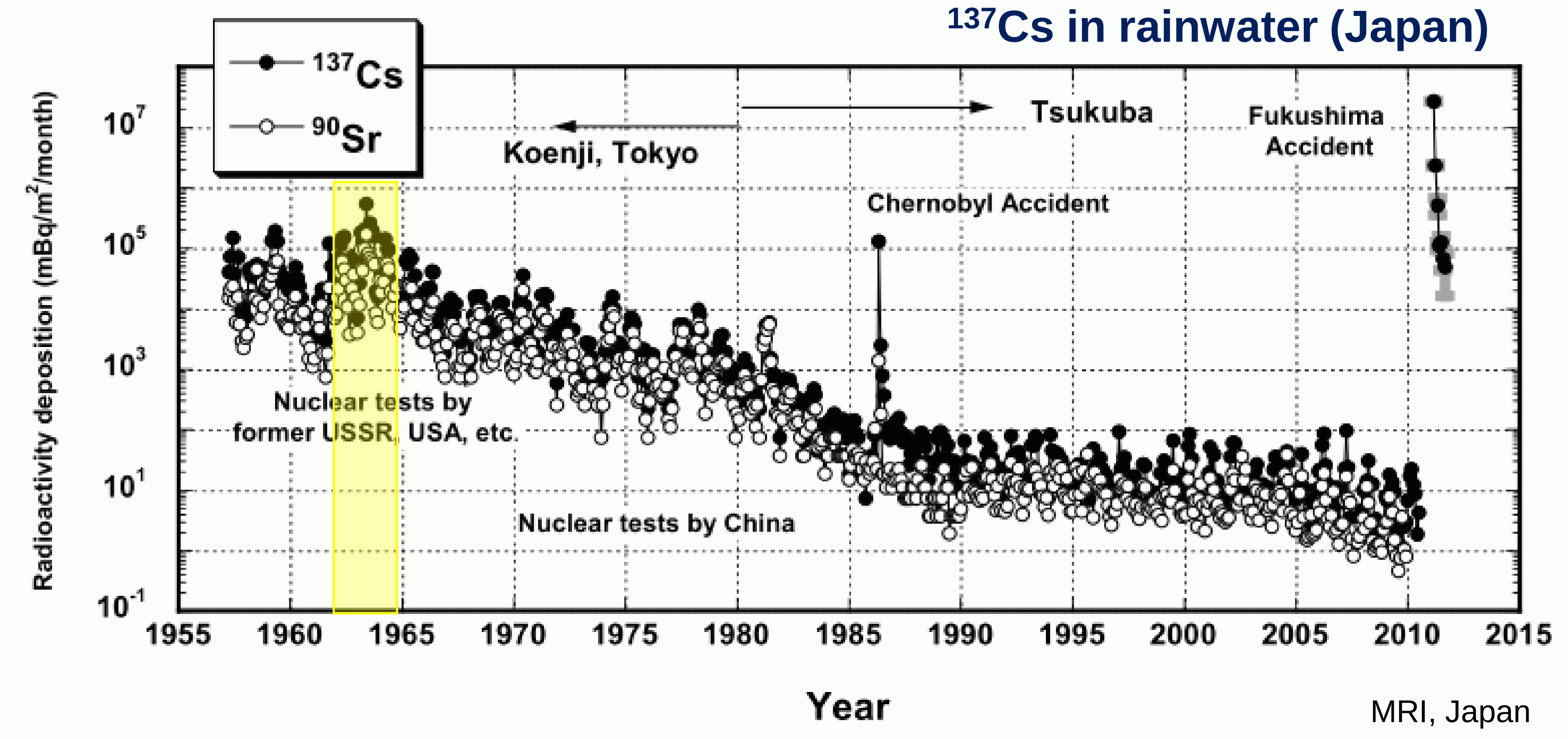
cf. Fukushima nearshore (April/2011): **180 Bq/kg**



MRI: http://www.mri-jma.go.jp/Dep/ge/ge_report/2011Artifi_Radio_report/Chapter2.html

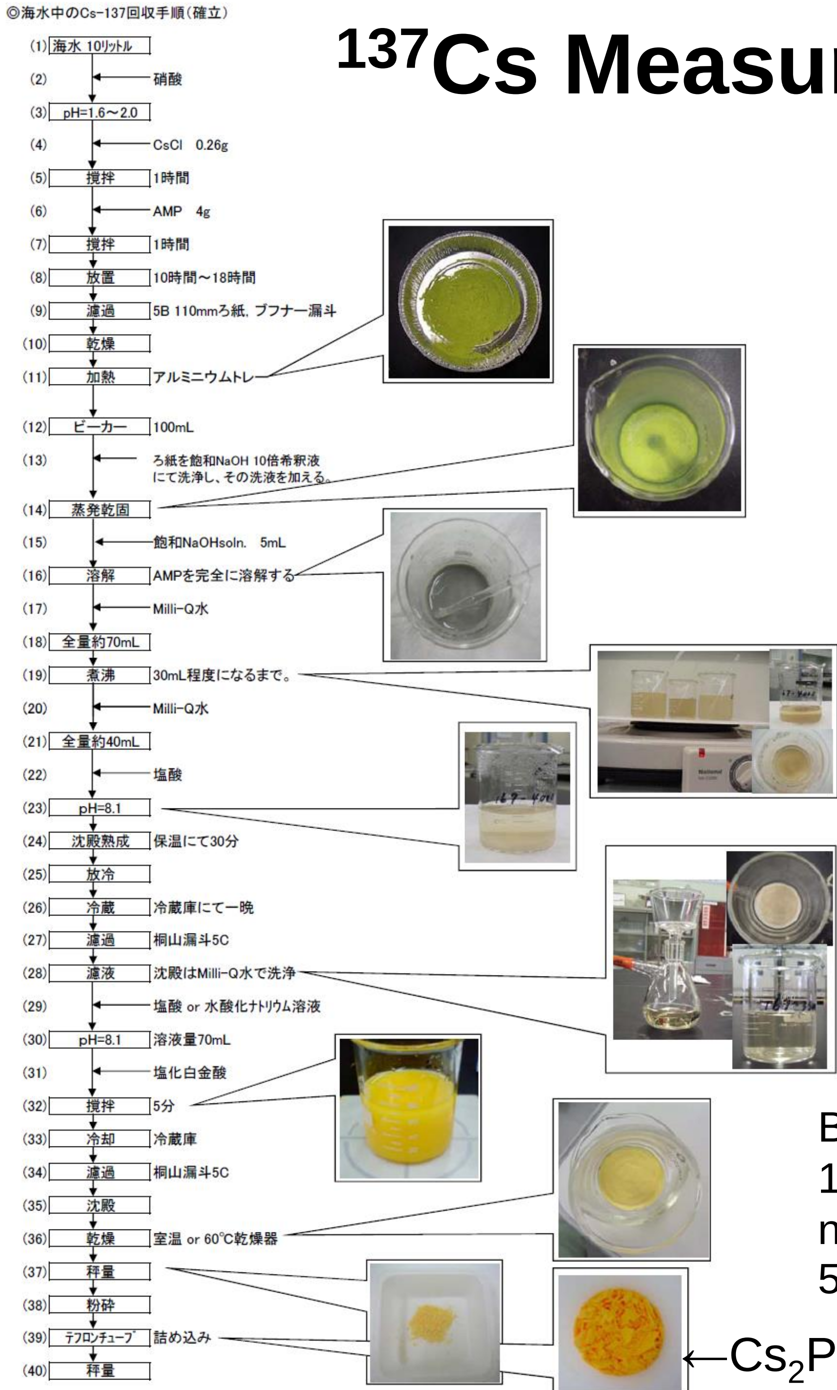
Global Fallout - Atmospheric Nuclear Testing

Global Fallout: Nuclear contamination of the entire Earth with anthropogenic radionuclides from atmospheric nuclear testing



MRI, Japan

^{137}Cs Measurements in Seawater



←Cs_2PtCl_6

Aoyama, Personal comn.

LLRL, Kanazawa Univ.
Ogoya underground laboratory

Background is less than 1/200 compared with normal detectors.
50-2000 keV 1.8 cpm

New Oceanic Circulation Tracers: U-236 & U-233

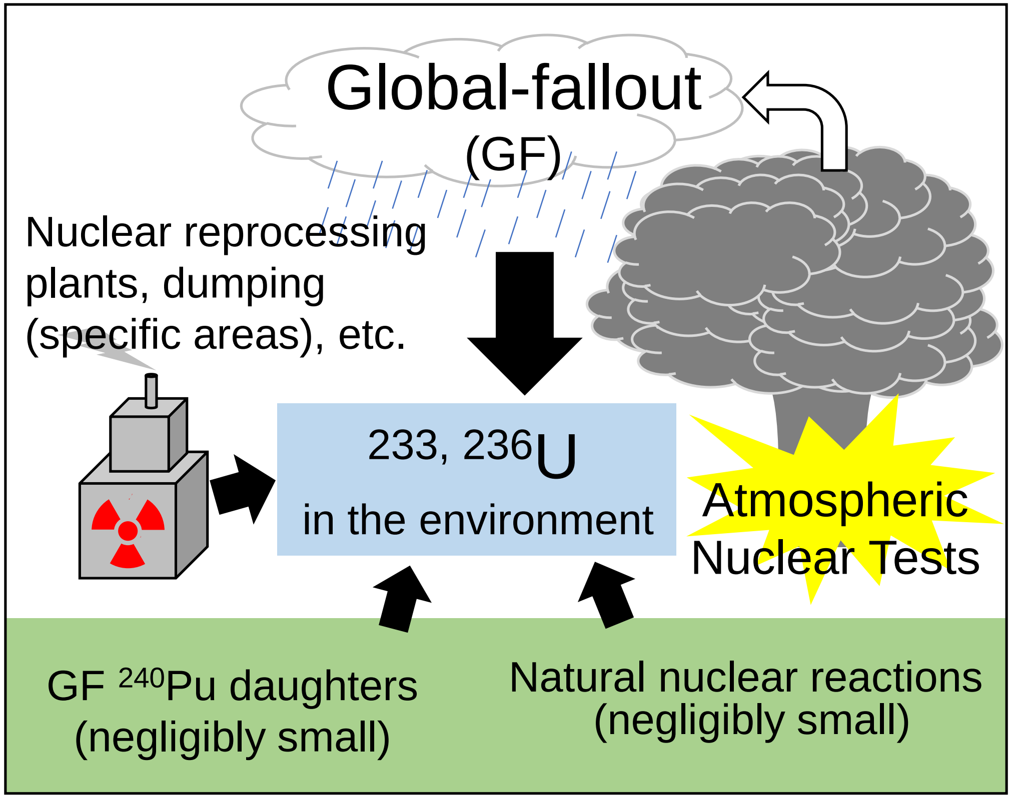
$^{233,236}U$ have long half-lives
(1.592×10^7 y, 2.37×10^7 y) cf. ^{137}Cs (30.2 y)

Uranium is a conservative (soluble) element in seawater
→ $^{233,236}U$ in seawater can be transported with water-mass
(Christl et al. 2012; Sakaguchi et al., 2012)

5-liter sample of seawater (sub-attograms of U) is enough for AMS measurements (Eigl et al. 2016; Hain et al., 2020)

Anthropogenic radionuclides
→ Clear origin and age of introduction to the earth's surface
(Sakaguchi et al., 2009; Winkler et al., 2012, Hain et al., 2020)

Simple concentration method
→ Available on-board ship
(Abe et al., in prep)



Production of ^{233}U and ^{236}U

$^{235}U(n, \gamma)^{236}U$ $^{238}U(n, 3n)^{236}U$

$^{235}U(n, 3n)^{233}U$

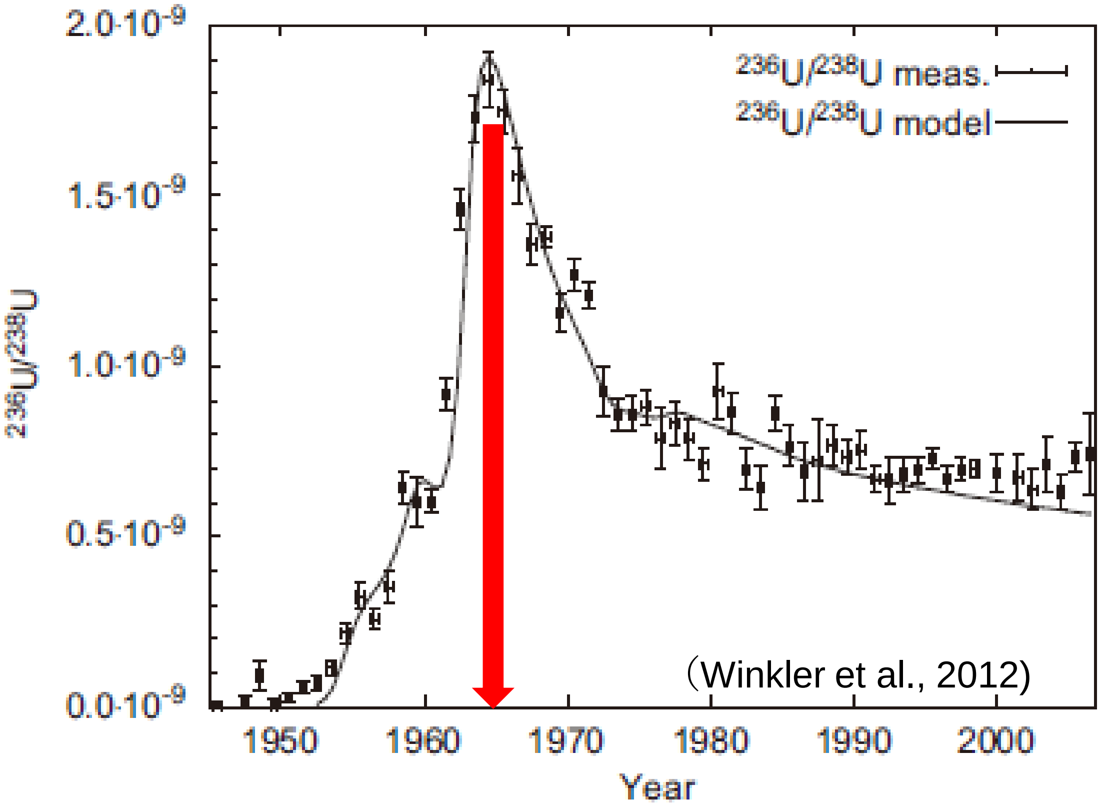
$^{232}Th(n, \gamma)^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U$

Reconstruction of ^{236}U Ocean Input

The $^{236}U/^{238}U$ ratio in surface seawater can be reconstructed using coral core samples

maximum deposition in 1964

(same variation as fission-produced Cs-137)

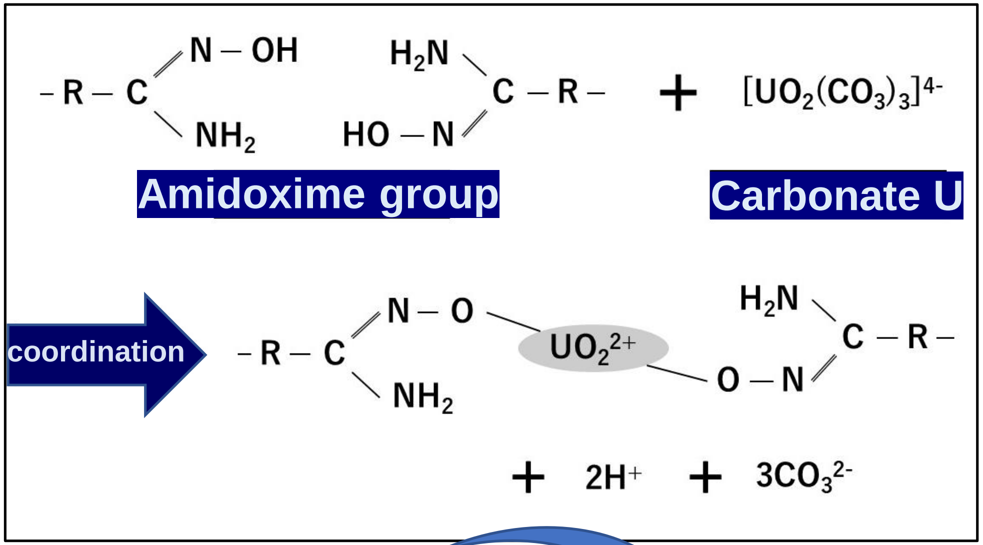


Reconstructed $^{236}U/^{238}U$ ratio in Caribbean surface seawater using a coral core

New Concentration Technique for U in Seawater

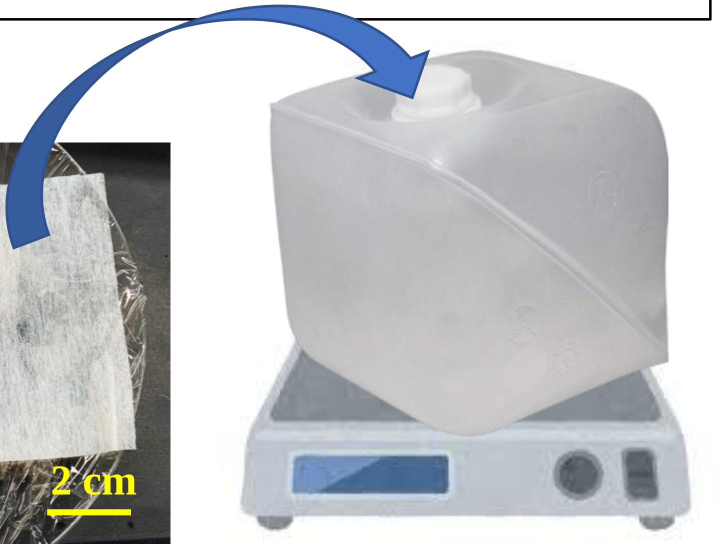
Amidoxime Adsorbents

- Produced by ‘tea-bag’
- radiation graft polymerization
- Concentrate U by a complexation with amidoxime group
- Easy to handle (fabric-like)



Electron beam irradiation

‘Teabag’ adsorbent!

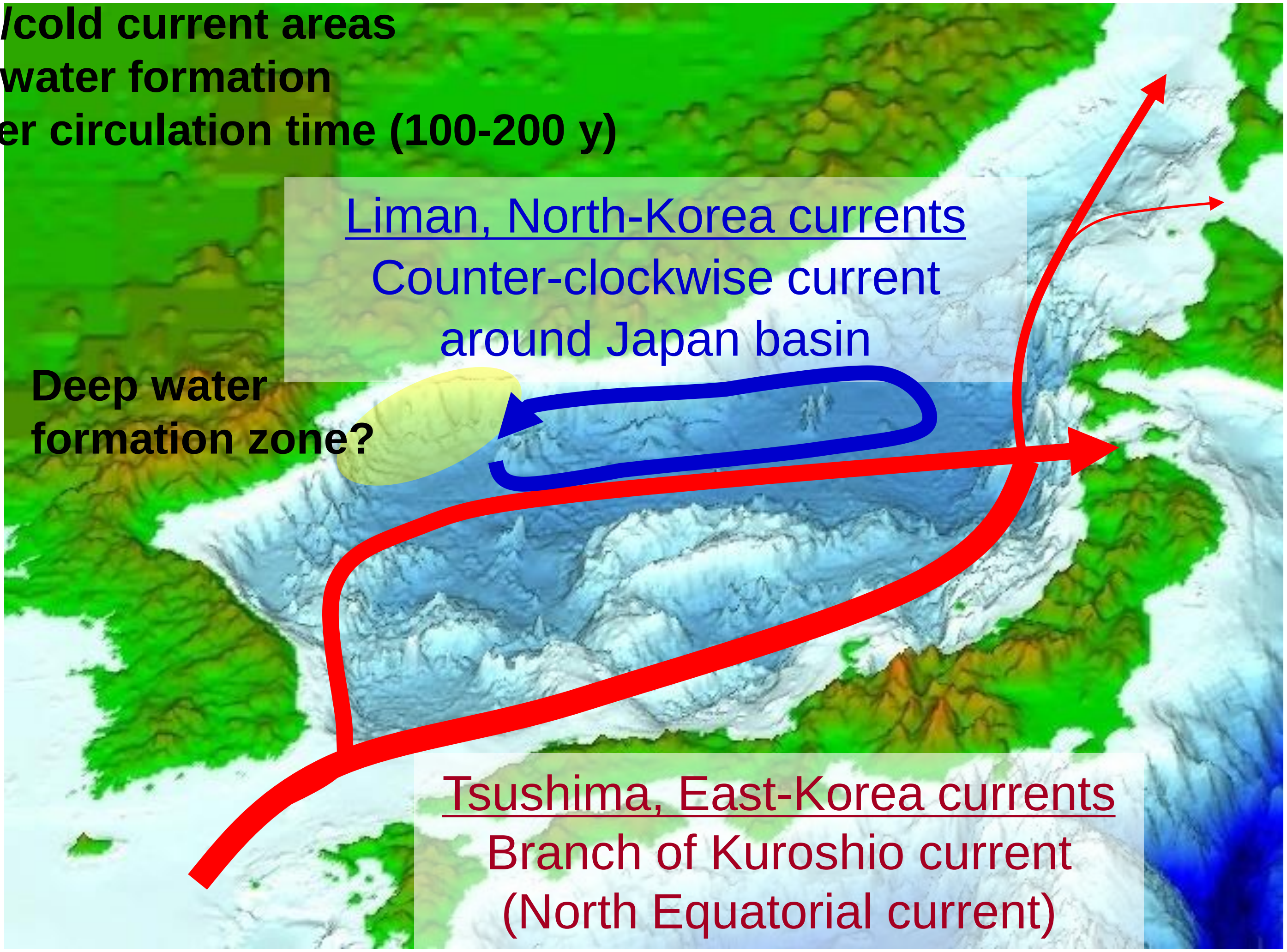


Concentrate U on-board ship

Seko et al., (2004); Tamada et al. (2007); Abe et al. in prep.

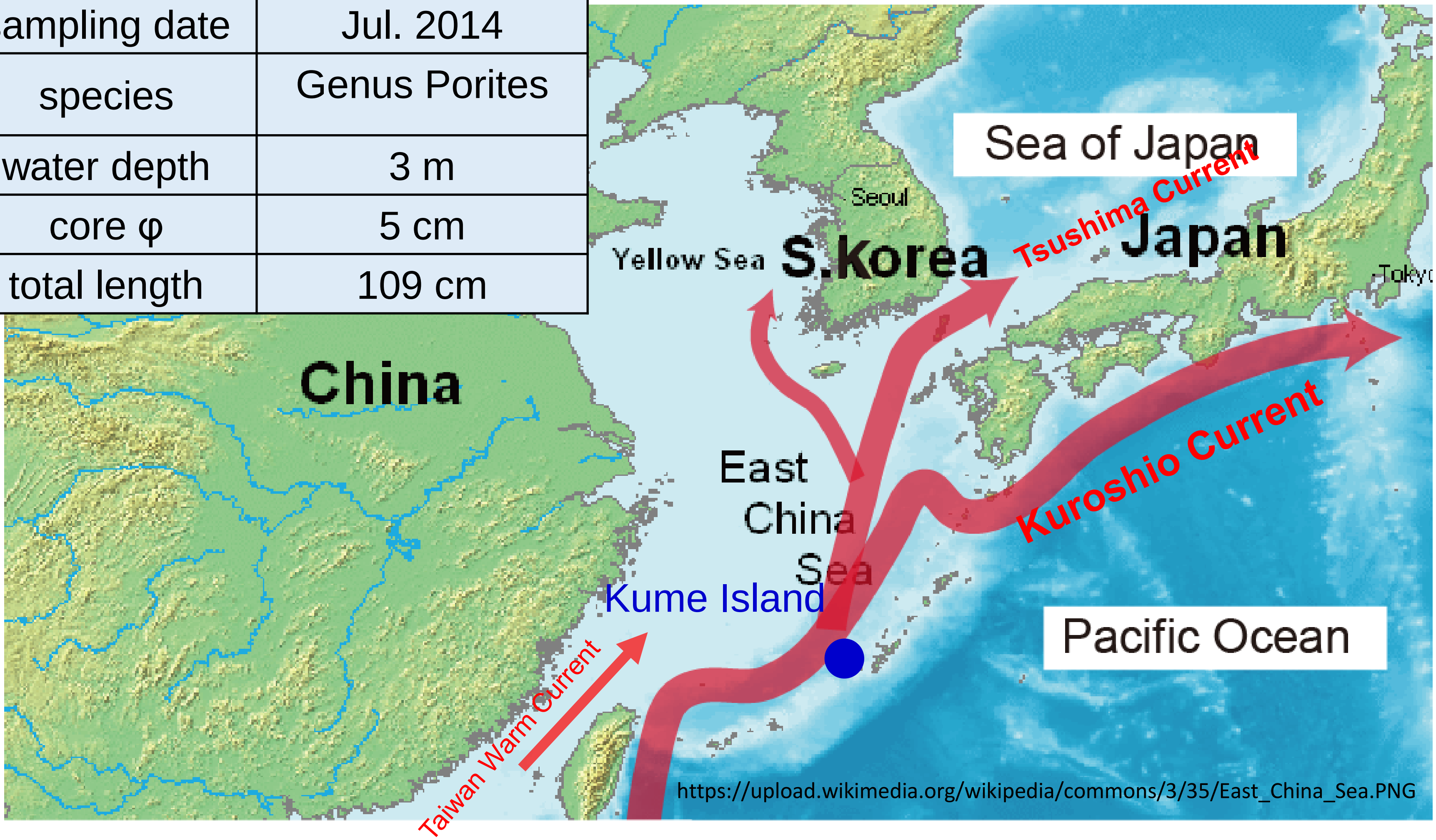
Surface Currents in the Japan sea

1. **Semi-closed system**
2. **Warm/cold current areas**
3. **Deep water formation**
4. **Shorter circulation time (100-200 y)**



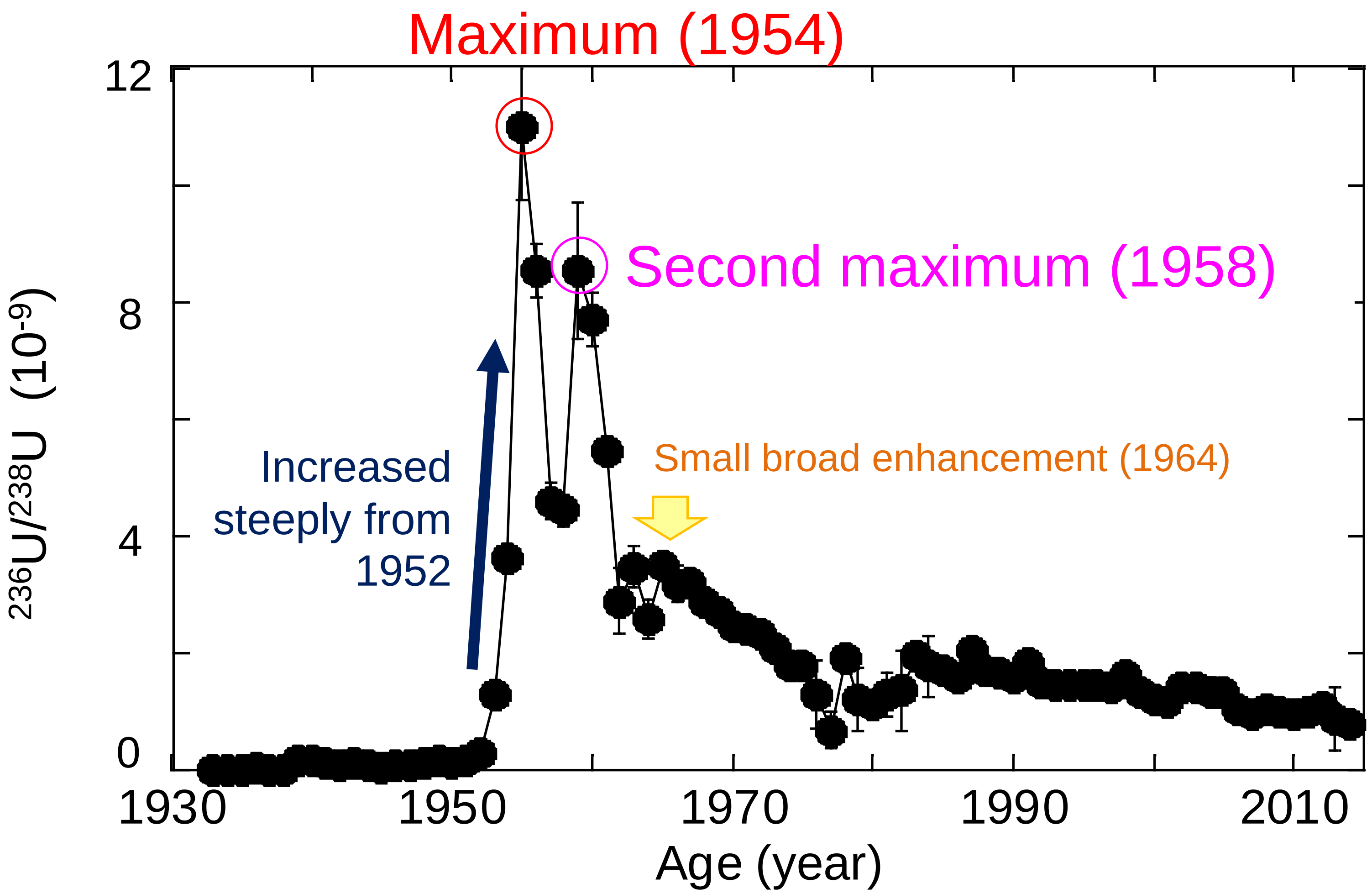
Coral Core Samples, Kume

sampling point	N 26º 19’7.5” E 126º 45’58.9”
sampling date	Jul. 2014
species	Genus Porites
water depth	3 m
core φ	5 cm
total length	109 cm



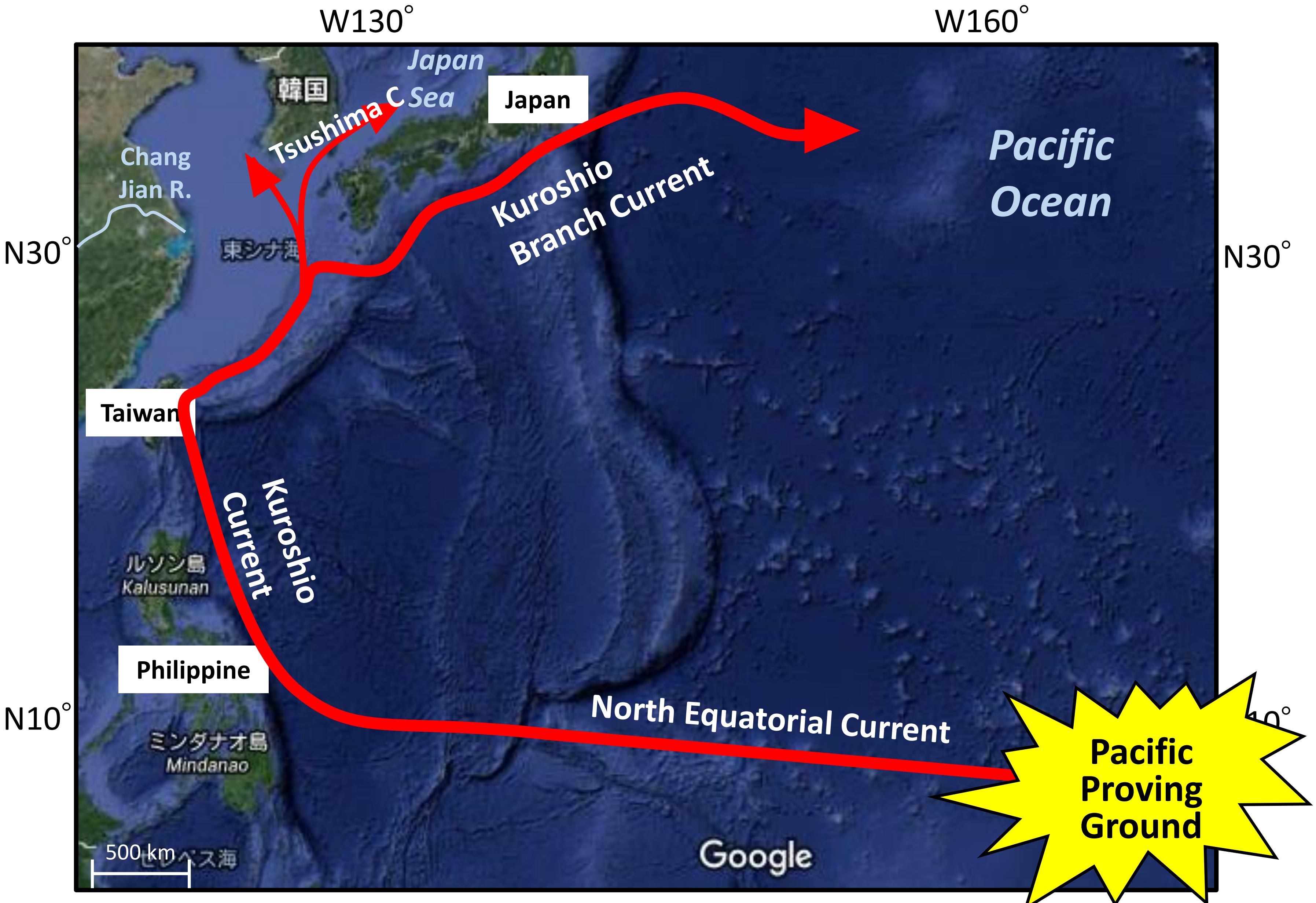
Results

$^{236}U/^{238}U$ in Surface Seawater, Kume



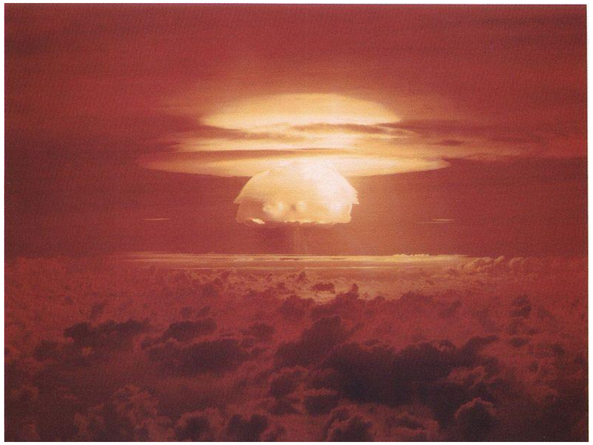
Nomura et al., 2016

^{236}U Input to the NWP from the PPG



Pacific Proving Ground Nuclear Testing

1952 - Operation Ivy



1954 - Operation Castle

1958 - Operation Hardtack

Year	Operation	Area	No. of Test	Yield (Mt)
1946	Crossroads	Bikini	2	0.05
1948	Sandstone	Eniwetok	3	0.1
1952	Ivy	Eniwetok	2	10.9
1954	Castle	Eniwetok, Bikini	6	48.2
1956	Redwing	Eniwetok	17	20.82
1958	Hardtack I	Eniwetok, Bikini	35	35.6

ANSCEAR (2000)

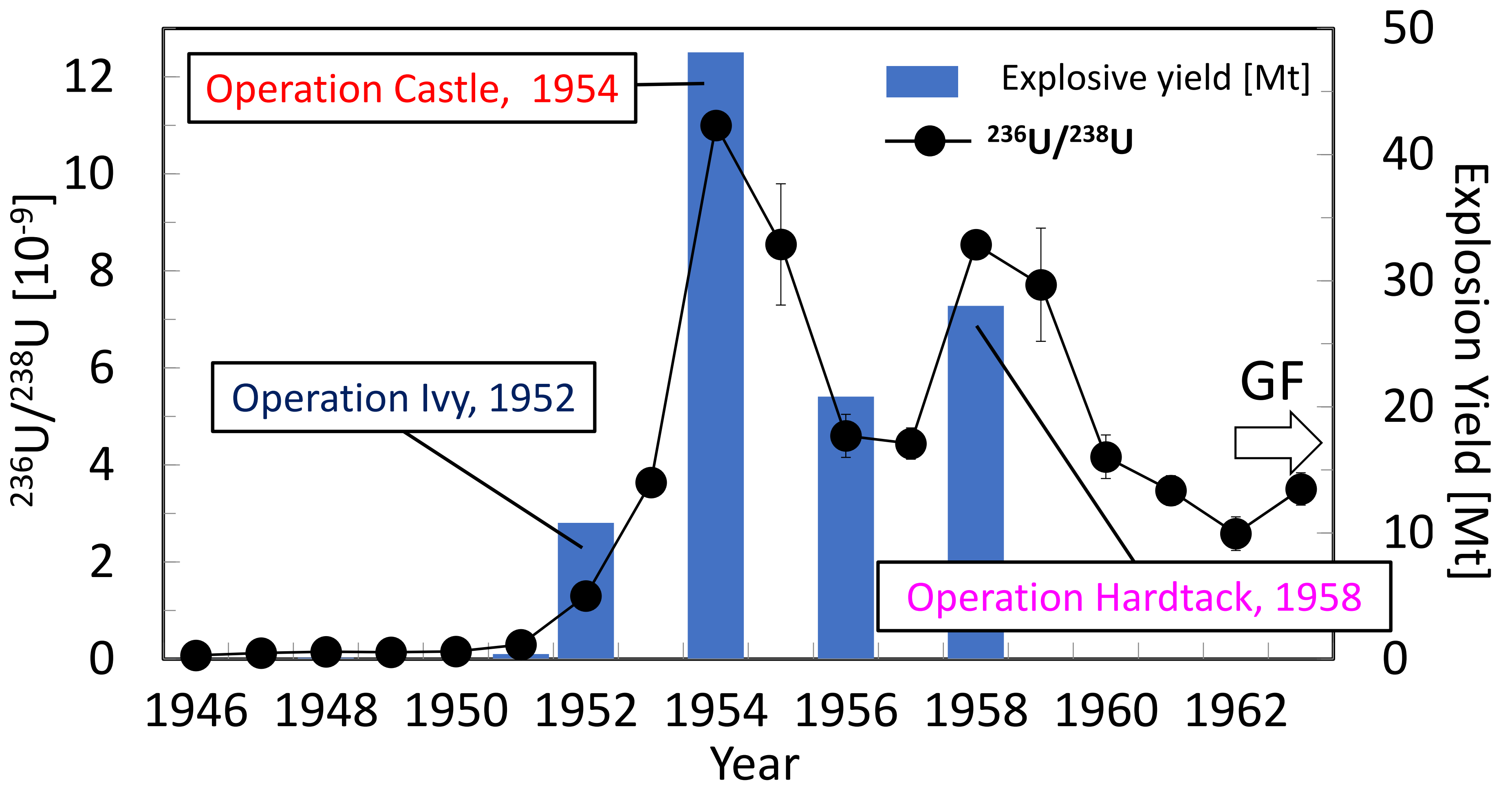
First hydrogen bomb test (1952)

Maximum explosion yield (1954)

Second largest explosion yield (1958)

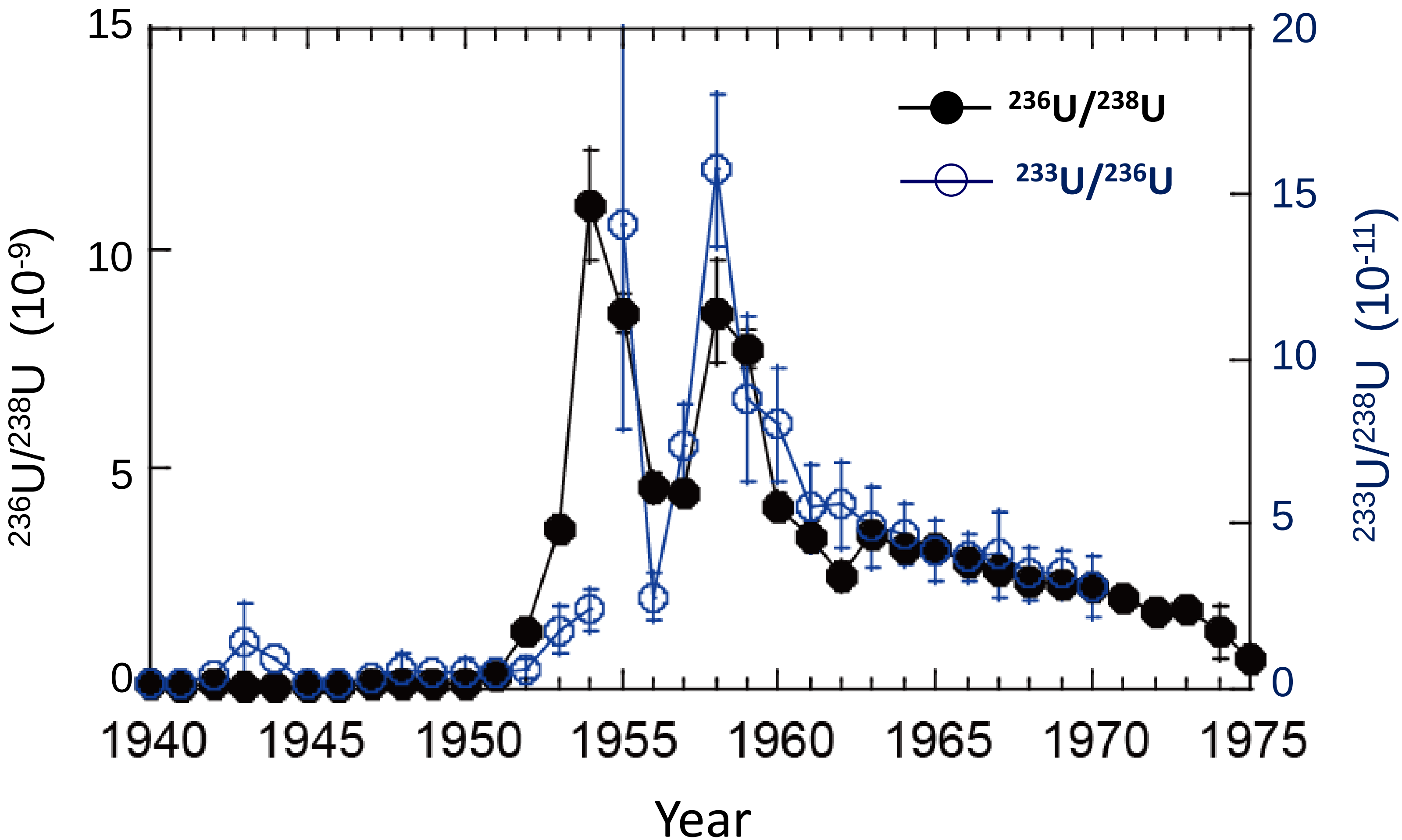
https://ja.wikipedia.org/wiki/%E3%82%A2%E3%82%A4%E3%83%93%E3%83%BC%E4%BD%9C%E6%88%A6#/media/%E3%83%95%E3%82%A1%E3%82%A4%E3%83%AB:IvyMike2.jpg
https://ja.wikipedia.org/wiki/%E3%82%AD%E3%83%A3%E3%83%83%E3%82%B9%E3%83%AB%E4%BD%9C%E6%88%A6#/media/%E3%83%95%E3%82%A1%E3%82%A4%E3%83%AB:Castle_Romeo.jpg
https://ja.wikipedia.org/wiki/%E3%83%8F%E3%83%BC%E3%83%89%E3%82%BF%E3%83%83%E3%82%AF%E4%BD%9C%E6%88%A6#/media/%E3%83%95%E3%82%A1%E3%82%A4%E3%83%AB:HardtackOak.JPG

$^{236}U/^{238}U$ in Surface Seawater, Kume



$^{236}U/^{238}U$ variation coincides well with explosion yield observed at PPG

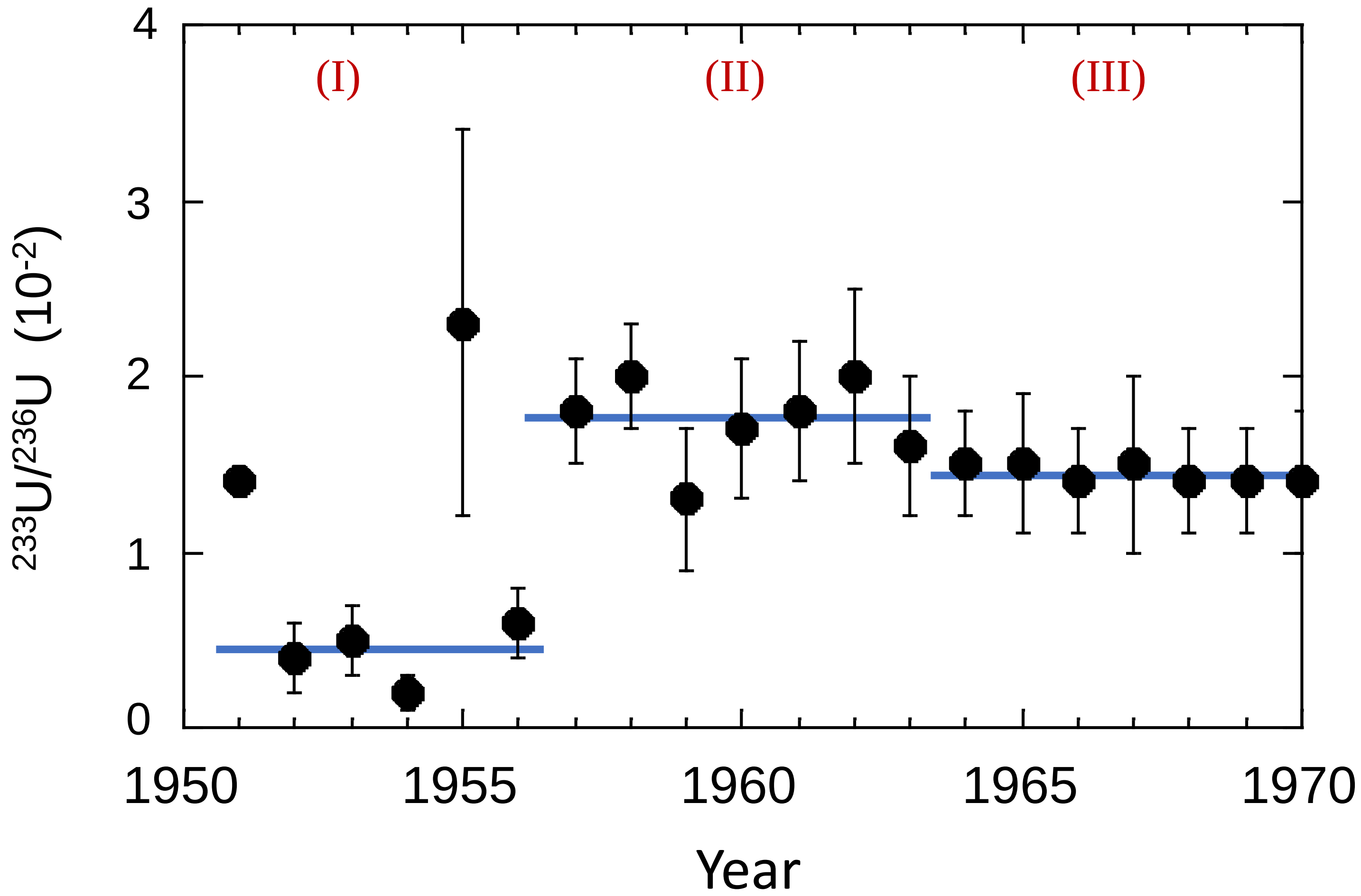
$^{233}U/^{238}U$ in Surface Seawater, Kume



$^{233}U/^{238}U$ ratios are 2 orders of magnitude smaller than those of $^{236}U/^{238}U$. However, the basic variations are the same for these ratios.

Nomura et al., 2016; Hain et al., 2020

$^{233}U/^{236}U$ in Surface Seawater, Kume



(I) Lower average ratio $(0.31 \pm 0.07) \times 10^{-2}$ compared with the other periods

Hain et al., 2020

Diffusion Simulation (FVM)

Finite Volume Method (FVM)

① simple system ② physical parameters can be retained

Reconstructed ^{236}U concentration from Kume island was used as input parameter for the very top layer

^{236}U concentration in each layer at each time

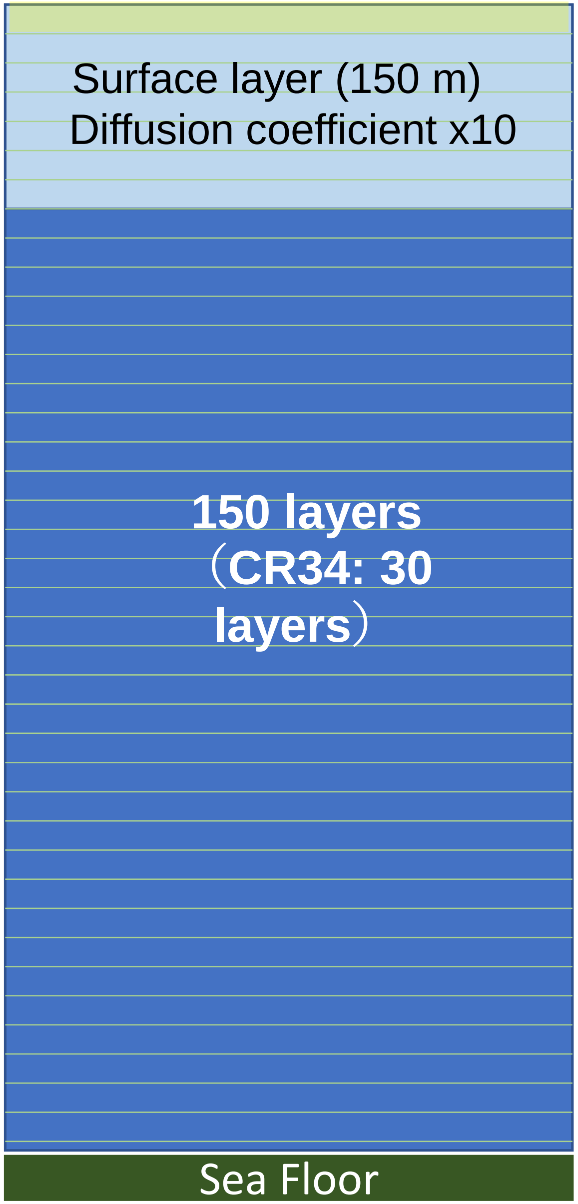
$$C_j(t+\delta t) = C_j(t) + dt\,[\{k_{j+1/2}(\,C_{j+1}(t) - C_j(t)\,) - k_{j-1/2}(\,C_j(t) - C_{j-1}(t))\}/dz^2 - \lambda C_j(t)]$$

$C_j(t)$: ^{236}U (atoms/kg) in the j-th FV (j=1–150) at time t

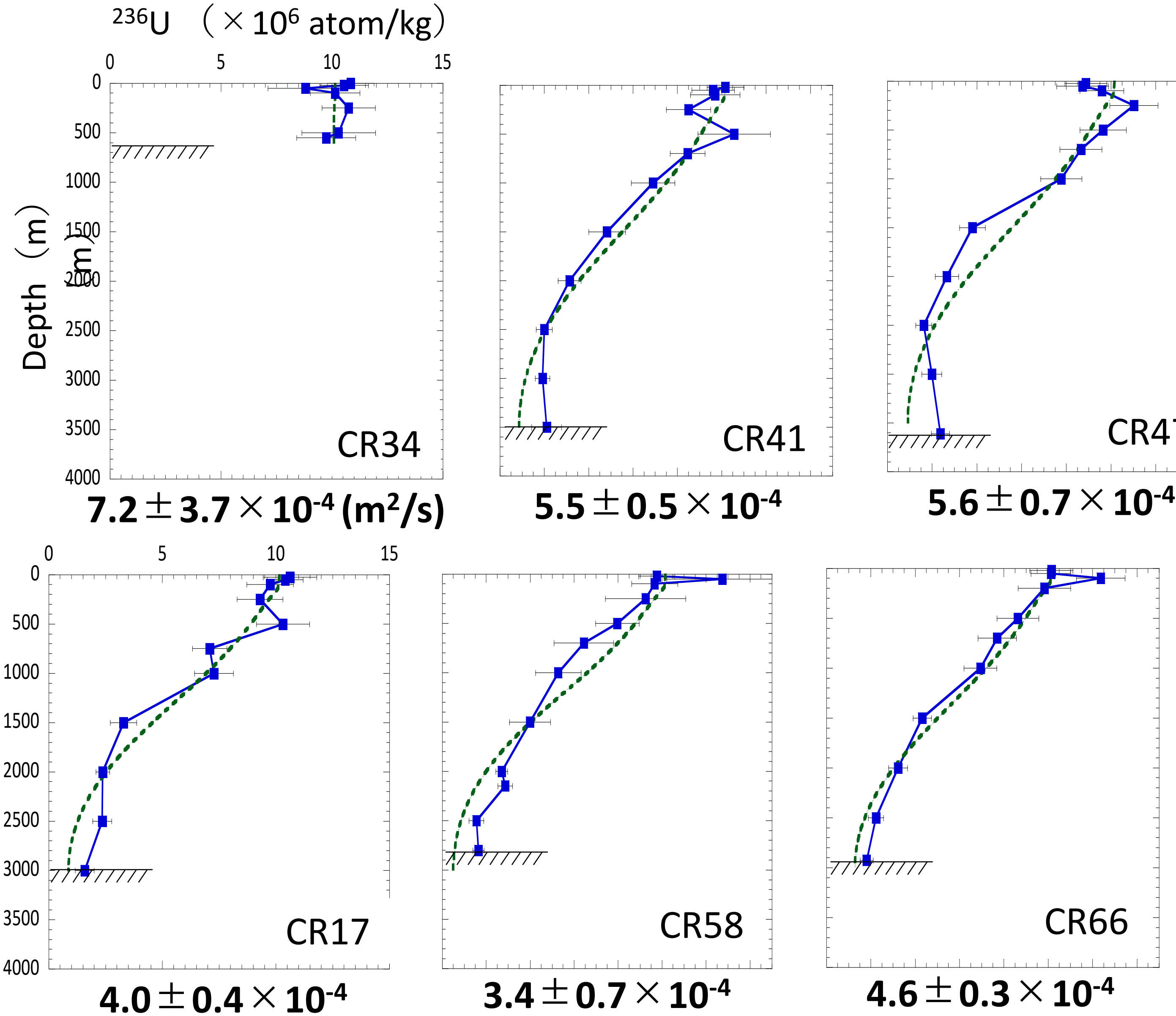
δt : time-step interval (s) [1/75 year, 16000 steps]

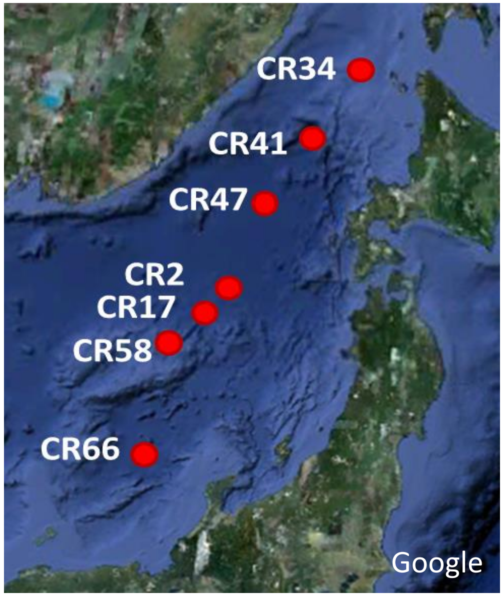
$K_{j+1/2}$: vertical diffusion coefficient (cm^2/s) for turbulent flow between the j- and (j+1)-th FVs（m^2/s）

λ : decay constant of ^{236}U（1/s）



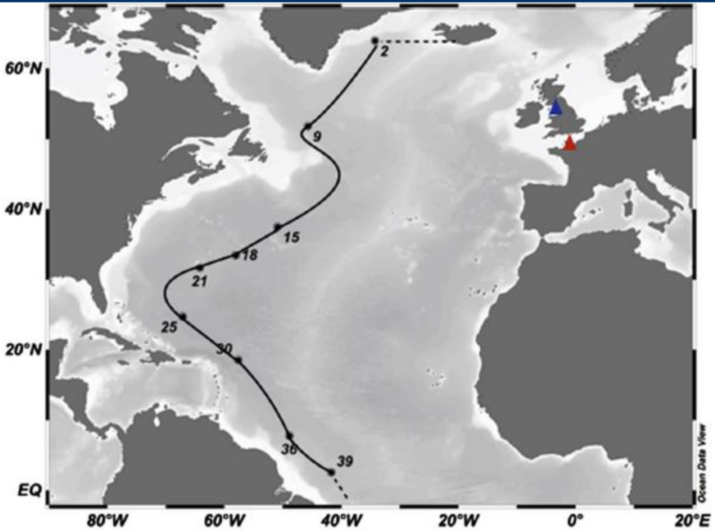
^{236}U Diffusion Simulation



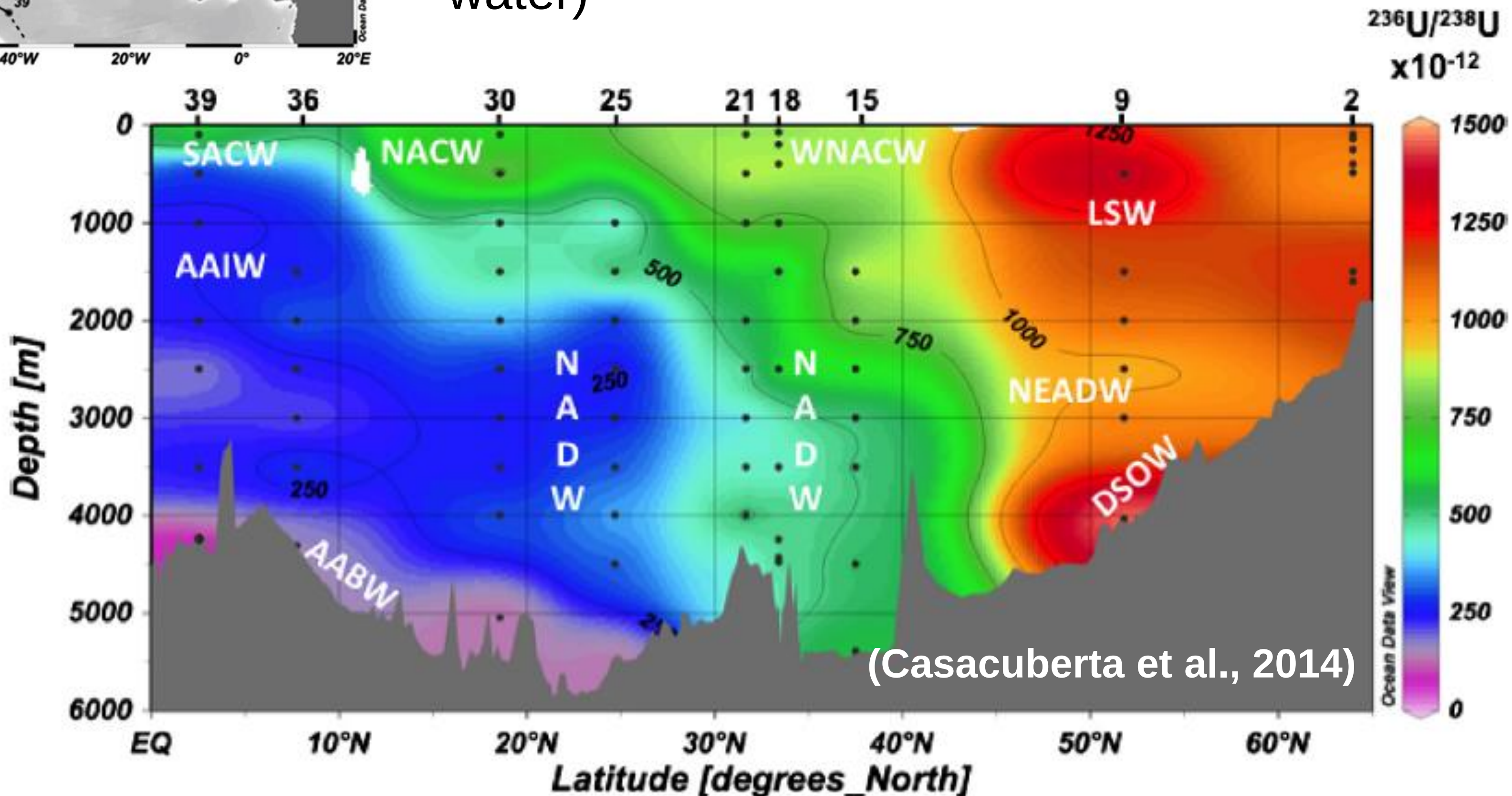


^{236}U concentration : ——— Fitting line : - - - - Sea Floor : ////////

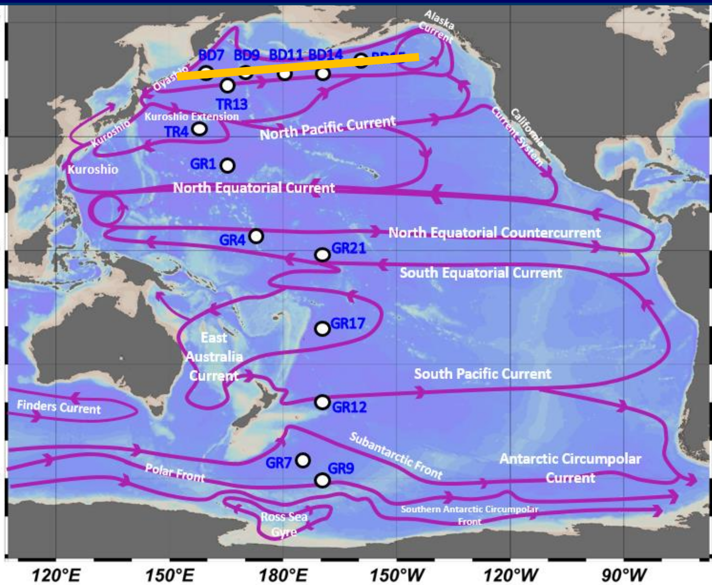
^{236}U in the North Atlantic Ocean



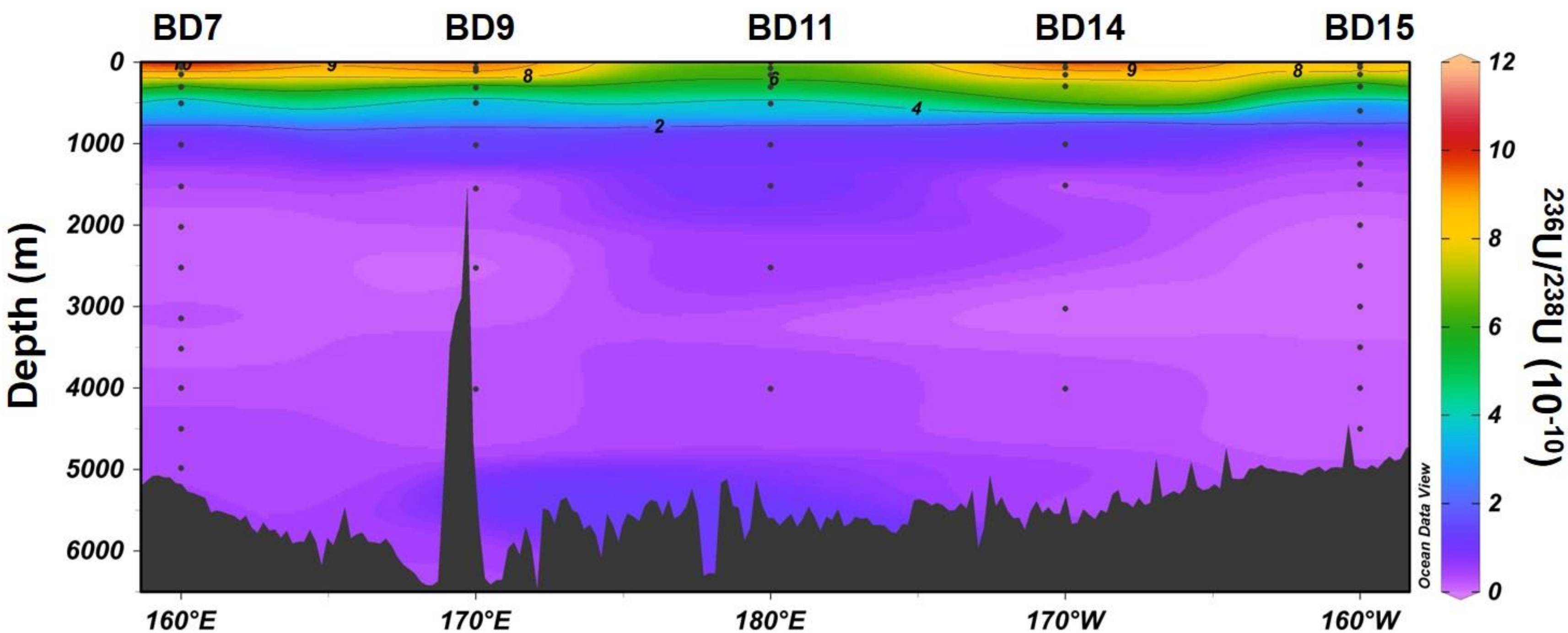
- High inventories due to influence from **nuclear reprocessing plants** in Sellafield (UK) and La Hague (France)
- High $^{236}U/^{238}U$ ratios at the bottom of northern stations (**subduction** of surface water)



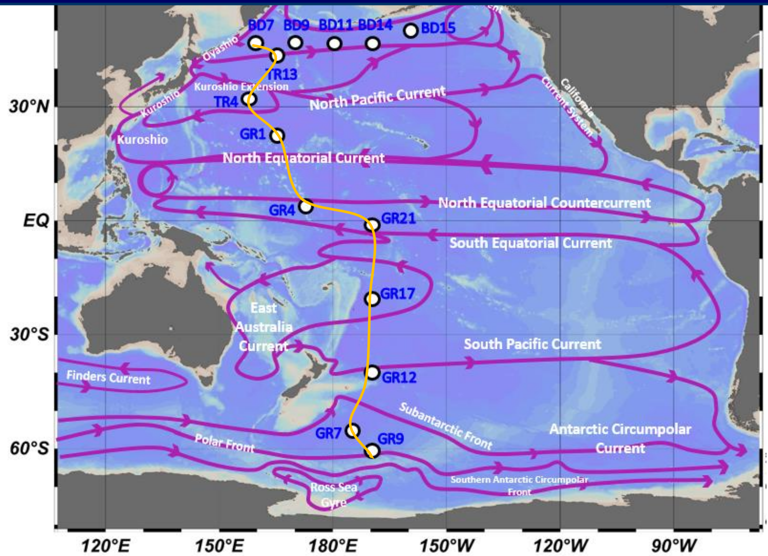
^{236}U in the North Pacific Ocean



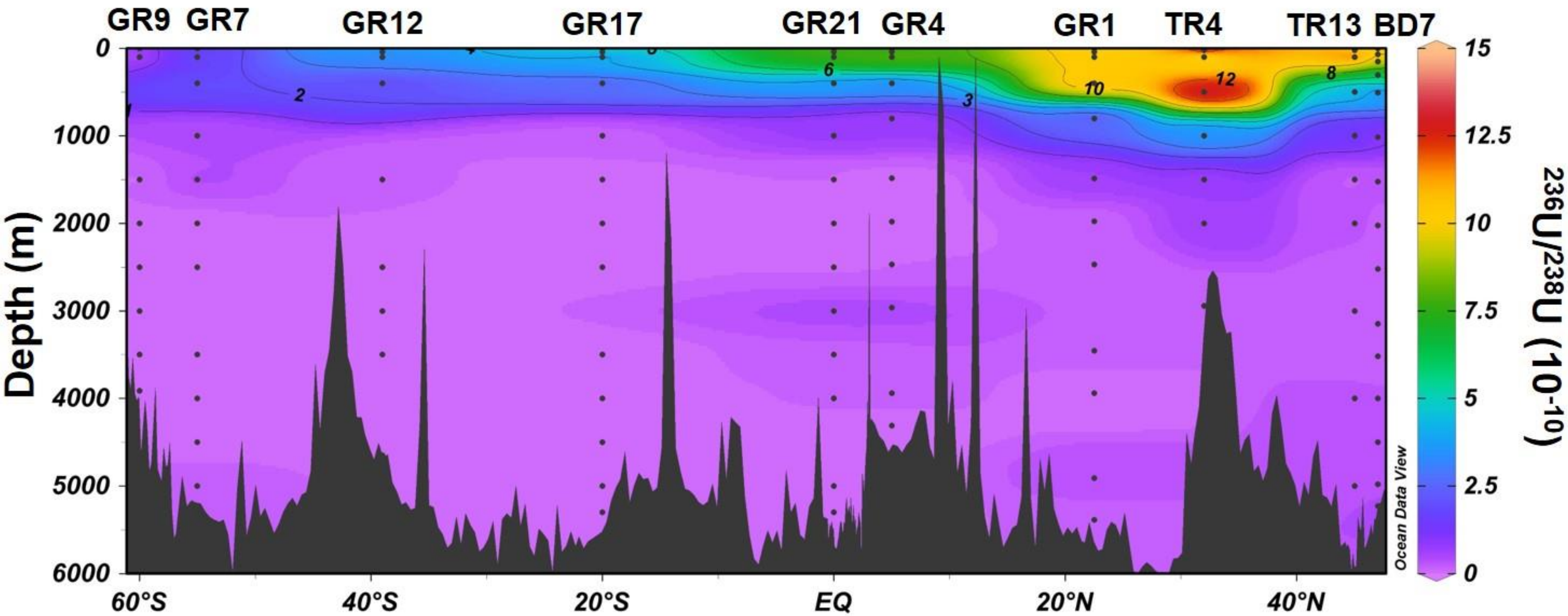
- High ^{236}U in the surface layer due to **global-fallout**
- Lower ^{236}U inventory than Atlantic
- ^{236}U is retained at the surface
- Quite **uniform distribution patterns** among sampling points



^{236}U in the West Pacific Ocean



- High ^{236}U in the **sub-surface layer** of the mid-North Pacific
- One order of ^{236}U concentration difference between north and south Pacific→**Very low ^{236}U inventory in the southern South Pacific**



Summary 1

- **Very low concentrations of $^{233,236}U$** have been successfully measured using small volume marine samples
- Variations in $^{236}U/^{238}U$ and $^{233}U/^{238}U$ atomic ratios and their concentrations in Northwest Pacific surface water were reconstructed
- Japan Sea water column **^{236}U depth profiles could be simulated using constructed values for ^{236}U** in the surface seawater.
- Combining U isotopes with other nuclides, such as ^{237}Np and ^{135}Cs, has **further potential to clarify the origin of water masses**

Further detailed observations are necessary.

Challenging Themes with AMS-^{237}Np

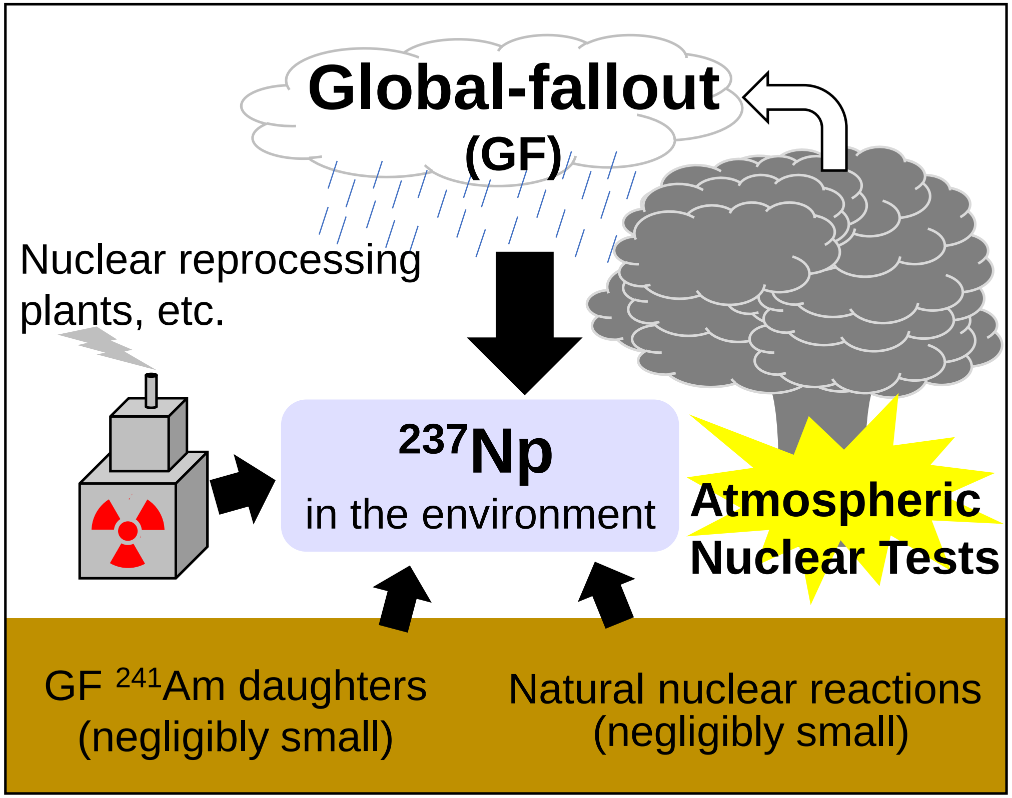
^{237}Np has a long half-life
(2.144×10^6 y)

Seawater samples of a few liters (attograms of ^{237}Np) are enough for AMS measurements
cf. 1800 L for α spectrometry (Holm et al., 1987)

Np is a conservative (soluble) element in seawater (Runde&Goff, 2005) → ^{237}Np in seawater can be transported with water-masses

Anthropogenic radionuclides
→Reconstructable origin and age of introduction to the earth's surface

$^{238}U(n,2n)^{237}U \rightarrow ^{237}Np$

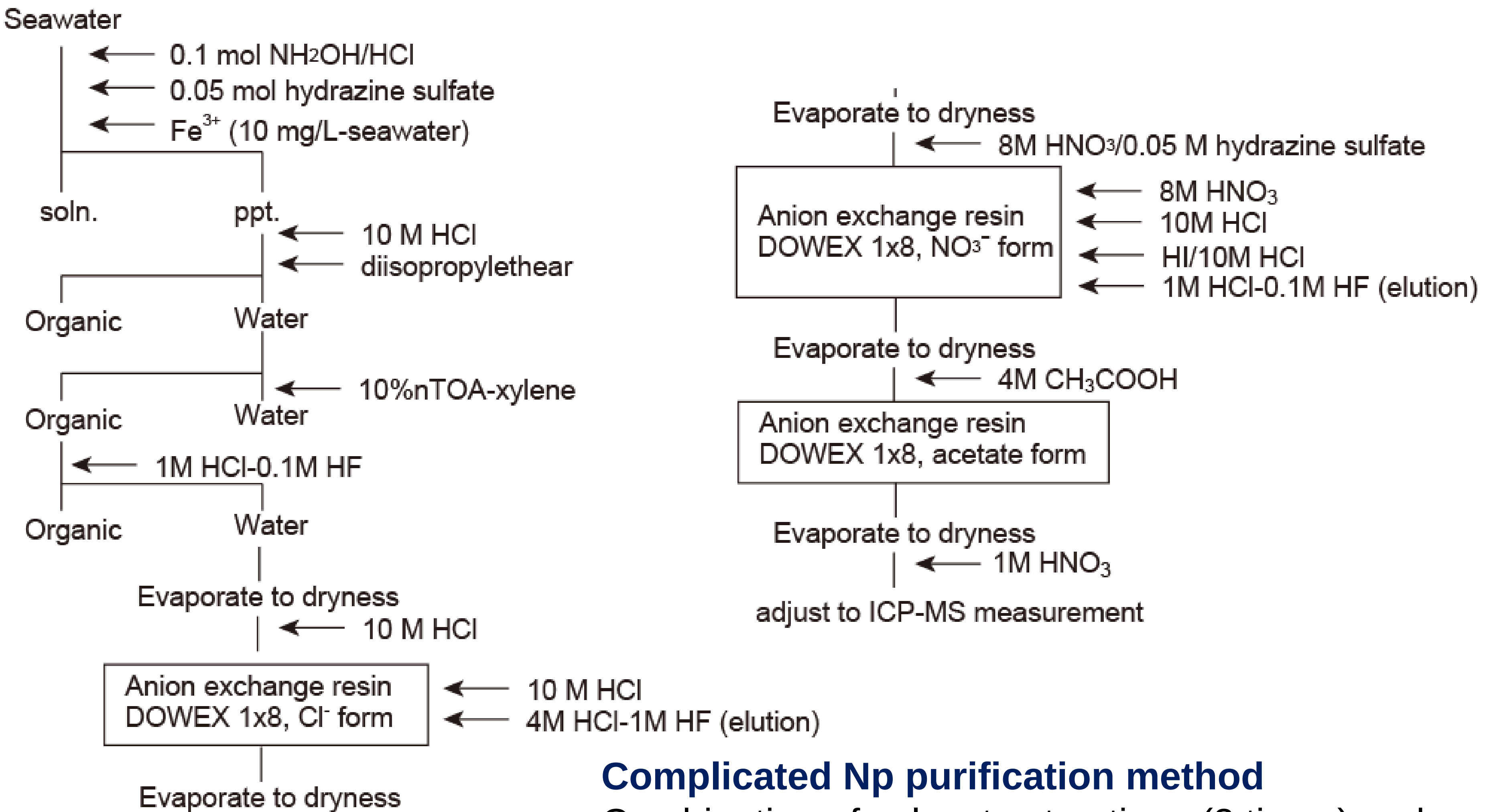


Important nuclides from the aspects of radiation protection and environmental research.

HOWEVER…there are very few comprehensive studies and little data on Np concentrations and distributions in the environment.

Np Chemical Separation Problems

Conventional (classic) method

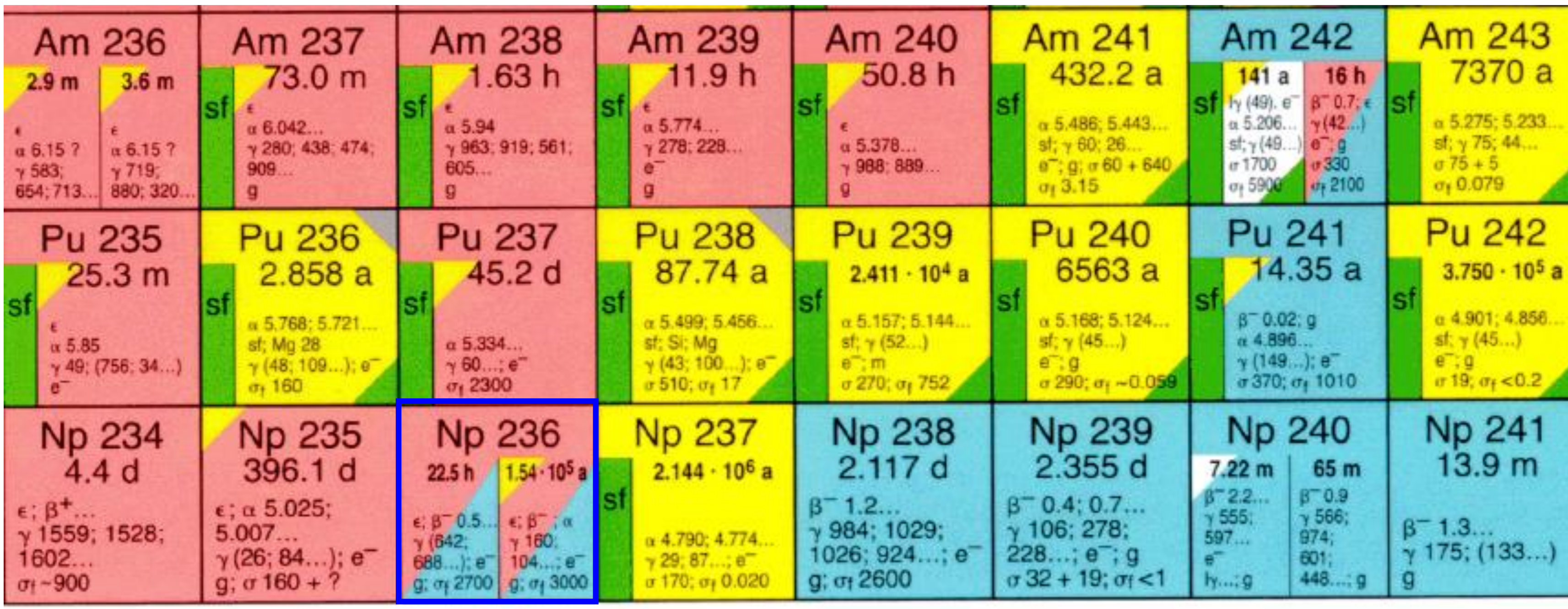


Complicated Np purification method

Combination of solvent extractions (2 times) and anion exchange resins (3 times)

Np AMS Measurement Problems

Appropriate yield tracer?



^{236}Np ($T_{1/2}$=1.54x10^5 y) able to be a good spike for ^{237}Np measurements

^{236}Np spike does not exist

Production of a Np Spike for AMS

Ideal nuclear reaction

^{232}Th (^{7}Li, 3n) **^{236g}Np**

High energy Li beam

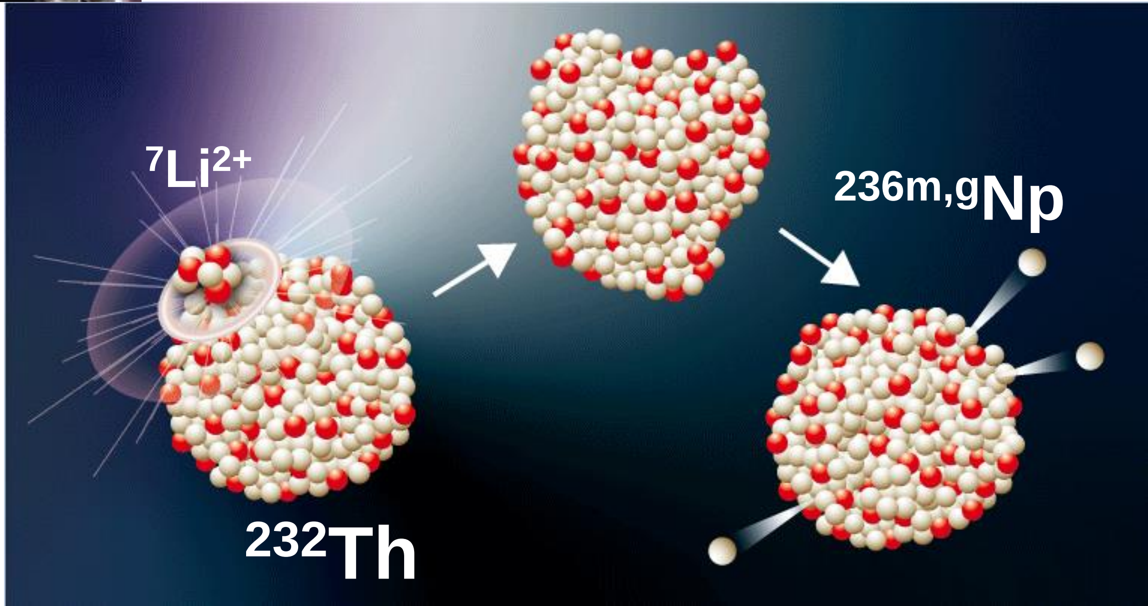
Long half-life Np

RIKEN
AVF Cyclotron

Interference side reactions

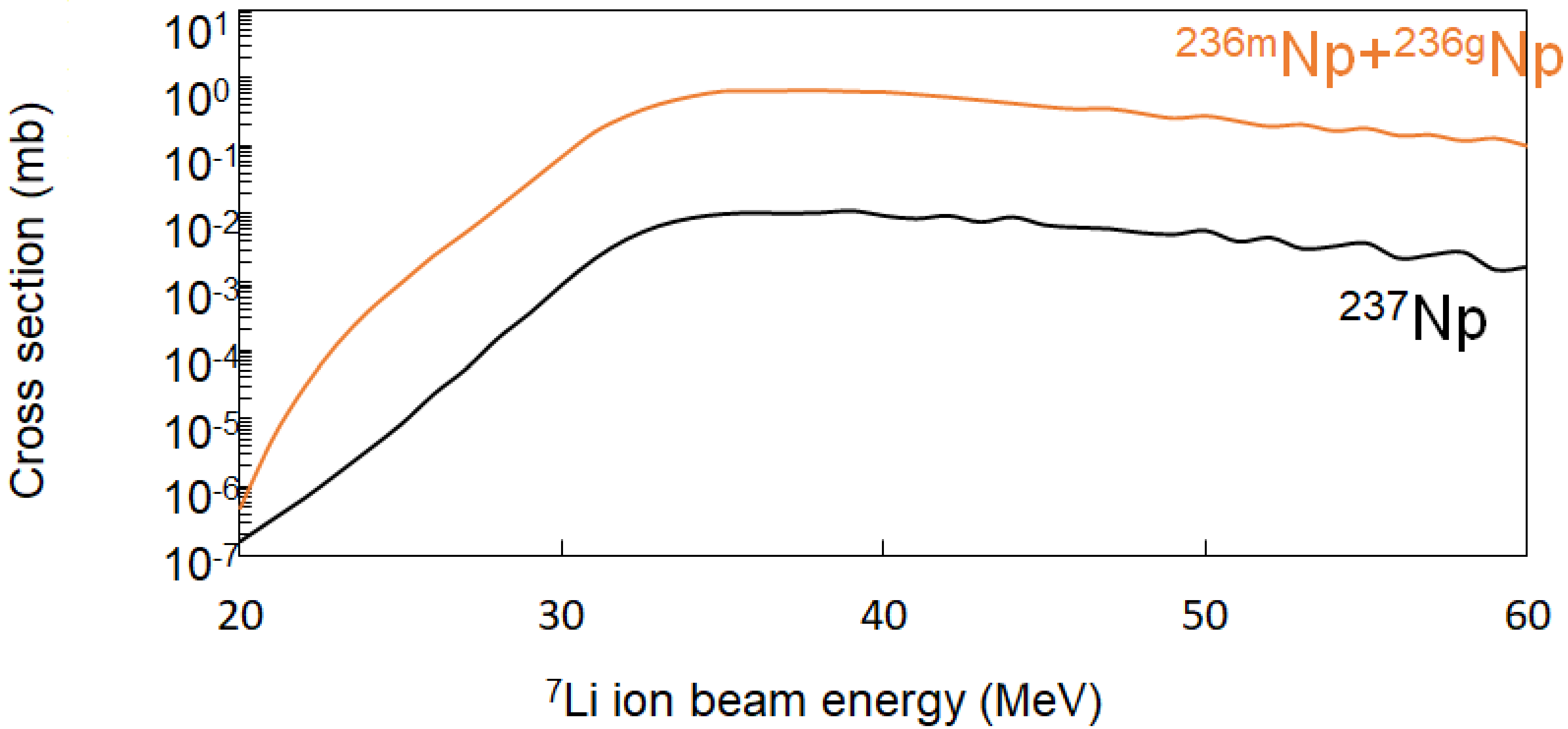
^{232}Th (^{7}Li, 3n) **^{236m}Np**

^{232}Th (^{7}Li, 2n) **^{237}Np**



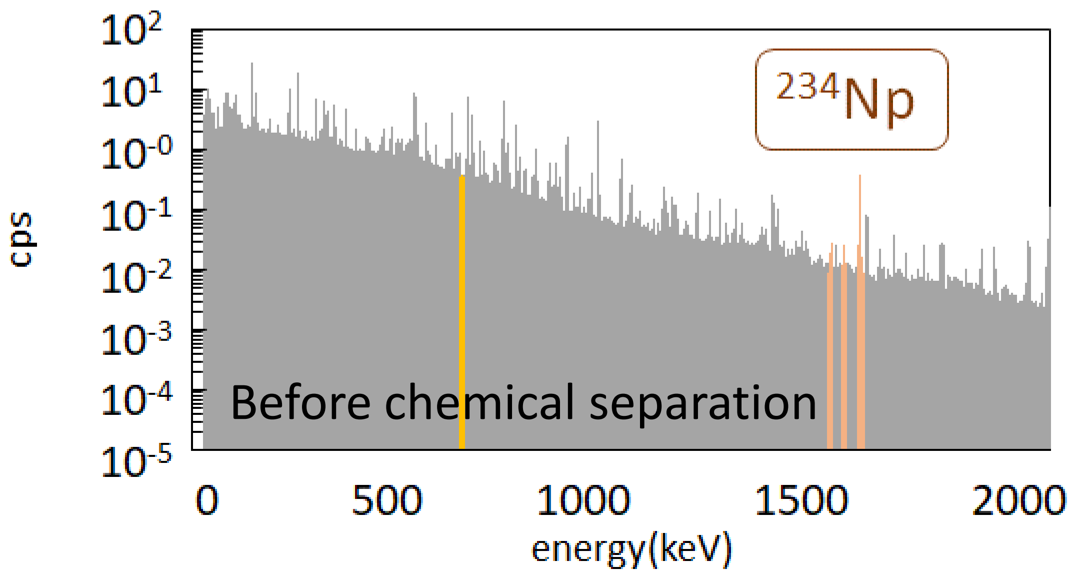
Production of a Np Spike for AMS

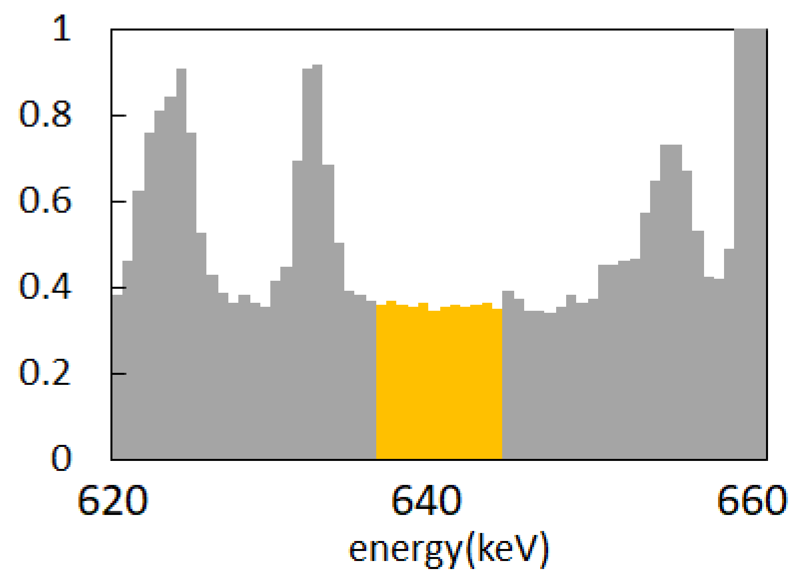
Simulation of Excitation Function by EMPIRE2



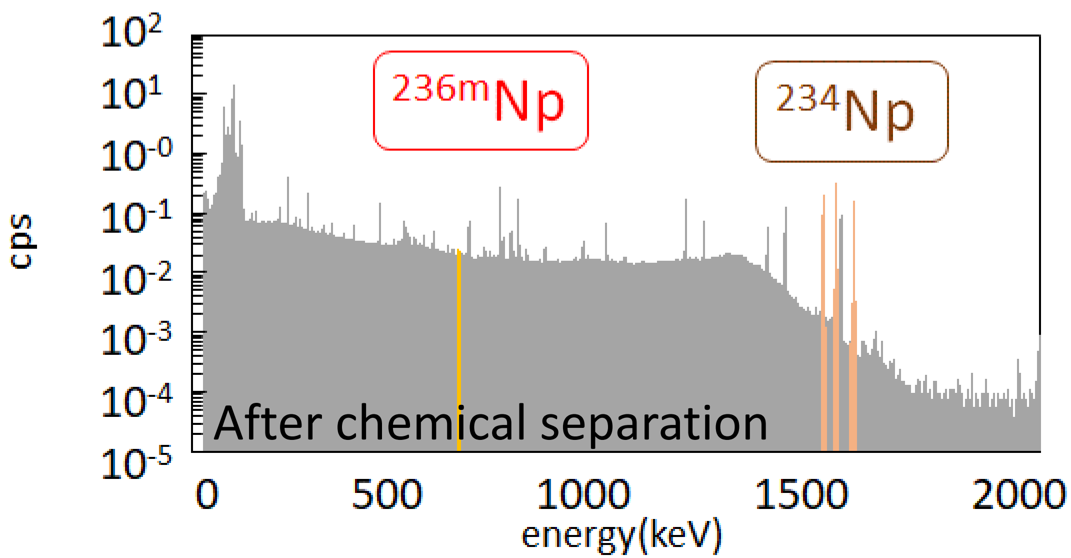
- Production ratio among nuclides are different through the bombing energy
- Larger ^{236g}Np and less ^{236m,237}Np
- No excitation functions exist for these reactions

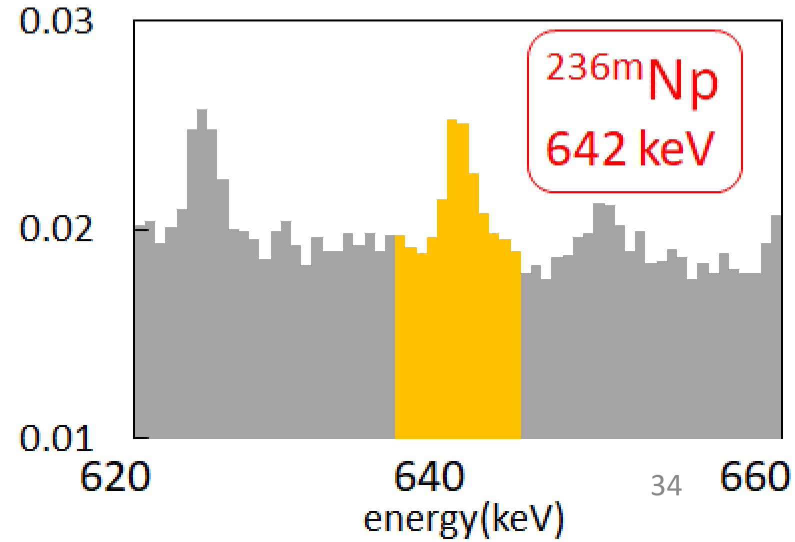
Preliminarily Results





We were able to confirm the production ^{236m}Np!





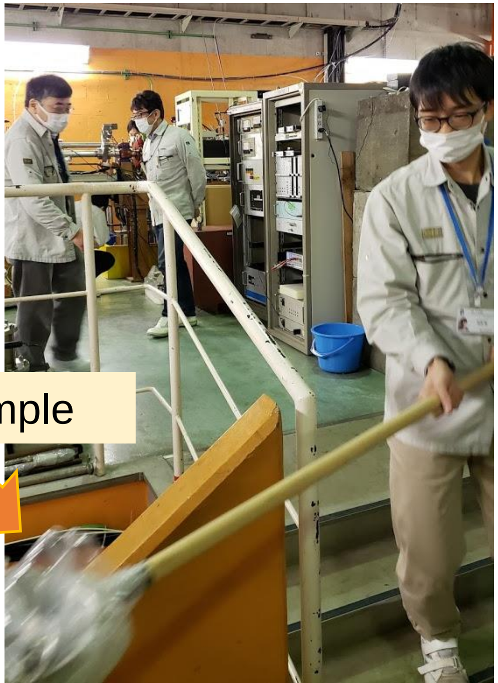
To Be Continued!

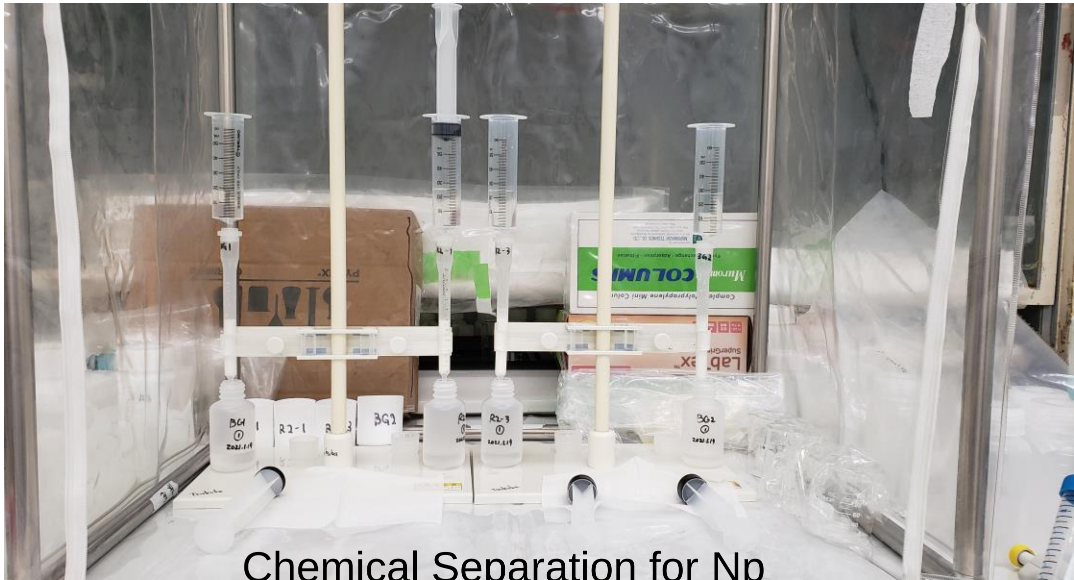
Th stack target preparation

We plan to distribute the Np spike for use in mass spectrometry (can also be used for ICP-MS)

Look forward to it!

Irradiated sample





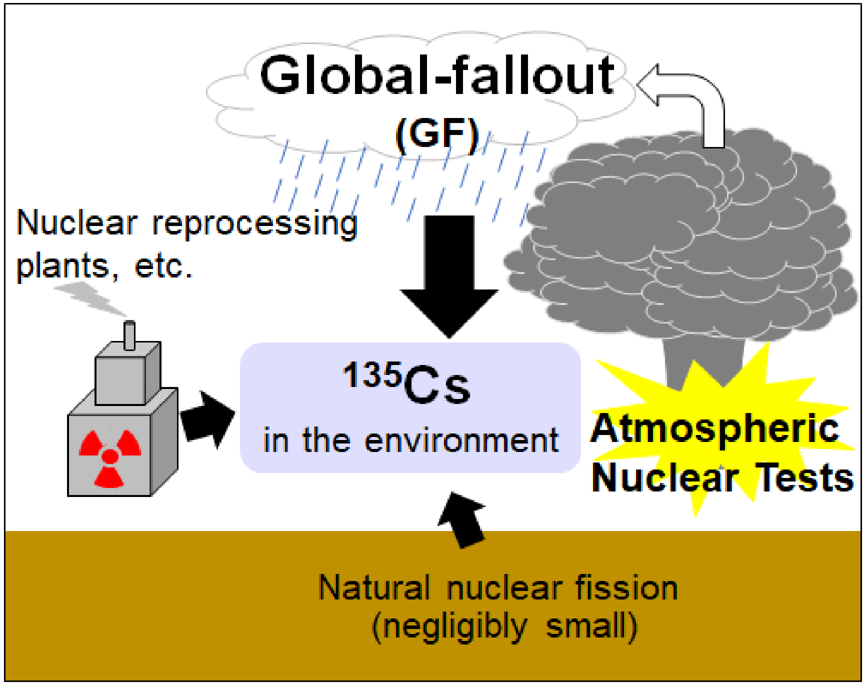
Chemical Separation for Np

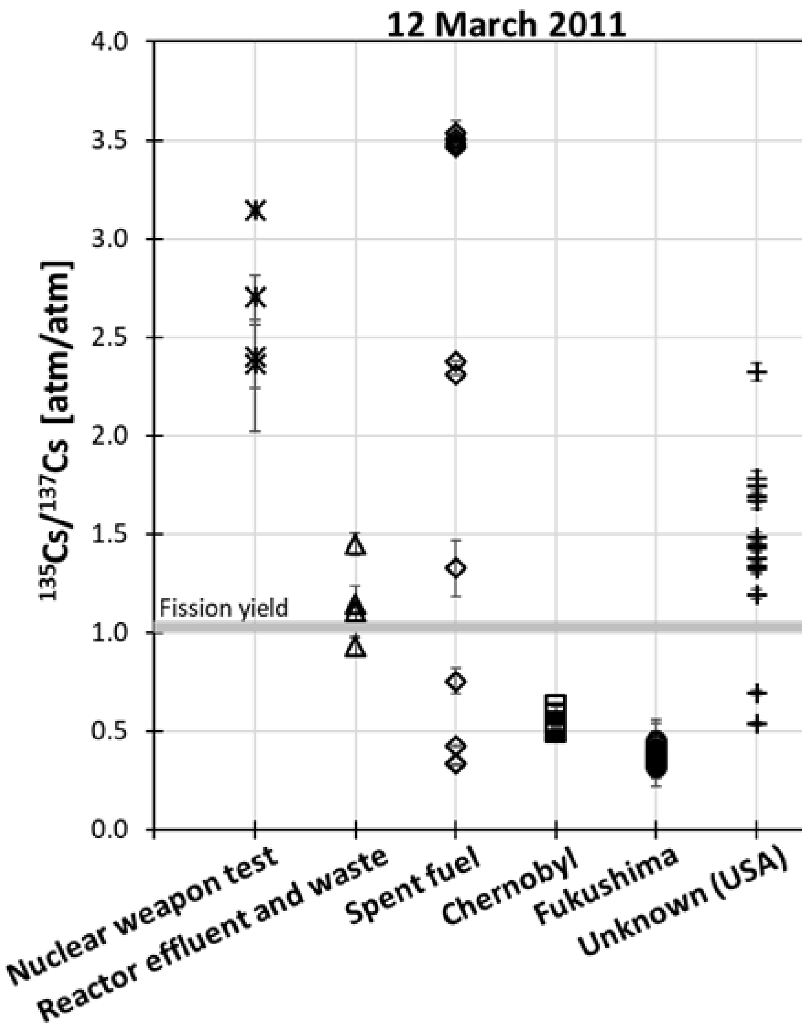
Challenging Themes with AMS-^{135}Cs

^{135}Cs has a long half-life
(2.3×10^6 y)   cf. ^{137}Cs (30.2 y)

Cs is a conservative (soluble) element in seawater

Anthropogenic radionuclides
(Fission product)
→the same origin as ^{137}Cs





Potential as an alternative environmental dynamic tracer to short half-life ^{137}Cs

D.C. Snyder (2012), B.C. Russell (2014,), V.F. Taylor (2008), L. Pibida (2004), M. Granet (2008) and 6 of others

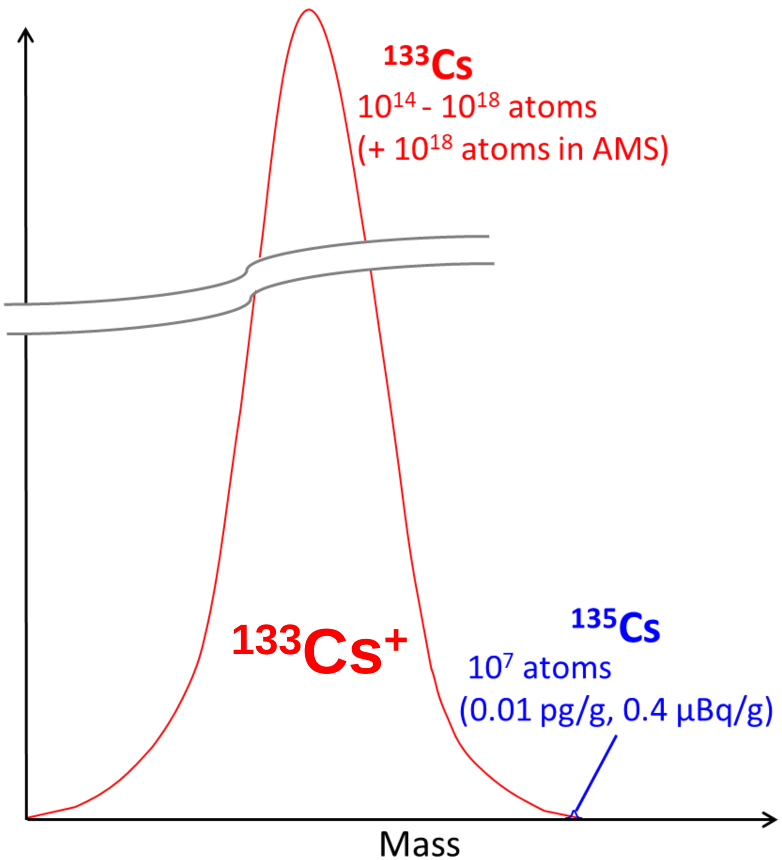
Why AMS ^{135}Cs Analysis?

Severe interference with some elements

$^{135,\,137}Cs/q$ **$^{135,\,137}Ba^+$, $^{95}Mo^{40}Ar^+$, $^{97}Mo^{40}Ar^+$ etc.**

Environment

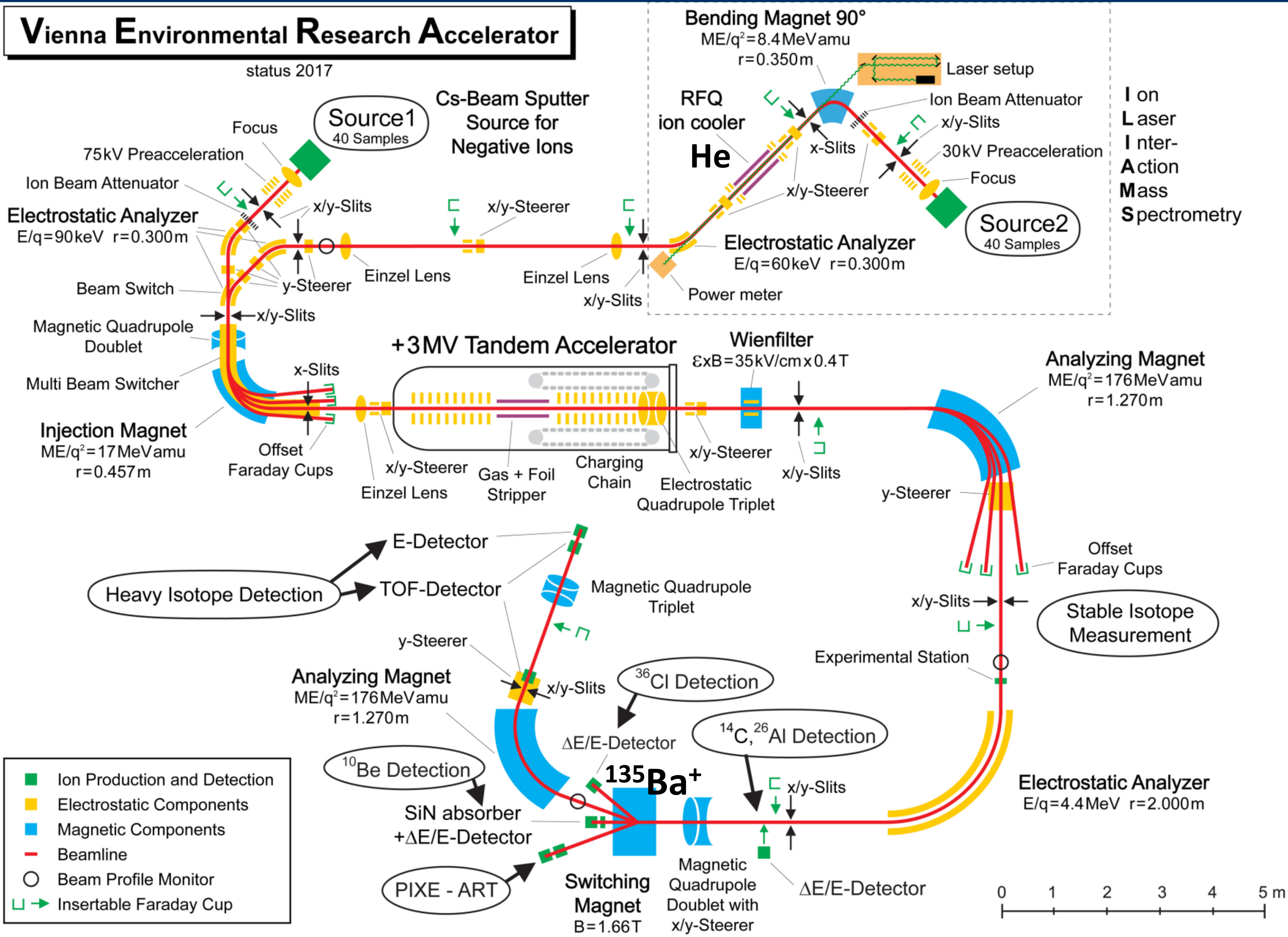
$^{135}Cs/^{133}Cs = 10^{-11} – 10^{-7}$



Instruments	$^{135}Cs/^{133}Cs$	
SF-ICP-MS	**$10^{-6} – 10^{-5}$**	Thermo Element 2XR
ICP-MS/MS	**$<10^{-8}$**	10^{-14} (Theoretical) Agilent 8800
ICP-CRC-MS	**10^{-10}**	Perkin Elmer DRCII
TIMS	**$10^{-10} – 10^{-9}$**	
RIMS	**$10^{-10} – 10^{-8}$**	
AMS	**10^{-15}** (Theoretical)	
ILIAMS	**6×10^{-12}**	VERA ILIAMS (3MV)

B.C. Russell et al. (2015), J. Zheng et al. (2013), V.F. Taylor et al. (2008), T. Lee et al. (1993), W. Bu et al. (2019), L.R. Karam et al. (2002), L. Pibida et al. (2004), J. Eliades et al. (2013)

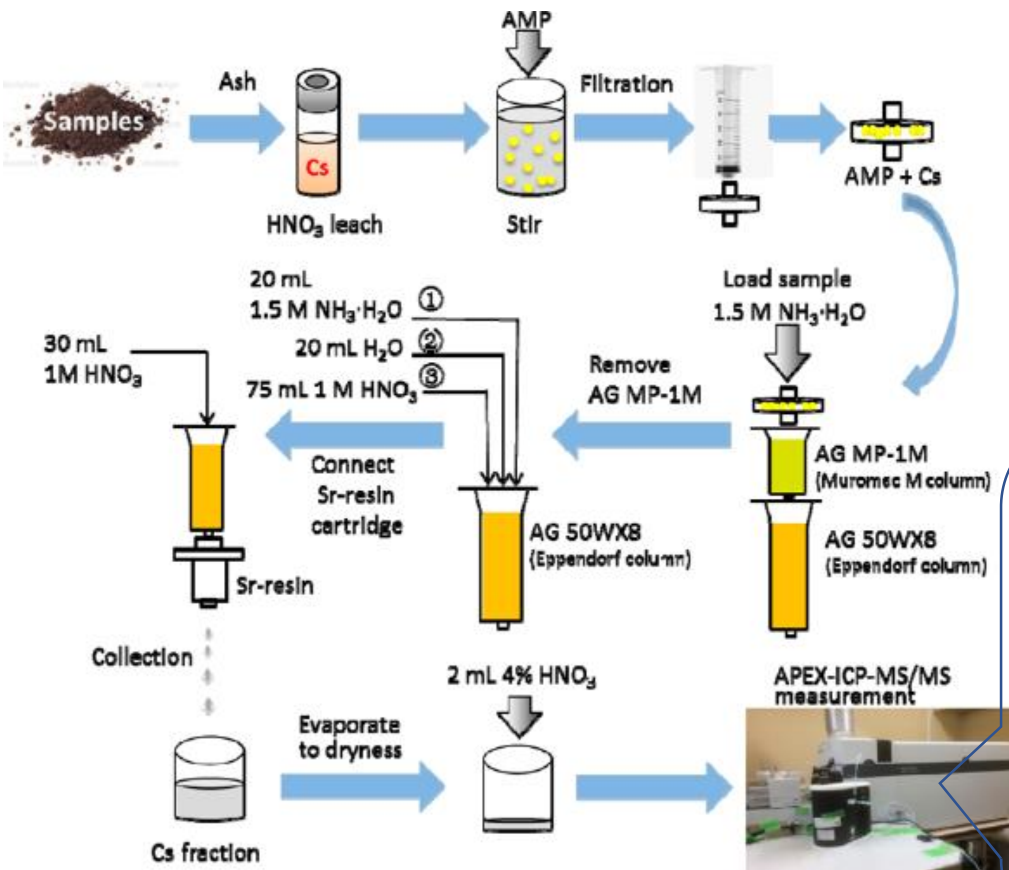
Ion Laser InterAction Mass Spectrometry- ILIAMS



https://isotopenphysik.univie.ac.at/fileadmin/user_upload/p_isotopenphysik/images_AMS_at_VERA/VERA_20170720.jpg

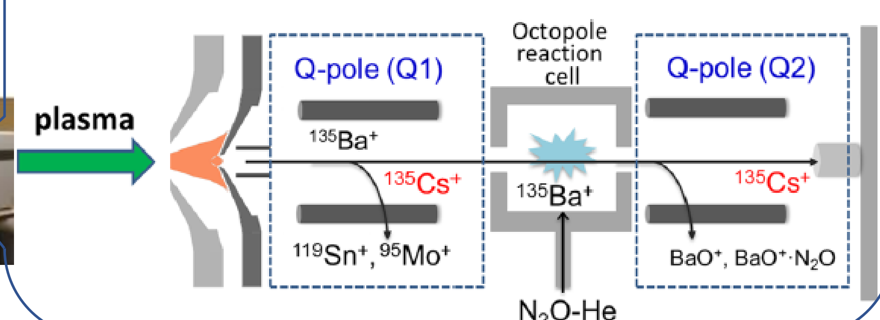
Chemical Separation Method for ^{135}Cs

Zheng et al. (2014; 2016) constructed a brilliant chemical separation method for ICP-QQQ-MS



HOWEVER . . .
it is still necessary to chemically separate Ba for AMS analyses

Measurement of 135Cs with ICP-QQQ-MS



Summary 2

- **New chemical separation** methods and **improved AMS system** enable the measurement of ultra-low level medium half-life radionuclides in the environment
- **Clarification of environmental dynamics** can be achieved from these studies by combining measurements and analyses of exotic nuclides (not only from the viewpoint of radiological protection)
- Global efforts should be made to develop this study field