Use of 10^{12} and 10^{13} ohm resistor amplifiers for uranium isotopic measurements by TIMS and MC-ICPMS

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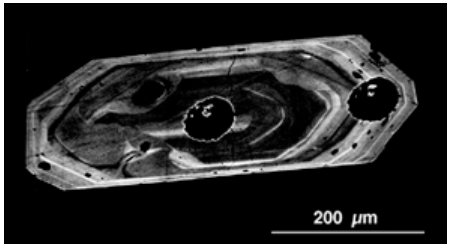
URANIUM ISOTOPE RATIOS

NUCLEAR DOMAIN

- Isotopic characterization at all steps of **nuclear fuel cycle**
- Validation of **neutronic calculation codes**
- IAEA **safeguards**
- **Nuclear forensics**. Source discrimination and datation (U-Th)
- Certification of nuclear materials (**metrology**)

EARTH SCIENCE

- **Datation**: U-Pb, U-Th
- **Sources discrimination**: paleoclimatology, hydrology
- Study of **isotopic fractionation** ($^{235}U/^{238}U$ fractionation)



ADVANTAGES OF 10^{12} ET 10^{13} RELATIVE TO SEM FOR MEASUREMENTS OF MINOR U ISOTOPES

Minor uranium isotope ratio measurements (^{234}U and ^{236}U)

- Isotopic ratios determined **on MC instruments** (TIMS, MC-ICPMS). Minor isotopes are generally measured **SEM** or **Daly electrode coupled to a photomultiplier**

Drawbacks: - Many settings must be performed (**linearity**, **dead time**, **gain** between SEM or Daly electrode and Faraday cup)

- Limited **time of life**

Advantages of 10^{12} et 10^{13} ohm amplifiers

- Increased by a factor 10 to 100 relative to 10^{11} ohm amplifier → the **signal to noise ratio** is increased by a **factor 3 to 10**
- Easy **calibration**, **flexibility** (choice of the amplifier resistor considering the application)
- **10^{12} ohm**: developed in 2007 (Tuttas et al.). **Applications**: K, Nd, Pb, Hf, S, W. Measured signals in the order of few mV but limited **below the mV**.
- **10^{13} ohm**: developed in 2013-2014. **Applications:** Nd, Pb, Sr. Signals lower than mV **and generally measured by SEM or Daly electrode**

MINOR URANIUM ISOTOPE RATIO MEASUREMENTS

- Systematic study of certified reference materials (IRMM)

	^{234}U	^{235}U	^{236}U	^{238}U
IRMM 183	0,0019688 %	0,32049 %	0,0147858 %	99,66276 %
IRMM 184	0,0052752 %	0,72096 %	0,000012356 %	99,2738 %
IRMM 185	0,0175913 %	1,96574 %	0,00028316 %	98,01639 %
IRMM 186	0,028479 %	2,98430 %	0,0032217 %	96,98399 %
IRMM 187	0,036935 %	4,5167 %	0,0068683 %	95,4395 %

- **TIMS (Triton Plus) and MC-IPMS (Neptune Plus) measurements**
- **Choice of the ohm resistor** considering the atomic abundance of ^{234}U and ^{236}U
- **Internal normalisation** $^{235}U/^{238}U$ to better compare the **performances** of 10^{12} and 10^{13} ohm resistors for **low signals**
- **Gain calibration** of 10^{13} relative to 10^{11} ohm resistors performed using **an Nd isotopic standard → reproducibility around 40 ppm**

10^{12} ET 10^{13} OHM TIMS MEASUREMENTS

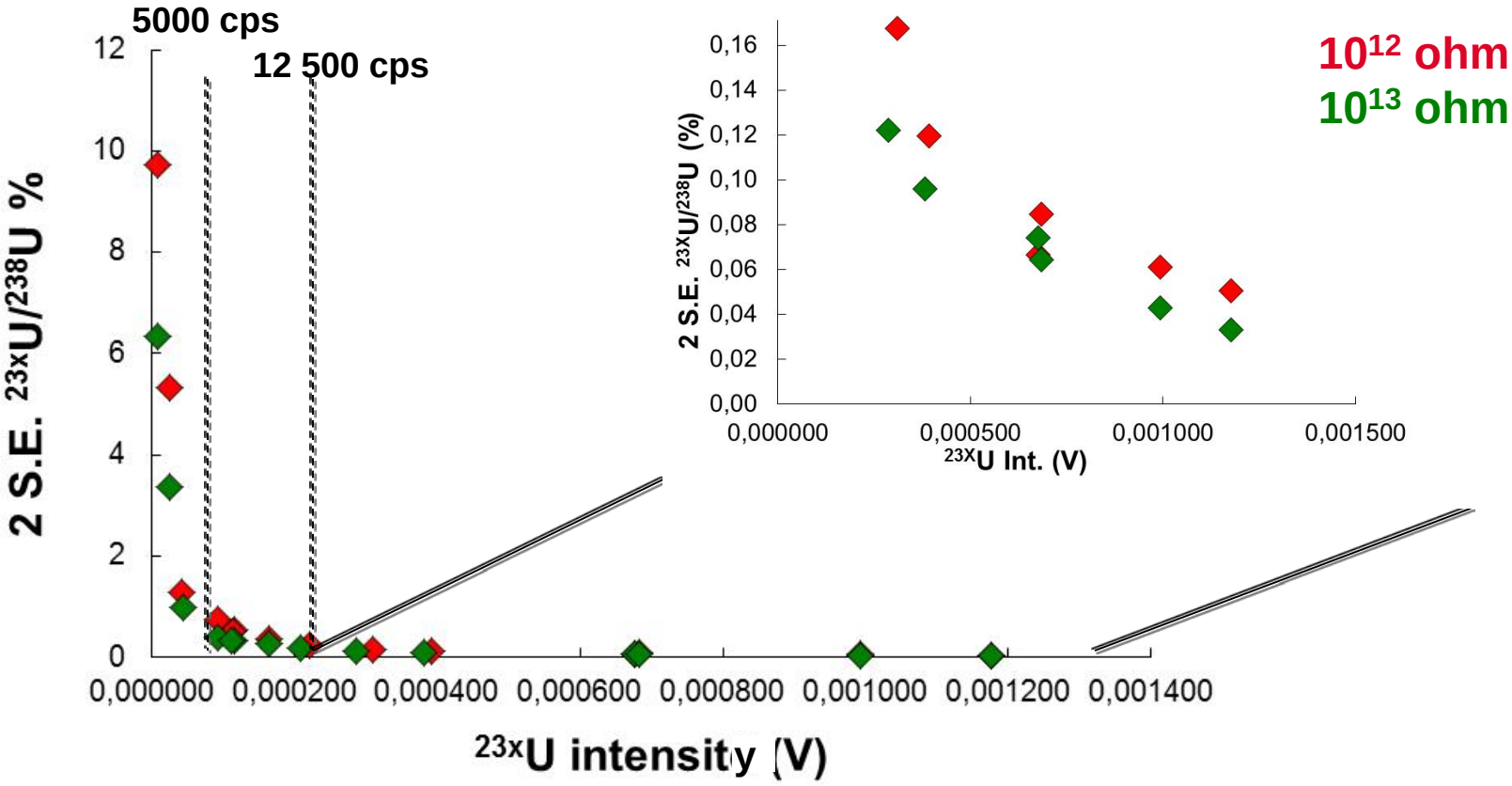
Details of measurement procedure by static multicollection

	L2	L1	Ax	H1	H2
	10^{12} ou 10^{13}	*10^{11}*	*10^{12} ou 10^{13}*	*10^{11}*	*10^{11}*
Seq. 1	^{234}U	^{235}U	^{236}U	237	^{238}U
Seq. 2	233.5	234.5	235.5	236.5	237.5
Seq. 3	234.5	235.5	236.5	237.5	238.5

- **^{238}U signal** between 3 and 4 volts**.** Number of **measurement cycles = 80** (integration time = 16.777 secondes).
- **Abundance sensitivity corrections**: measurements of half masses (233.5 and 234.5 for 234 mass and 235.5 and 236.5 for 236 mass measured on the same ohm resistors)

10^{12} ET 10^{13} OHM TIMS MEASUREMENTS

- **Internal** reproducibility obtained according to the ion beam intensity



- **Signals between 0.08 and 0.2 mV (5000 to 12500 on SEM)** Comparison of measurements **10^{12}, 10^{13} ohm** and SEM → IRMM 183 et 184

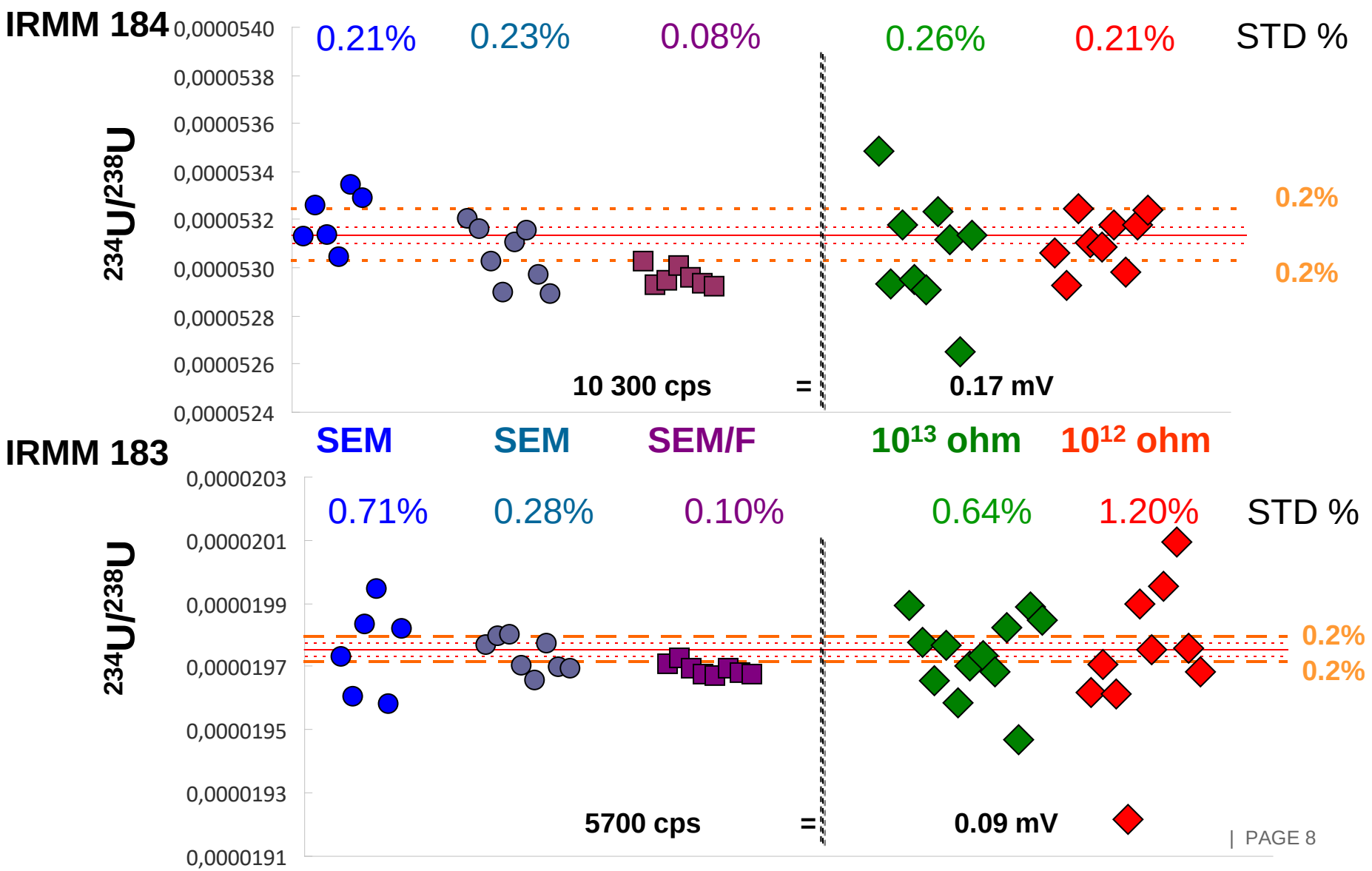
TIMS: COMPARISON 10^{12}, 10^{13}, SEM (5000 to 12 500 cps)

- **Measurement procedure by dynamic multicollection with axial SEM (+ electrostatic filter)**

	L2	L1	Ax (SEM)	H1	H2	H3
Seq. 1			^{234}U			^{238}U
Seq. 2			^{235}U		^{238}U	
Seq. 3	233.5	234.5	235.5			
Seq. 4	^{234}U	^{235}U	^{236}U	^{238}U		
Seq. 5	234.5	235.5	236.5			

- **^{238}U signal** between 3 and 4 volts**.** Number of **measurement cycles = 40** (integration time = 16.777 secondes for ^{234}U and ^{236}U and 8.839 secondes for ^{235}U and ^{238}U)
- **Abundance sensitivity corrections**: measurements of half masses (235.5 and 236.5 for 236 mass measured on SEM)
- **Internal correction of Gain F/SEM gain**: ^{235}U measured on SEM (Seq. 2) and Faraday (Seq. 4)

TIMS: COMPARISON 10^{12}, 10^{13}, SEM (5000 à 12 500 cps)



MC-ICPMS MEASUREMENTS

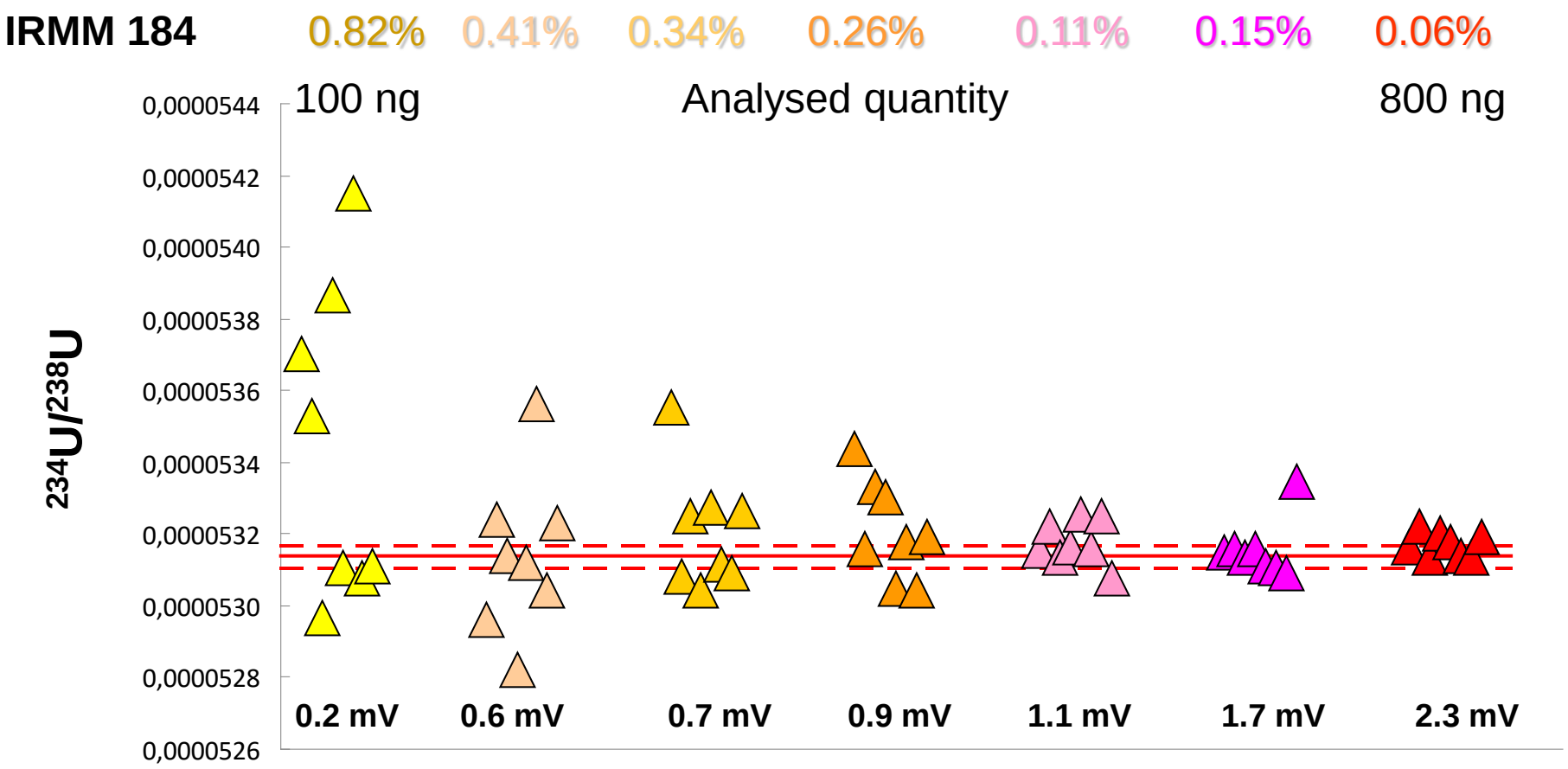
Measurement procedure by multicollection

	L2	L1	Ax	H1	H2
	10^{12}	10^{11}	10^{11}	10^{11}	10^{11}
Seq. 1	^{234}U	^{235}U	^{236}U	237	^{238}U
Seq. 2	233.5	234.5	235.5	236.5	237.5
Seq. 3	234.5	235.5	236.5	237.5	238.5

- **^{238}U signals** between 4 and 45 volts**.** Number of **measurement cycles = 30** (integration time = 8.4 secondes)
- **Abundance sensibility corrections**: measurement of half masses (233.5 and 234.5 for 234 mass and 235.5 and 236.5 for 236 mass measured on the same ohm resistors)
- **Measurements of the certified isotopic standard IRMM 184** at different signals measured on the ^{234}U mass on 10^{12} ohm resistor amplifier

MC-ICPMS MEASUREMENTS

- **External reproducibility and accuracy on the IRMM 184 standard**



- Measurements of **234, 235 et 238 on Faraday cups**
- Method **validation : accuracy < 0,1%** (signal of 2.3mV signal on ^{234}U)

CONCLUSIONS AND PERSPECTIVES

- **New analytical procedures for the determination of uranium isotope ratios by TIMS with measurements of 234 and 236 uranium isotopes on 10^{12} Ω et 10^{13} Ω resistors**
  - **Flexibility**
  - **Robustness** in comparison to SEM measurements
  - **Reproducibility** better than those obtained by SEM for signals > 12 500 cps (=0.2 mV)

- **MC-ICPMS measurements and measurements of 234 isotope on 10^{12} Ω**
  - Necessity to take into account of **baseline corrections and abundance sensibility corrections**
  - **Reproducibility** obtained lower than 0,1% for signals in the order of few mV

- **Perspectives**
  - **MC-ICPMS** measurements of uranium minor isotopes on **10^{13} Ω**
  - Development **of coupling between separative techniques and MC-ICPMS MC** with measurements of uranium minor isotopes on **10^{12} Ω**

Thanks for your attention

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