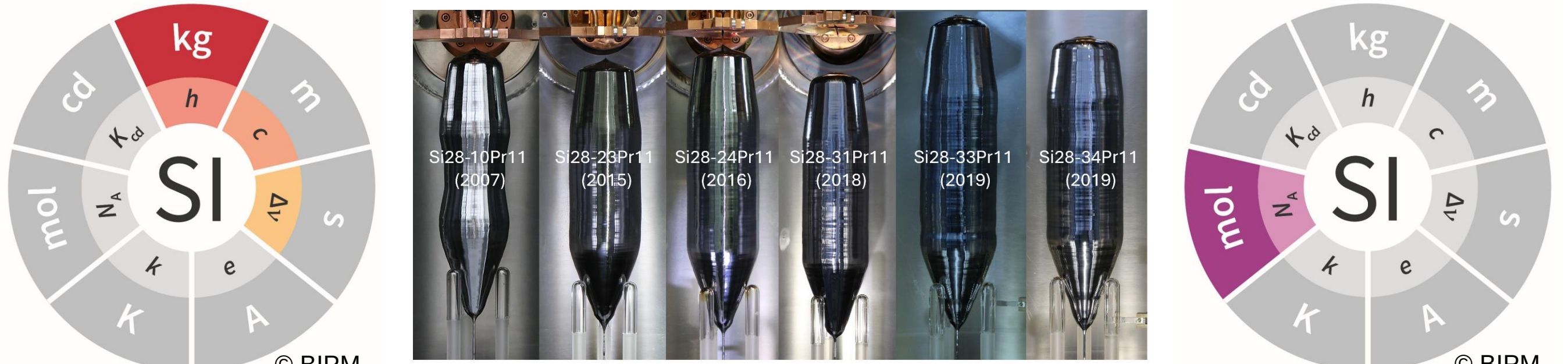


High resolution isotope ratio mass spectrometry: From the dissemination of the kilogram and the mole towards supporting the characterization of quantum bits

Introduction A key parameter for the revision of the SI base units kilogram and mole in 2019 and their ongoing realization and dissemination via the X-ray crystal density (XRCD) method is the determination of the molar mass M and isotopic composition $x(^i\text{Si})$ of ultra-pure silicon crystals highly enriched in ^{28}Si with lowest associated uncertainty [1].

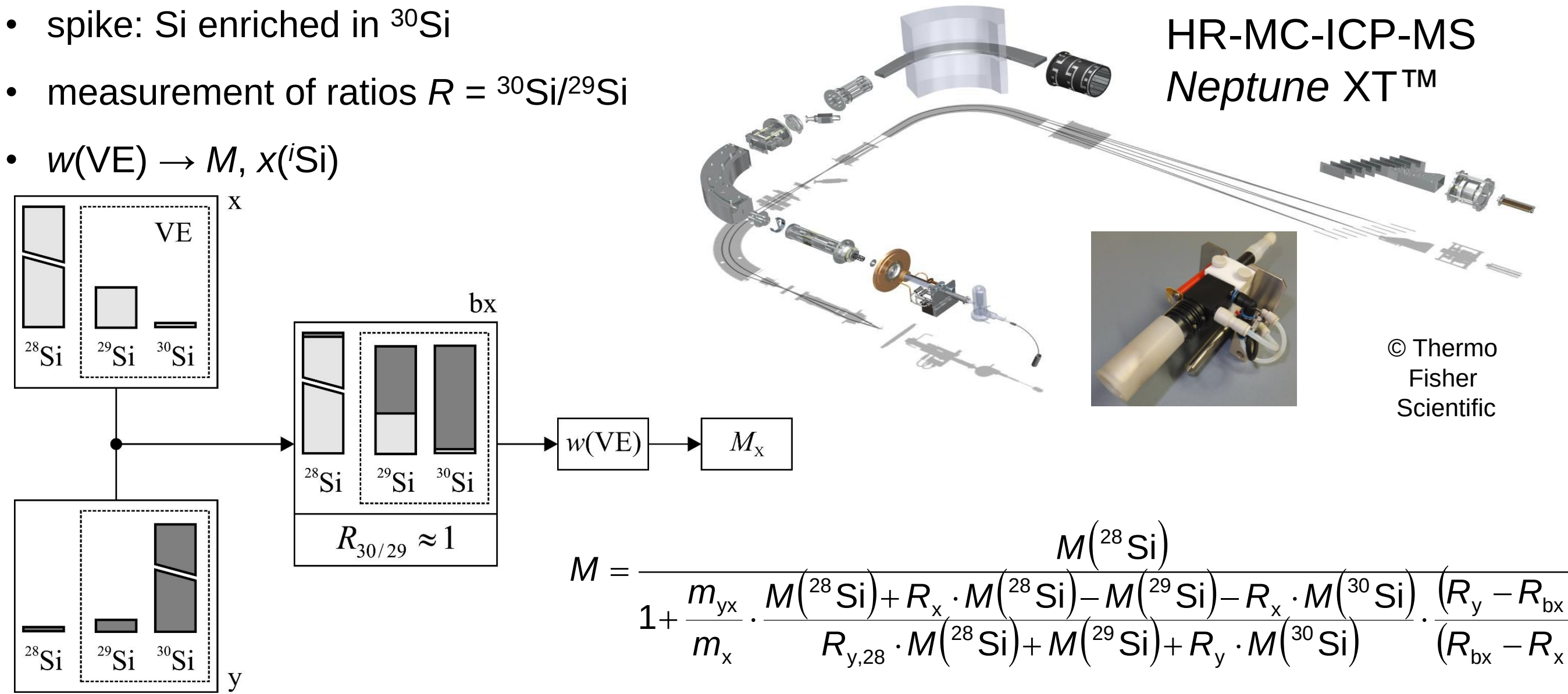


The International Avogadro Coordination and PTB produced six crystals (≈ 5 kg each; $x_{\text{rel}}(^{28}\text{Si}) > 0.999\,9$ mol/mol) each providing two spheres (1 kg each). A pool of twelve spheres exists, representing primary standards for key comparisons and dissemination purposes.

High resolution isotope ratio mass spectrometry for the measurement of the isotopic composition has been continuously improved using the principle of the virtual-element isotope dilution mass spectrometry (VE-IDMS) together with an ab-initio experimental determination of calibration factors K for isotope ratios [2]. With these tools, the uncertainty associated with M has been reduced by more than two orders of magnitude over one decade down to $u_{\text{rel}}(M) < 3 \times 10^{-9}$ – which is unique in chemistry. This method, successfully adopted and applied by several other NMIs and DIs in a CCQM-pilot study (CCQM-P160), still serves as the state-of-the-art practice to obtain $M(\text{Si})$ and $x(^i\text{Si})$ [3]. The characterization of $M(\text{Si})$ and $x(^i\text{Si})$ of the last two spheres (Si28-34Pr11) is pending and will be done with the combination of wet chemistry sample preparation and high resolution multicollector-inductively coupled plasma mass spectrometry (MC-ICP-MS) with improved technical performance. Preliminary studies predict that this material is both highly enriched in ^{28}Si ($x(^{28}\text{Si}) > 0.999\,97$ mol/mol) as well as strongly depleted in ^{30}Si ($x(^{30}\text{Si}) < 1.4 \times 10^{-7}$ mol/mol). The elevated challenge compared to previous crystals is the enlarged ratio $x(^{29}\text{Si})/x(^{30}\text{Si}) > 170$ mol/mol, which is very difficult to measure along with sufficiently small associated uncertainties.

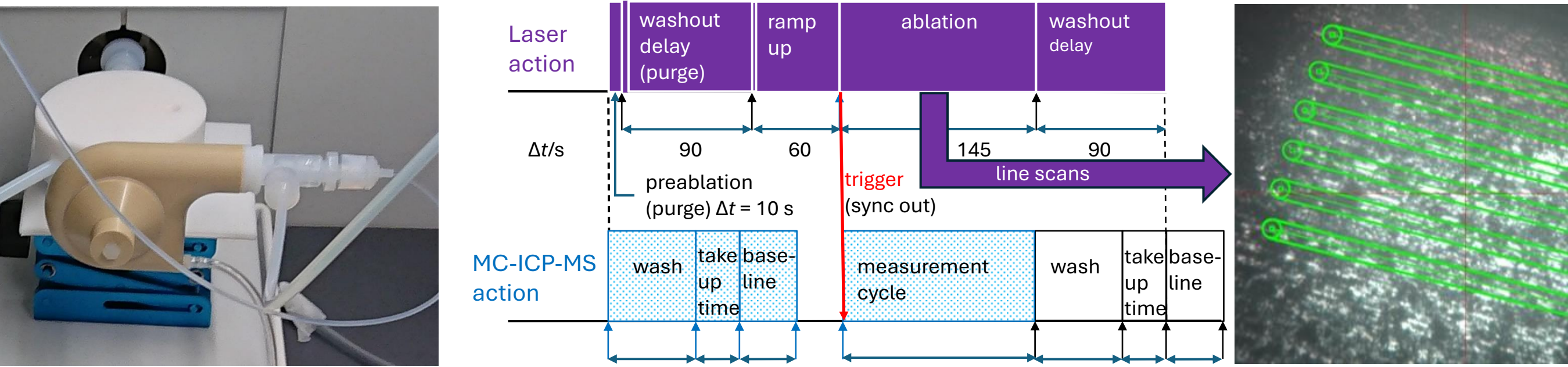
Experiment Solid Si samples: Etching, dissolving in TMAH ($w(\text{Si}) \approx 4000$ $\mu\text{g/g}$). The measurement of M and $x(^i\text{Si})$ is done with a HR-MC-ICP-MS applying the VE-IDMS-principle:

- virtual “element” VE ($^{29}\text{Si} + ^{30}\text{Si}$)
- spike: Si enriched in ^{30}Si
- measurement of ratios $R = ^{30}\text{Si}/^{29}\text{Si}$
- $w(\text{VE}) \rightarrow M, x(^i\text{Si})$



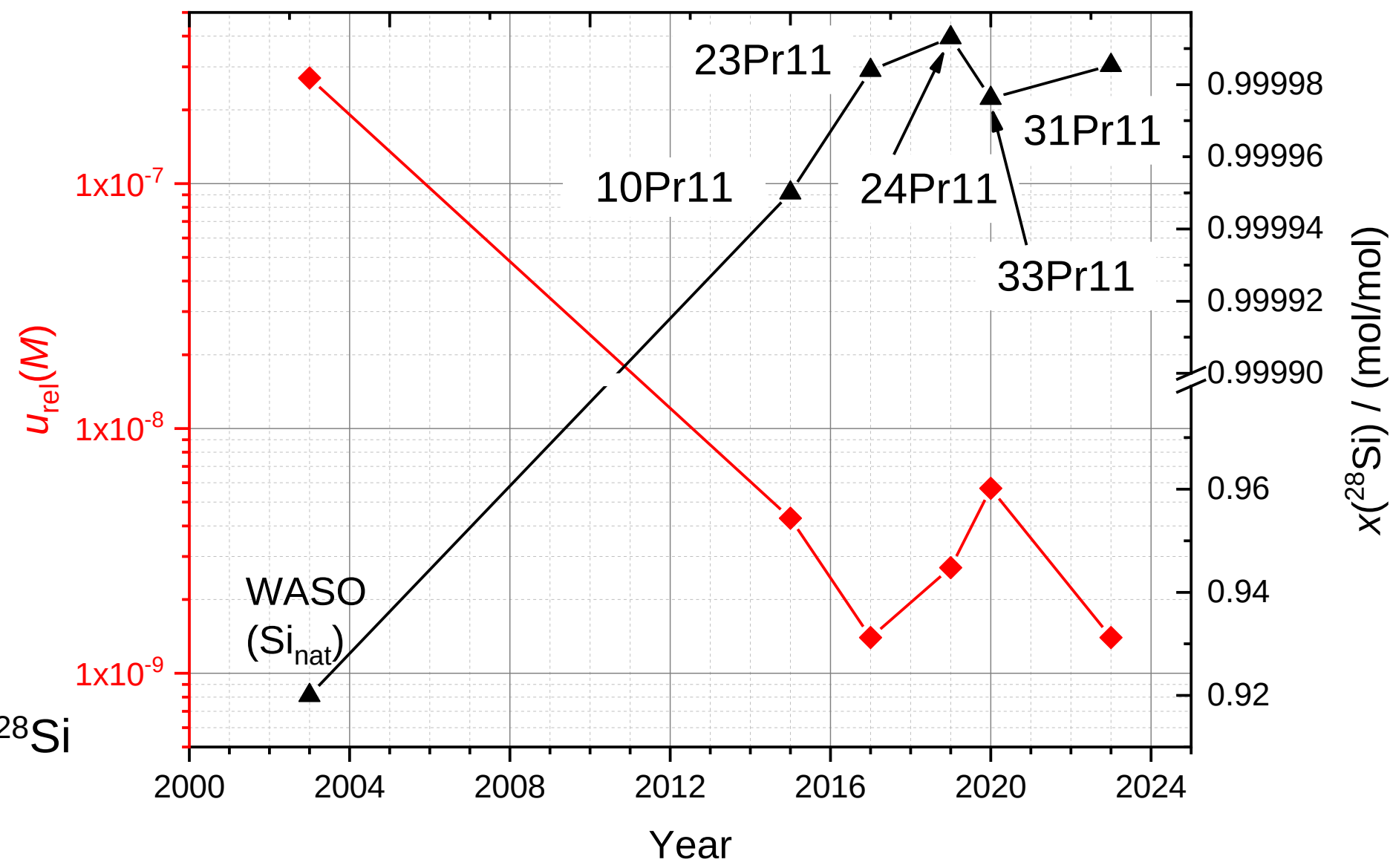
Laser ablation combined with liquid sample introduction [4]:

- laser: solid state Nd:YAG, 213 nm, 20 Hz, 4 ns/pulse
- scan type: line scan ($10\,\mu\text{m} \times 5000\,\mu\text{m}$)
- sample: Si_{nat} (WASO04), two-volume cell



Results Silicon crystals highly enriched in the ^{28}Si isotope were used in a complementary approach determining the Planck constant h and Avogadro constant N_A used for the redefinition of the kilogram and mole, respectively, via the silicon route (XRCD):

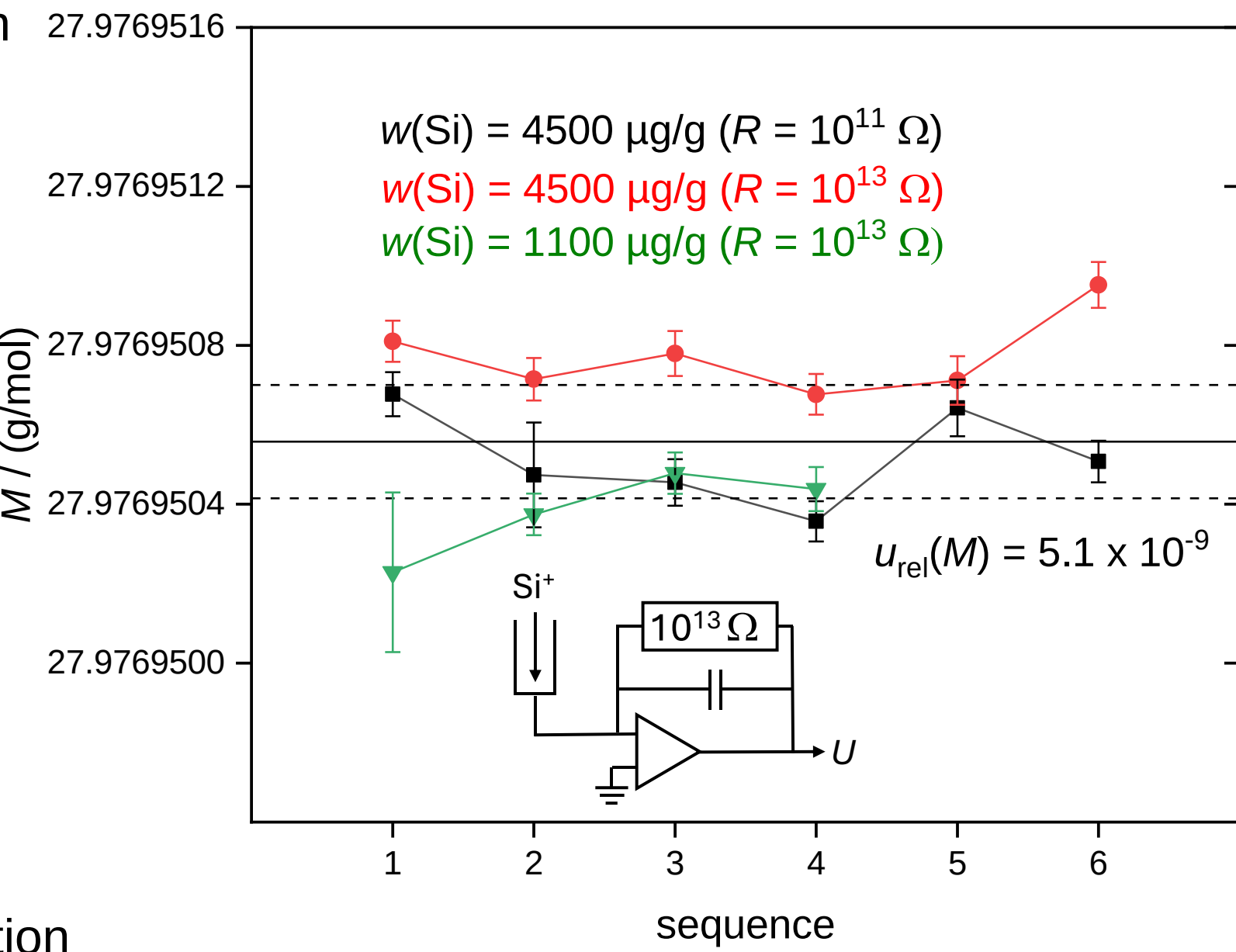
- reduction of uncertainty of $M(\text{Si})$ and $x(^i\text{Si})$ over the years: two orders of magnitude!
2003: $u_{\text{rel}}(M(\text{Si}_{\text{nat}})) = 3 \times 10^{-7} \rightarrow 2023: u_{\text{rel}}(M(\text{Si28})) = 1.4 \times 10^{-9}$
- homogeneity studies $\rightarrow x(^i\text{Si})$ no significant local variations
- complete straightforward dissolution in TMAH: plasma energy focusing onto Si
- validation of the VE-IDMS method and absolute K factor determination independently by other NMIs and during a CCQM-pilot study:
CCQM-P160
- main aspects as a prerequisite for an Si primary standard with lowest $u_{\text{rel}}(M(\text{Si}))$:
 - crystal purity
 - crystal homogeneity
 - extreme enrichment in ^{28}Si



crystal	M g/mol	$u_{\text{rel}}(M)$ $\times 10^{-9}$ ($k = 1$)	$x(^{28}\text{Si})$ mol/mol	$x(^{29}\text{Si})$ $\times 10^{-5}$ mol/mol	$x(^{30}\text{Si})$ $\times 10^{-7}$ mol/mol	Year
Si28-10Pr11	27.976 970 12(12)	4.3	0.999 957 52(12)	4.136(11)	11.21(14)	2015
Si28-23Pr11	27.976 942 666(40)	1.4	0.999 984 470(39)	1.492 1(38)	6.095(48)	2017
Si28-24Pr11	27.976 933 787(77)	2.7	0.999 993 104(31)	0.653 6(28)	3.600(88)	2019
Si28-33Pr11	27.976 950 48(16)	5.7	0.999 976 24(19)	2.357(24)	1.97(78)	2020
Si28-31Pr11	27.976 941 464(41)	1.4	0.999 985 350(37)	1.4364(36)	2.861(88)	2023

Seven orders of magnitude variation

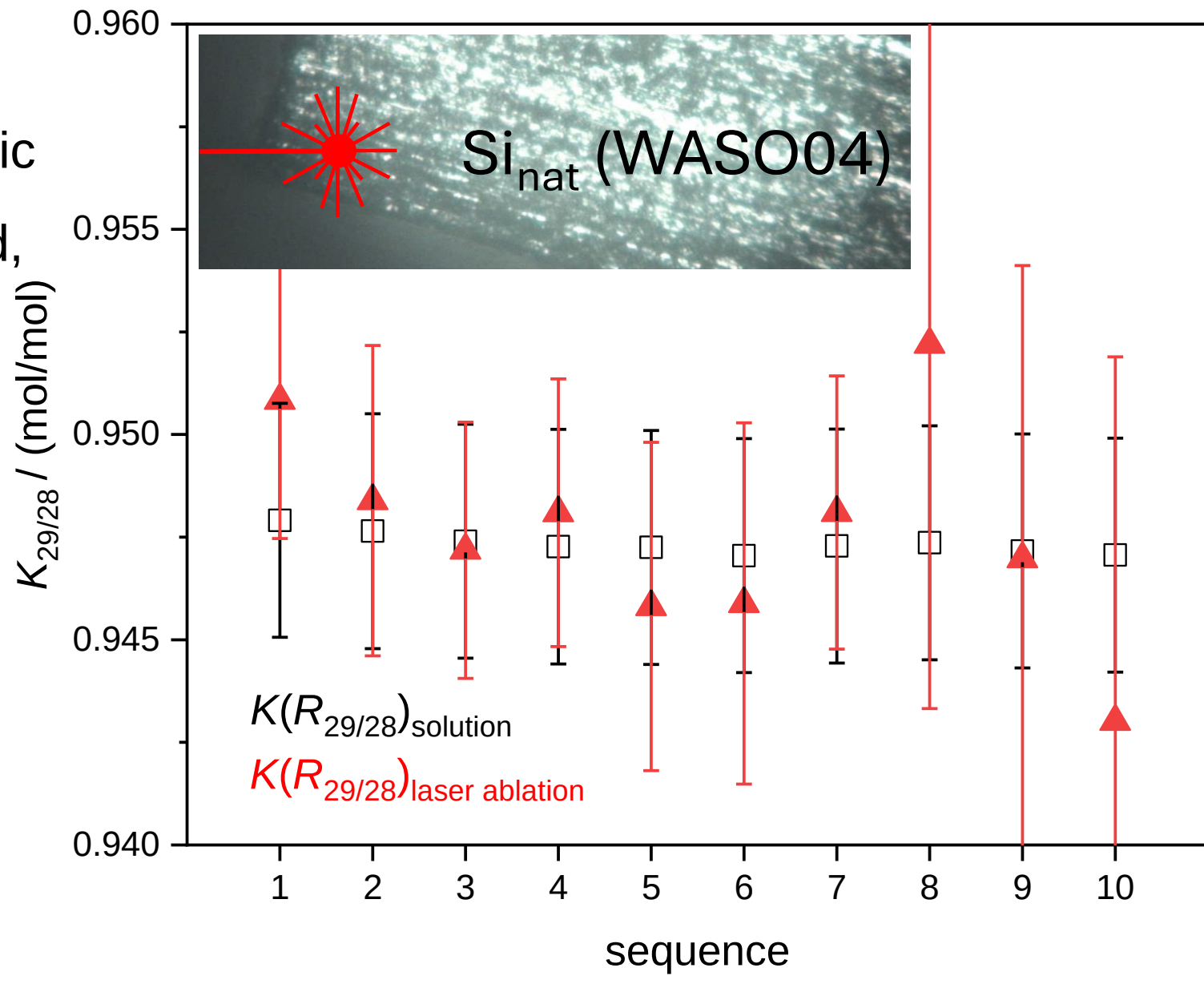
- in isotopic abundance of ^iSi
- high concentration of $w(\text{Si})$
 $\approx 4000\,\mu\text{g/g}$ necessary with $10^{11}\,\Omega$ resistors in the feedback loop of Faraday cup detectors
- use of $10^{13}\,\Omega$ resistors (^{29}Si , ^{30}Si)
- reduction of sample amount by $\frac{1}{4}$ (time- and cost-efficient) [5]



Combination of LA source with solution

sample introduction [4]:

- optimization of sample signal stability (intensity and fluctuation) by systematic study of laser parameters: scan speed, laser energy, He flow, spot size
- solid Si crystal sample (WASO04) suitable for K factor determination
- $u_{\text{rel}}(K(^{29}\text{Si}/^{28}\text{Si})) = 0.58\%$
- $u_{\text{rel}}(K(^{30}\text{Si}/^{28}\text{Si})) = 0.60\%$
- $u_{\text{rel}}(K(^{30}\text{Si}/^{29}\text{Si})) = 0.47\%$



Conclusion The validated experience and knowledge of the measurement of the isotopic composition of Si crystals highly enriched in ^{28}Si can serve as a basis for an SI

traceable characterization and calibration of new quantum materials (qubits) which might be produced in a larger scale, thus the reported experiences of measurements of highly enriched Si can be regarded as a basic fundament for scientific “spin-off” in quantum technological applications [6].

References

- [1] K. Fujii et al, *Metrologia*, 53 (2016) A19.
- [2] O. Rienitz, A. Pramann, D. Schiel, *Int. J. Mass Spectrom.*, 289 (2010) 47.
- [3] A. Pramann, O. Rienitz, *Metrologia*, 61 (2024) 025005.
- [4] T. Ren et al., submitted to *J. Anal. At. Spectrom.* (2025).
- [5] A. Pramann, O. Rienitz, *J. Anal. At. Spectrom.* 39 (2024) 1540.
- [6] R. Acharya, *Communication Materials*, 5:57 (2024).

