

A century of isotope ratio measurements and their role in the international system of units



Introduction

High-precision isotope measurements have played an important role in science, starting with the early mass spectrometric measurements of hydrogen in the 1920s. The observation of a slightly lighter hydrogen by mass spectrometry, compared to chemical measurements, led to the search and the eventual discovery of deuterium. In his 1935 Nobel lecture Harold Urey wrote that “without [this discrepancy], it is probable that we would not have made a search for it and the discovery of deuterium might have been delayed for some time”.

Isotope measurements not only enhance the International System of Units (SI) but also provide ways to measure other quantities. Policy decisions for climate change rely on isotope ratio measurements but the isotopic composition of CO₂ allows not only to identify the sources of carbon emissions but can act as a paleo-thermometer of fossils. More generally, isotope ratio measurements allow to establish time-scales for geological processes, glean evolution histories of celestial bodies, or distinguish natural chemicals from artificial.



Inspired by Wien's 1886 discovery that beams of positively charged gases can be deflected with powerful magnetic fields, in 1912 Thomson and Aston successfully separated and photographed two spectral lines in pure neon sample, marking them as neon-20 and neon-22.

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Oxygen (1920) Amount of substance

Among the most common ways of realizing the amount of substance is by measuring their mass, which requires molar mass (atomic weights). For a long time, however, many *local* atomic mass scales were in use and discussions for a unified atomic mass scale occupied scientists for more than a century.

The O = 16 atomic mass scale emerged as the standard by the early 20th century, but the discovery of oxygen isotopes made apparent that spectroscopy methods used the oxygen-16 scale (isotopic scale) whereas chemists relied on the average mass of oxygen (chemical scale). By the mid 1930s, this was further compounded with the observation that the isotopic composition of oxygen varies in nature, making oxygen an unsuitable primary standard. A consensus was reached between the International Union of Pure and Applied Physics (IUPAP) and Chemistry (IUPAC) in 1960 to establish carbon-12 as the new standard, a decision that was adopted by the General Conference on Weights and Measures (CGPM) in 1971 when it included amount of substance in the SI.

The 1914 Nobel Prize for chemistry recognized the value of precise atomic weights, but such precision was lost due to a lack of uniform adoption of international standards.

Bodenstein *et al* (1922) Zweiter Bericht der Deutschen Atomgewichts-Kommission. *Ber. Dtsch. Chem. Ges.* **55**, 8–85 © 1922 Wiley

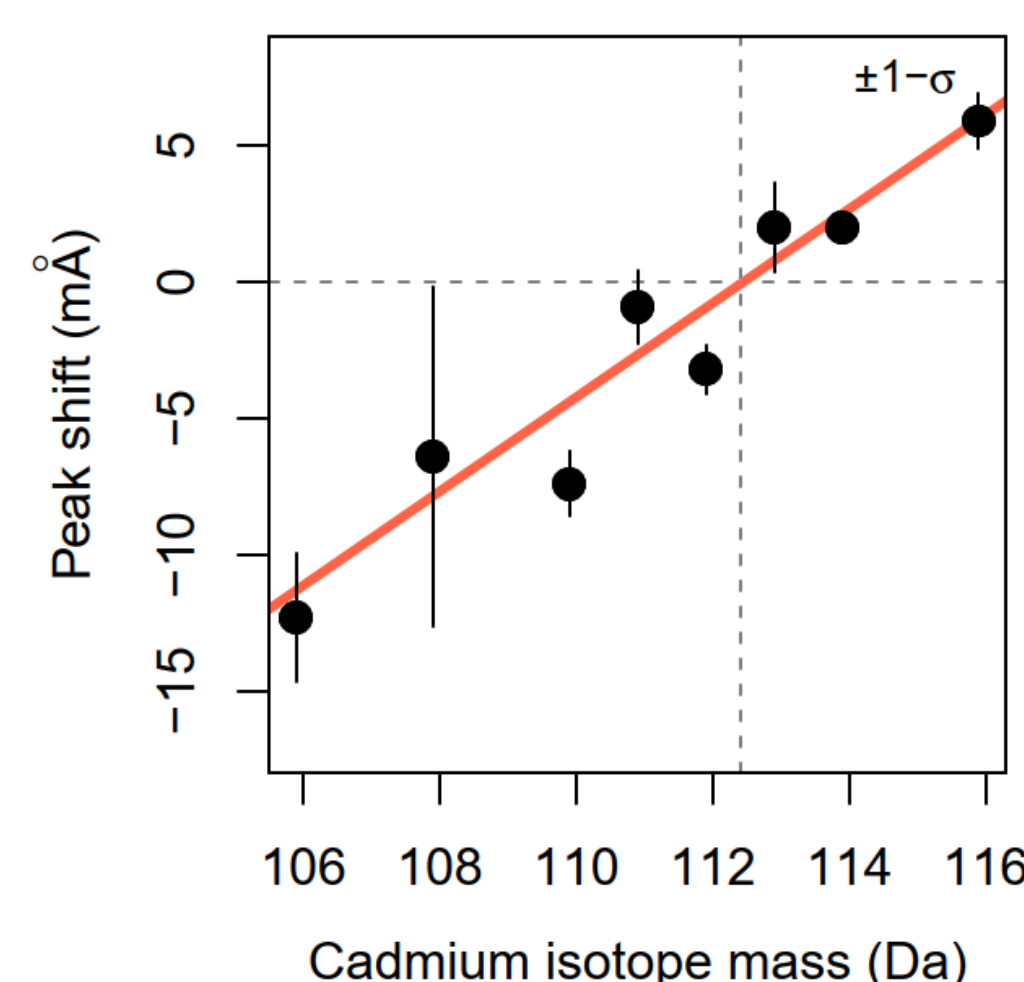
	Deutsch-land 1921	Schweiz 1921	Internat. 1921
Kr	82.92	82.9	82.92
Nb	93.5	93.5	93.1
Pb	207.2	207.2	207.20
Ra	226.0	226	226.0
Rb	85.5	85.5	85.45
S	32.07	32.07	32.06
Sc	45.10	44.1	45.1
Si	28.8	28.8	28.1

Cadmium (1940s) Wavelength standard

In the search for a natural standard of length based on light emitted by various gases or metal vapors, Michelson identified the red line of cadmium vapor while working at the International Bureau of Weights and Measures (BIPM). It showed a well separated bright line of half-width of 6.5 mÅ whose sharpness and reproducibility was unequalled at the time. In his 1907 Nobel Lecture Michelson noted that “we now have a natural standard of length, the length of a light-wave of incandescent cadmium vapor”. By the 1940s, interferometry had emerged as the standard method for length measurements. However, the wavelength of this light varied for each isotope of cadmium and this realization prompted the 9th CGPM (1948) to seek new ways of defining the metre, leading to the 1960 definition based on a single specified isotope, krypton-86.

Starting with the 1930s, much work was done to compare the length of the standard meter with the wavelength of light. With all eight stable isotopes of cadmium made available from isotopic separation at the Oak Ridge National Laboratory, it was shown that the wavelength of the red cadmium light varied with the isotopic composition of cadmium. (10 Å = 1 nm)

Wise & Vander Sluis (1956) Preliminary report on the isotopic structure of the cadmium primary standard of wavelength. *J. Opt. Soc. Am.* **46**, 587–589



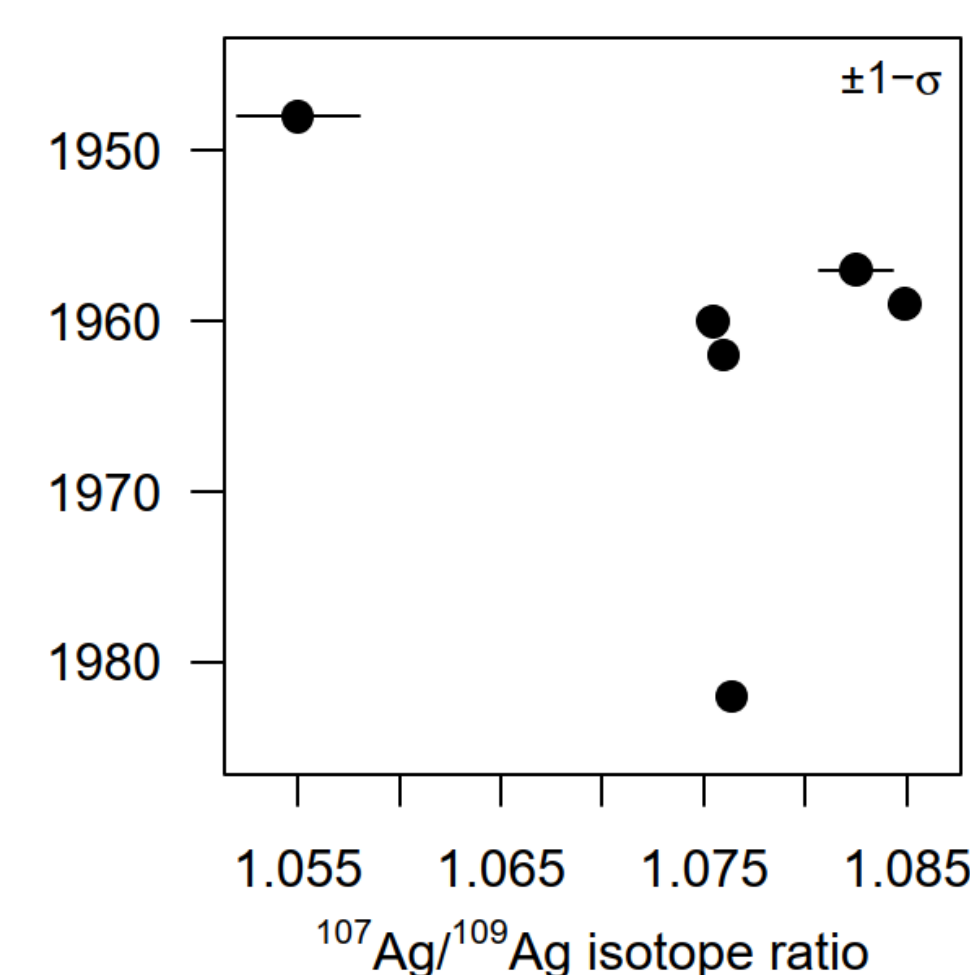
Silver (1960s) Faraday constant

The 2nd International Electrical Congress (Chicago, 1893) defined the *international ampere* as the quantity of current capable of depositing 1118 µg of silver per second. This definition was linked to the chemical equivalent of pure silver thus requiring the molar mass of silver.

Throughout the 1960s and 1970s, the CODATA adjustment of the fundamental physical constants grappled with discrepancies in the Faraday constant estimates, raising the possibility of systematic errors in the molar mass of silver. While silver ampere was replaced by then, silver coulometry continued to provide one of the most precise estimates of the Faraday constant up until the 1980s.

Silver isotope ratio measurements were not reliable before 1960s which is why silver coulometry measurements of the Faraday constant were set aside in the 1973 CODATA adjustment of the fundamental physical constants. These results were also inconsistent with the values implied by proton gyromagnetic ratio measurements. New silver isotope measurements at the National Institute of Standards and Technology (USA) in the 1980s afforded a 5-fold reduction in the uncertainty of the Faraday constant and a strong validation of the other measurement techniques.

Bower *et al* (1982) Recalculation of the Faraday Constant due to a new value for the atomic weight of silver. *J. Res. Natl. Bur. Stds.* **87**, 21–22



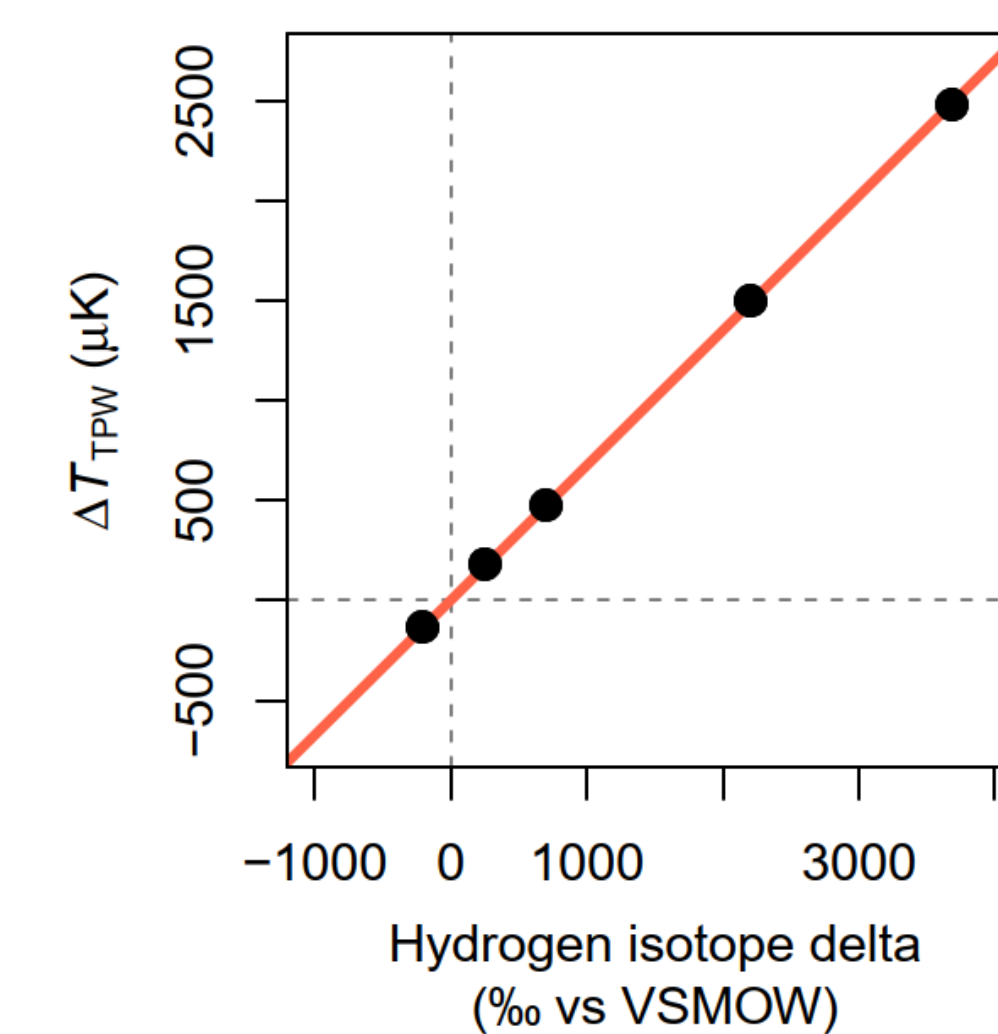
Hydrogen (2000s) Triple point of water

Variations in the isotopic composition of substances used as fixed points in the International Temperature Scale (ITS-90) can significantly impact their phase transition. Indeed, the triple point temperature estimates of the two most abundant molecules in natural water (H₂¹⁶O and H₂¹⁸O) differ by 300 mK – four orders of magnitude beyond typical measurement uncertainty for the triple point temperature.

Variation in the isotopic composition of water remains one of the major contributors to uncertainty in the realization of the triple point of water. This led the 23rd CGPM (2007) to clarify that the definition of the kelvin refers to water of isotopic composition that is identical to the Vienna Standard Mean Ocean Water (VSMOW) reference material.

Variations in the isotopic makeup of water have a substantial impact on its triple point temperature. Natural waters have isotopic composition of hydrogen that varies approximately from –500 ‰ to +100 ‰ relative to the VSMOW. This affects the triple point temperature of the water from –300 µK to +70 µK.

Faghihi *et al* (2015) Accurate experimental determination of the isotope effects on the triple point temperature of water. I. Dependence on the ²H abundance. *Metrologia* **52**, 819–826



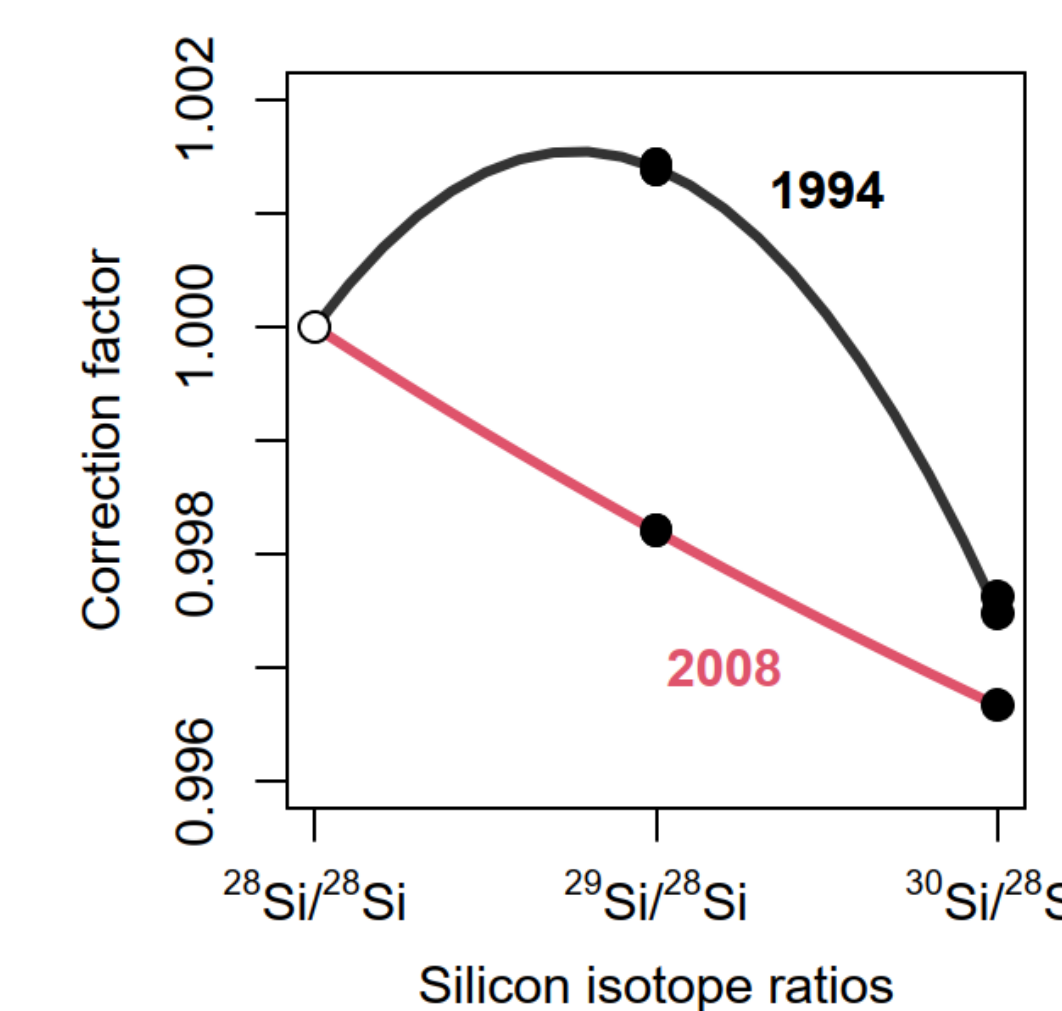
Silicon (2000s) Plank and Avogadro constants

Several National Metrology Institutes devoted considerable effort to determining the Planck constant needed to redefine the kilogram. However, in the early 2000s the estimates from the Kibble balance (NIST) and x-ray crystal density methods (International Avogadro Coordination, IAC) differed enough to halt the redefinition of the SI for a decade. This bias was later found to be due to an overlooked error in the calibration of silicon isotope ratio measurements from the 1-kg natural silicon crystal sphere. Although this delayed the redefinition of the SI, it also raised the awareness of these measurements by the International Bureau of Weights and Measures (BIPM) with the creation of the Isotope Ratio Working Group by the Consultative Committee for Amount of Substance (CCQM) in 2018.

Calibration of silicon isotope ratios remains the single biggest source of uncertainty in all mass spectrometry measurements.

Shown here are the silicon isotope ratio correction factors employed for the 2005 IAC results along with the corrected values a decade later, which resolved a long-standing discrepancy between the Kibble balance and x-ray crystal density methods.

Valkiers *et al* (2011) Si primary standards for the calibration of ion-current ratios in the molar-mass measurement of natural Si single crystals. *Metrologia* **48**, S26–S31



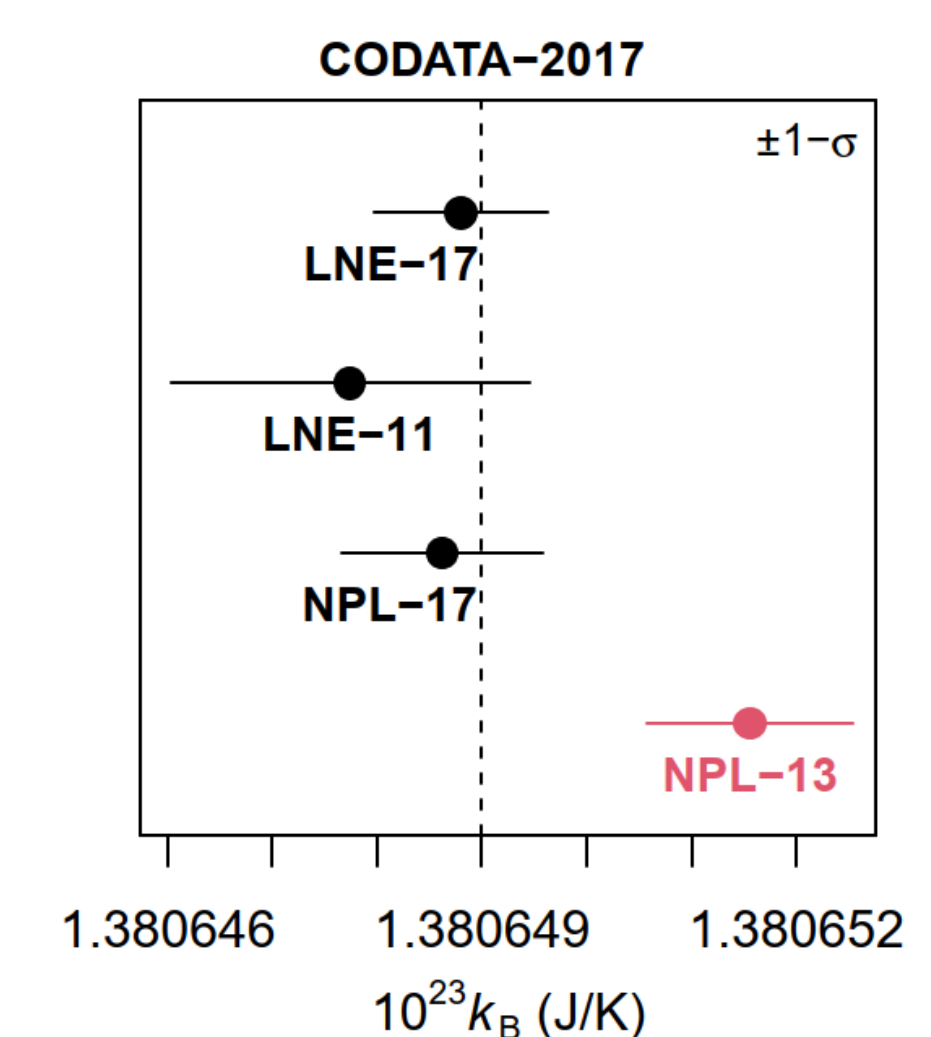
Argon (2010s) Boltzmann constant

One of the most accurate determination of the Boltzmann constant (k_B) uses acoustic gas thermometry which measures thermodynamic temperature by determining the speed of sound in helium or argon.

In 2013, the National Physical Laboratory (NPL, UK) reported the most precise measurement of the Boltzmann constant at the time, by argon acoustic gas thermometry, noting a significant difference between the 2011 estimate from France (LNE). The isotopic composition of argon remained the largest uncertainty component in this measurement. Subsequent investigations, however, revealed errors in the molar mass measurements which led to a significantly lower value of k_B , by 3-sigma, and an agreement with the LNE result.

Measurements of argon isotope ratios have played a key role in determining the value of the Boltzmann constant with several acoustic gas thermometry studies devoting significant efforts to re-evaluate the argon molar mass. Shown here is the outcome of a careful re-estimation of the molar mass of the argon sample used in the NPL-13 study which has led to significant improvements of the Boltzmann constant.

De Podesta *et al* (2017) Re-estimation of argon isotope ratios leading to a revised estimate of the Boltzmann constant. *Metrologia* **54**, 683–692



Epilogue

Despite the importance of isotope ratio measurements in the SI, the foundations upon which isotope ratio metrology is built are not as deep as one might think. Indeed, the 2019 redefinition of the SI spurred many new advances. Yet, plenty of work still remains. As an example, three independent silicon isotope ratio measurements of the same quartz sample (NBS 28) disagree with one another by *two orders* of magnitude beyond what their uncertainties suggest, even though all three were carefully calibrated using the state of the art methods.

Ren *et al* (2021) Certification of a natural silicon reference material with SI-traceable isotopic composition. *Geostds. Geoanal. Res.* **45**, 755–766

Reproducibility has been, and continues to be, the business of metrology

The history of metrology holds many valuable lessons for initiatives towards more reliable results. While a lack of reproducibility means that we must independently replicate the results before they can be accepted as true, it may also herald new discoveries and stimulate scientific progress.

Milton & Possolo (2020) Trustworthy data underpin reproducible research. *Nature Physics* **16**, 114–119

The 150th anniversary of the Metre Convention provides a timely opportunity to acknowledge how isotope ratio measurements have reinforced the International System of Units, and, if history is any guide, they are poised to shape the future of the SI.