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Letter to the editor

Silicon isotope amount ratios and molar masses for two silicon isotope reference materials: IRMM-018a and NBS28

Abstract

A new 2 kg batch of SiO_2 crystals, IRMM-018a as well as the existing NBS28 silica sand (or RM 8546, obtained by I. Friedman from U.S. Geological Survey) have been characterised for their “absolute” silicon isotope composition and molar mass. The amount-of-substance measurements needed for that purpose were performed on the IRMM amount comparator (Avogadro II) on samples from these batches, which were converted to gaseous silicon tetra-fluoride (SiF_4). The isotope amount ratio measurements were calibrated by means of synthesized isotope amount ratios realized in the form of synthetic Si isotope mixtures, the measurement procedure of which makes them SI-traceable.

IRMM-018a is intended to be used as Isotope Reference Material for isotope amount measurements in geochemical and other isotope abundance studies of silicon. It is distributed in samples of about 0.1 mol and will replace IRMM-018 (exhausted).

Keywords: Isotope reference materials; Silicon; Silicon tetra-fluoride; Si isotope abundances; Gas mass spectrometry; Molar mass

1. Introduction

Highly precise mass spectrometric measurements of silicon isotope amount ratios enable to detect natural variations between specimens resulting from different chemical, physical, geochemical or biological processes. It are these variations that open new fields of study in geochemistry, chemical technology, solid state physics, archaeology and analysis of trace elements. Results of these measurements must be comparable, i.e. be measured on the same measurement scale which means traceable to a common stated reference, otherwise they are declarations of isolated figures only, and therefore literally “incomparable”. As in other fields, credible values carried by Isotope Reference Materials (IRMs) are very useful as the needed common stated references. Such references are the values of the units used and realized in these Reference Materials. If measurement results are traceable to the values of the SI units, traceability to the SI system of units is realized. The Isotope Measurements Unit at IRMM (EC-JRC, Geel, Belgium) has been one of the world centres over the last 40 years where synthetic isotope amount ratios (isotope mixtures) are prepared for use as “stated metrological references” in order to serve the calibration of isotope amount ratio measurements.

Many isotope measurements are “differential” measurements: isotope amount ratios are compared against a value assigned by consensus for this ratio carried by a “Reference Material”, thus realizing the “zero-point” of what is commonly called a δ-scale. Differential measurements are an excellent tool for studying “differences” i.e. changes, processes. However, the long term comparability of measurement results in space and in time cannot be guaranteed because (reference) materials are never stable in the long range (e.g. sooner or later they must be replaced). Values which are traceable to the definition of SI units (such as the mole) are more stable than values defined by materials. To achieve that, a very good strategy is based on calibrating a transparent and highly reproducible isotope mass spectrometric measurement system and the associated measurement procedure by means of isotope amount ratio values synthesized in synthetic isotope mixtures. Synthetic isotope amount ratios can be prepared with a small uncertainty by ratio gravimetry. Typically, combined uncertainties of 0.01% can be obtained. Such procedures need to be well understood, i.e. uncertainty sources need to be identified meticulously in the entire process of measurement as well as along the entire traceability chain.

Preference is hereby given to ‘transparent’ measuring systems described in detailed measurement procedures, e.g. systems suffering from minimal spectral or other interferences with very repeatable mass discrimination.

Excellent tools in this context are gas source electron impact mass spectrometers and thermal ionisation mass spectrometers which use near-monoenergetic ions. The

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Table 1
Measured ion current ratios on IRMM-018a and NBS28 ($U = ku_c$, with $k = 1$)

	IRMM-018a SiO_2	NBS28 SiO_2
$I(^{29}SiF_3)^+/I(^{28}SiF_3)^+$	0.05076091 (76)	0.05075662 (79)
$I(^{30}SiF_3)^+/I(^{28}SiF_3)^+$	0.03365602 (74)	0.03365761 (76)

determination of an amount-of-substance ratio is done via an electric current ratio measurement.

2. Experimental

Two silica materials IRMM-018a (Optipur Merck) and NBS28 (a silica sand, also named NIST RM 8546) were calibrated using such synthetically prepared amount ratios of the three Si stable isotopes (^{28}Si, ^{29}Si and ^{30}Si) in a series of gas mass spectrometric measurements near the highest attainable accuracy [1–3].

After careful homogeneisation, both IRMM-018a and NBS28 were converted to SiF_4 gas, because highly repeatable amount-of-substance ratio measurements can be performed on SiF_4. These conversions needed to be rigorously free of any isotopic contamination since, evidently, no alterations of the isotopic composition, or even suspicion of alteration, can be tolerated in the preparation process. This was ensured by selecting chemical reactions for the preparation of SiF_4 which have a very high yield (>99.5%).

The Si amount-of-substance measurements on the prepared SiF_4 gas were made on the Finnigan MAT 271 mass spectrometer as modified to IRMM requirements and now called “the IRMM amount comparator (Avogadro II)” [3]. Over the years this instrument was used to achieve highly improved and SI-traceable values for isotope amount ratios and molar masses with associated measurement uncertainties of several elements (S, Xe, Kr, C) [4–6].

The ion currents of $^{28}SiF_3{}^+$, $^{29}SiF_3{}^+$ and $^{30}SiF_3{}^+$ at $m/e = 85$–87, originating from the SiF_4 sample were measured on a single Faraday collector. In gas mass spectrometry, the measured ion currents, $I(^{i}SiF_3)^+/I(^{28}SiF_3)^+$ are proportional to the corresponding amount-of-substance ratio, $n(^{i}Si)/n(^{28}Si)$ in the sample, but not exactly equal to them:

$$n(^{i}\mathrm{Si})/n(^{28}\mathrm{Si}) = K_{i/28}[I(^{i}\mathrm{SiF}_3)^+/I(^{28}\mathrm{SiF}_3)^+] \quad \text{with } i = 29 \text{ or } 30.$$

The conversion of the measured ion current ratios (Table 1) into amount-of-substance ratios (Table 3), is affected by isotope mass fractionation during the inlet of the gas from the original container through different steps into the ion source as well as during the generation and transport of the ions until and including the detection stage. Mixtures of chemically pure and highly enriched isotopes [1] with known isotope composition are used to determine the “overall” conversion factor K_{res} (from which $K_{i/28}$ is a component), of the measured ion current ratios (Table 2). Such isotope measurements, using synthetic isotope mixtures (of course of the same element as the element to be measured), result in the smallest combined uncertainty achievable, and which can hence serve to “calibrate” other measurements. This approach gives the measurement results a “primary” character because they are located in the traceability chain right after the link from the definition of the unit to its realisation. These measurement results establish “absolute” i.e. SI-traceable molar mass values in materials, and turn these materials into Isotope Reference Materials for high-accuracy isotope abundance or isotope amount ratio measurements, useful in geochemical and other studies of silicon.

Table 2
“Overall” conversion factor for converting ion current ratios into “amount-of-substance” ratios, with $U = ku_c$, with $k = 1$

$K_{res\text{-}1}$ for $I(^{29}SiF_3)^+/I(^{28}SiF_3)^+$	1.001306 (37)
$K_{res\text{-}2}$ for $I(^{30}SiF_3)^+/I(^{28}SiF_3)^+$	0.996315 (58)

3. Results

From the two “absolute” isotope amount ratios $n(^{i}Si)/n(^{28}Si)$ with $i = 29$ or 30 (Table 3) of IRMM-018a and NBS28, the δ^{29}Si and δ^{30}Si values can be calculated as follows:

$\delta^{i}\mathrm{Si}_{\mathrm{IRMM\text{-}018a/NBS28}} = \{[n(^{i}\mathrm{Si})/n(^{28}\mathrm{Si})]_{\mathrm{IRMM\text{-}018a}}/[n(^{i}\mathrm{Si})/n(^{28}\mathrm{Si})_{\mathrm{NBS28}}] - 1\} \times 1000$, yields:
$\delta^{29}\mathrm{Si}_{\mathrm{IRMM\text{-}018a/NBS28}} = +0.08 \pm 0.12‰$,
$\delta^{30}\mathrm{Si}_{\mathrm{IRMM\text{-}018a/NBS28}} = -0.05 \pm 0.16‰$ both with $U = ku_c$, and $k = 1$.

From these measurements it can be concluded that there is no significant difference between all the values for the Isotope Reference Materials IRM-018a and NBS28.

A comparison of the molar masses of IRMM-018a and NBS28 with those of other SiO_2 materials [7] is given in Table 4. All isotope ratios are in good agreement, but the combined uncertainties of the values reported in this work are two orders of magnitude smaller than those of the values previously reported.

Table 3
Silicon isotope amount-of-substance ratios, and amount-of-substance fractions and the corresponding molar masses for IRMM-018a and NBS28, certified after calibration of the measurement procedure by means of Si synthetic isotope mixtures ($U = ku_c$, with $k = 1$)

	IRMM-018a	NBS28
Amount-of-substance ratio		
$n(^{29}Si)/n(^{28}Si)$	0.0508272 (20)	0.0508229 (20)
$n(^{30}Si)/n(^{28}Si)$	0.0335320 (21)	0.0335336 (21)
Amount-of-substance fraction		
^{28}Si	0.9222036 (25)	0.9222059 (25)
^{29}Si	0.0468730 (18)	0.0468692 (18)
^{30}Si	0.0309234 (19)	0.0309249 (19)
Molar mass, M(Si) (g mol^{-1})	28.0855284 (40)	28.0855276 (40)

Table 4
Molar masses of the two different SiO_2 materials (IRMM-018a and NBS28), after calibration of the measurement procedure by means of Si synthetic isotope mixtures ($U = ku_c$, with $k = 1$), compared to other SiO_2 samples

Substance	M(Si) ($g\,mol^{-1}$)
Igneous rocks and minerals	28.08549 (39)
Opaline sinter	28.08541 (48)
Chalcedonic sinter	28.08553 (39)
Hot springs	28.08552 (36)
Opaline phytoliths	28.08557 (51)
Sponge spicules	28.08534 (44)
Diatomite	28.08555 (44)
Chert	28.08558 (52)
Silicified algal matter	28.08568 (47)
Clay minerals	28.08549 (50)
Diagenic quartz	28.08551 (36)
Shale	28.08552 (36)
Sandstone	28.08552 (37)
IRMM-18a (SiO_2)	28.0855284 (40)
NBS28 (silica sand)	28.0855276 (40)

4. Conclusion

The increasing importance of isotope measurements in fields such as geology or archeology now reaches beyond the confines of pure research, and has increased the demands on their quality and comparability. Primary Isotopic Reference Materials like IRMM-018a, with values independent of human arbitrariness, contribute to anchor the values of isotope reference materials and therefore of all measurements calibrated by these RMs. Therefore they offer the basis for a truly international structure for results of isotope measurements.

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