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Revised $\delta^{30}\text{Si}$ consensus values for BHVO-2, big batch, diatomite and IRMM-018 secondary reference materials using literature compilation

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Secondary isotope standards play a vital role in the assessment of measurement accuracy across studies and the evaluation of long-term reproducibility. Here we compile almost two decades of measurements of the Si isotope secondary standards BHVO-2 (17 years), Big Batch, Diatomite and IRMM-018 (all 18 years) reported in the literature and provide updated consensus Si isotope values for these materials. The revised mean consensus $\delta^{30}\text{Si}$ values and uncertainties (95% CI) are $-0.29 \pm 0.004\text{‰}$, $-10.56 \pm 0.03\text{‰}$, $+1.25 \pm 0.005\text{‰}$ and $-1.65 \pm 0.04\text{‰}$ for BHVO-2, Big Batch, Diatomite and IRMM-018, respectively. Comparisons of the updated and original mean isotope values for these secondary standards show no or small differences: 0.00‰ for BHVO-2 and IRMM018, -0.05‰ for Big Batch, and -0.01‰ for Diatomite, but with substantially reduced uncertainty (95% CI) for each material.

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Introduction

The development of high-precision methods for stable silicon (Si) isotope measurement has opened new fields of study in the natural sciences, allowing studies of silicon dynamics and mass balance in systems ranging from marine¹ and fresh waters² to terrestrial³ and extraterrestrial⁴ systems. The metrics of data quality for early Si isotope studies were the measurement precision of replicated analyses of unknowns and the slope of the covariation defined by the data in a three isotope plot of $\delta^{29}\text{Si}$ vs. $\delta^{30}\text{Si}$ (e.g.^{3,5,6}). Subsequent efforts established consensus values for the silicon isotope composition of several secondary reference materials,^{5,7–9} allowing assessment of measurement accuracy and long-term reproducibility for the growing global network of investigators. Here we reassess consensus values for four commonly used Si isotope secondary reference materials by compiling measurements of these materials reported in the literature. Our effort is an expansion of efforts by Mao *et al.*,¹⁰ Zhang *et al.*¹¹ and Jochum *et al.*,¹² who used data from the GeoReM database to assess isotopic

reference values and or the chemical composition of a variety of reference materials.

The primary standard for silicon isotope measurements is NBS-28 (a silica sand, NIST RM 8456) with four commonly used solid secondary standards being Big Batch (a laboratory-produced cristobalite⁵), Diatomite (a cleaned and calcined natural diatomite⁵), BHVO-2 (a Hawaiian basalt, USGS rock reference material⁷) and IRMM-018 (a quartz⁵). Consensus values for these materials were established ~17–18 years ago by Reynolds *et al.*⁵ and Abraham *et al.*⁷ Since then, many studies have reported values for these materials to evaluate the accuracy of their measurements of unknown samples. Here we assemble those literature values to refine the consensus values for these four secondary standards.

Approach

Reynolds *et al.*⁵ reported consensus values for Big Batch, Diatomite and IRMM-018, while Abraham *et al.*⁷ and Savage *et al.*¹³ are most cited for the consensus value for BHVO-2. We used Web of Science v5.14 in early February 2026 to identify publications that cite these three papers and that report values for one or more of these secondary standards. This procedure captures manuscripts published through 2025. Mean $\delta^{30}\text{Si}$ values and their uncertainty (where reported) were compiled, resulting in 66 measures of Big Batch, 154 measures of Diatomite, 83 measures of BHVO-2 and 45 measures of IRMM-018. While straightforward and reproducible, we acknowledge this approach may have missed some relevant publications.

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Data analysis

Our analysis generally follows the recommendations for analyzing data from several laboratories when developing consensus isotope values.¹⁴ Specifically, we follow procedures laid out in Ellison *et al.*,¹⁵ in which data from each participating laboratory (each published study in our case) is first examined and outliers removed, after which a weighted average of the remaining values is calculated with weights corresponding to $1/X^2$ where X is the uncertainty in the average value from a given lab. Ellison *et al.*¹⁵ recommend using the standard error of the mean (SEM) when calculating weights. Here the standard deviation (σ_{SD}) is used. The choice of $1/\sigma_{SD}^2$ rather than $1/SEM^2$ as weights is based on the following considerations: (a) publications reporting only a few measurements of a secondary standard receive equal weight as those reporting many measurements, (b) more precise analyses still receive more weight than those with larger data scatter, and (c) laboratories reporting averages of a large number of measurements ($N > 250$) generally do not seem to be significantly closer to the mean than those with small N (< 10), indicating that there is some inter-laboratory variability not explained by the random intra-laboratory scatter, such that more conservative uncertainties on the values reported by individual laboratories need to be chosen to avoid giving undue preference to reports with large N .

All calculations were done in EXCEL Version 2108 augmented by the Real Statistics Resource Pack software (Release 9.5.5). Copyright (2013–2025) Charles Zaiontz. <http://www-real-statistics.com/>.

The data were first sorted by measurement instrumentation. The vast majority of studies used multicollector inductively coupled plasma mass spectrometry, MC-ICP-MS (100% for

Table 1 Statistics for the regression of mean $\delta^{30}\text{Si}$ values as a function of publication year and of $2\sigma_{SD}$ values against publication year for the four secondary standards. For each regression the F statistic for a linear model and the associated p value are reported^a

Standard	$\delta^{30}\text{Si}$		$2\sigma_{SD}$	
	F	p	F	p
BVHO2	$F_{1,81} = 1.60$	0.20	$F_{1,80} = 1.61$	0.21
Big batch	$F_{1,64} = 0.53$	0.46	$F_{1,62} = 1.72^a$	0.19 ^a
Diatomite	$F_{1,152} = 0.38$	0.53	$F_{1,150} = 0.19$	0.66
IRMM-018	$F_{1,43} = 0.45$	0.50	$F_{1,43} = 0.45$	0.51

^a Excludes $2\sigma_{SD}$ value of 1.0 from ETH in ref. 22 which is anomalously large (see Fig. S1).

BHVO-2, 86% for Big Batch, 94% for Diatomite and 95% for IRMM-018). Measurements by isotope ratio mass spectrometry (IRMS) comprised 14%, 6% and 5% of the studies reporting means for Big Batch, Diatomite and IRMM-018, respectively. A single report for Big Batch, Diatomite and IRMM-018 employed inductively coupled mass spectrometry (ICP-MS). The distribution of reported values for measurements by IRMS and ICP-MS are shown against whisker plots of the entire data set in Fig. S3. The IRMS and ICP-MS values show considerable scatter across the range of values for all three secondary standards, though IRMS values for Big Batch appear skewed towards more positive values compared to the median of the overall dataset. Welch tests comparing IRMS and MC-ICP-MS values for each secondary standard showed no significant differences ($p > 0.05$, two-tailed tests) for Diatomite and IRMM-018 and weak significance for Big Batch ($p = 0.044$, two tailed test). Statistical testing was not applied to the single values obtained by ICP-MS

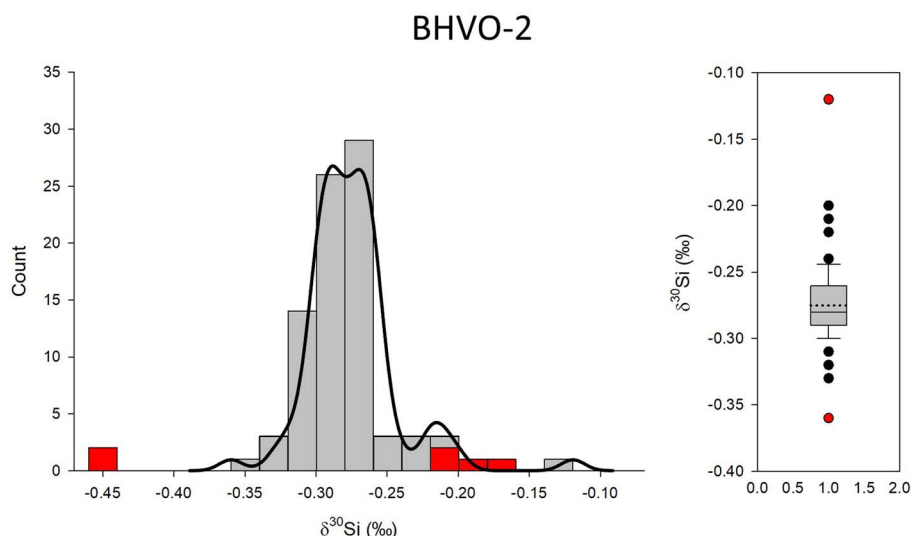


Fig. 1 Left: Histogram of reported mean $\delta^{30}\text{Si}$ values from the literature for the secondary Si isotope standard BHVO-2. Red bars are the original data from Abraham *et al.* (2008)⁷ used to define the current consensus value for this material. In that study mean values represent the results from analyses performed on separate days by a single laboratory. Black line is the probability density function. Right: Whisker plot of all data. Horizontal box boundaries represent the upper quartile (Q3) and lower quartile (Q1) with the median as the solid horizontal line and the mean as the horizontal dashed line. Whiskers represent the 90th and 10th percentiles. Data that fall outside this range are shown as individual points. Red points are considered outliers by the criteria outlined in the main text.

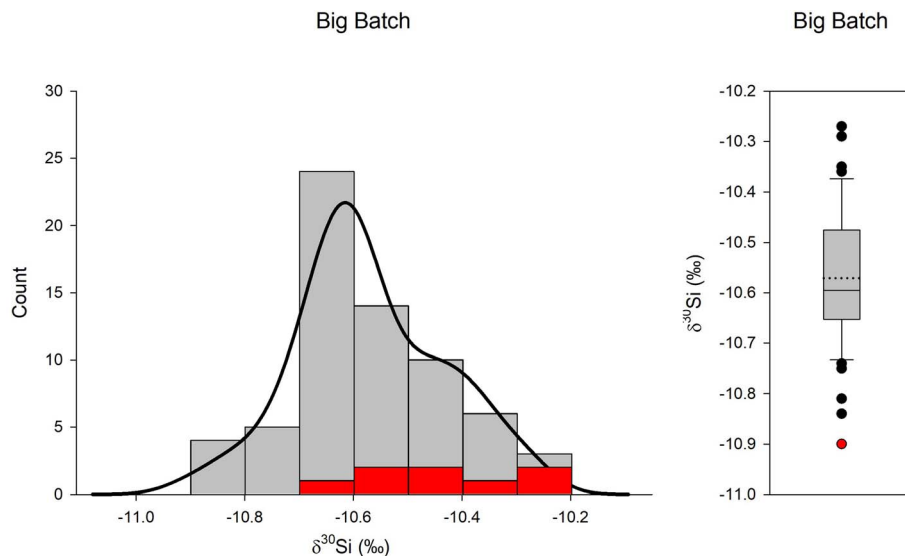


Fig. 2 As in Fig. 1 for the secondary standard Big Batch. Here the original data used to define the current consensus value are from Reynolds *et al.*⁵ They represent the mean values obtained by each of the eight laboratories participating in that study.

relative to other instruments. As there was no consistent difference between measurements by IRMS and MC-ICP-MS across the three secondary standards, values from all studies were included in the analysis of the overall dataset.

Reported average values for each standard and their uncertainties ($2\sigma_{\text{SD}}$) were plotted over time to assess whether values for any standard showed systematic temporal variation (Fig. S1–S2, SI). None of the time series showed a statistically significant trend over time (Table 1).

Histograms of the mean values for each standard and the associated probability density functions are shown in Fig. 1–4. Each probability density function was modeled using kernel

density estimation with the optimal bandwidth (h) based on Silverman's approximation¹⁶ as:

$$h = 0.9 \min \left(2\sigma_{\text{SD}}, \frac{\text{IQR}}{1.34} \right) N^{-1/5}$$

where $2\sigma_{\text{SD}}$ is the standard deviation, IQR is the interquartile range and N is the number of observations.

The histograms also show the original data used to establish the current consensus values.^{5,7} For BHVO-2, each datum is the mean $\delta^{30}\text{Si}$ value from separate analytical runs from the single laboratory where the measurements were performed.⁷ (Note that these values are represented as a single mean in

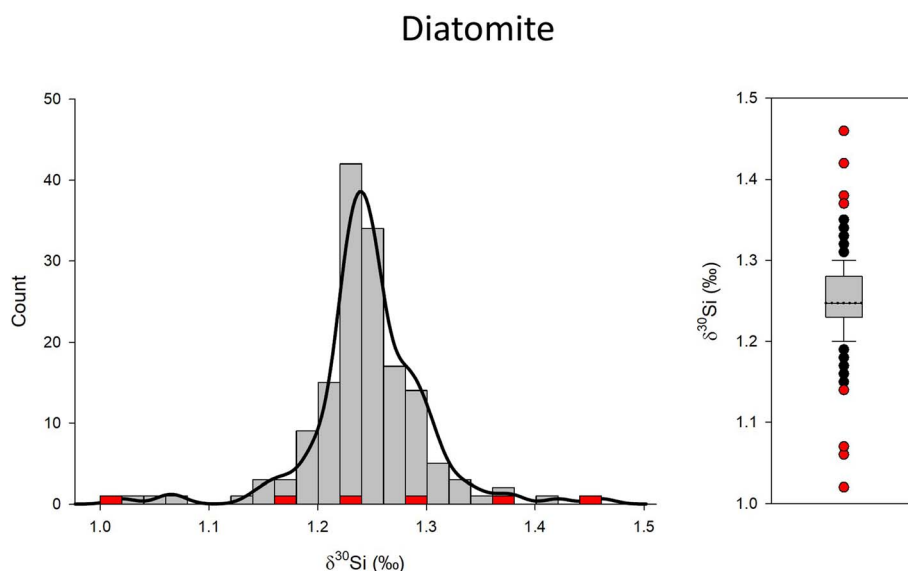


Fig. 3 As in Fig. 2 except for the secondary standard diatomite. Here the original data used to define the current consensus value are from Reynolds *et al.*⁵ They represent the mean values obtained by each of the eight laboratories participating in that study.

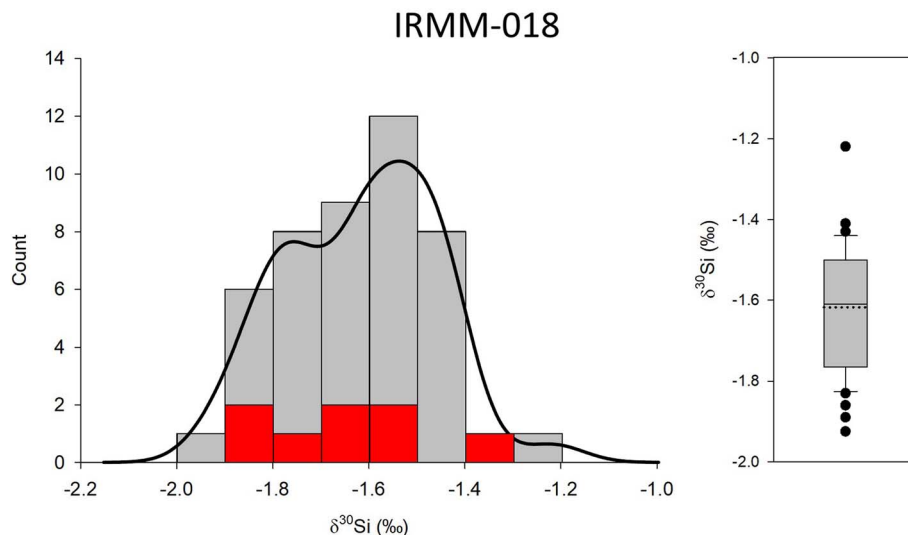


Fig. 4 As in Fig. 2 except for the secondary standard IRMM-018. Here the original data used to define the current consensus value are from Reynolds *et al.*⁵ They represent the mean values obtained by each of the eight laboratories participating in that study.

Table 2 Statistical results for secondary standards (arithmetic means) based on the updated literature compilation (SEM = standard error of the mean; MAD = mean absolute deviation)

	Standard	Mean $\delta^{30}\text{Si}$ (‰)	$1\sigma_{\text{SD}}$	SEM	Median $\delta^{30}\text{Si}$ (‰)	MAD	N
With outliers	BHVO-2	-0.28	0.03	0.003	-0.28	0.02	83
	Big batch	-10.57	0.13	0.017	-10.60	0.07	66
	Diatomite	+1.25	0.05	0.004	+1.25	0.02	154
	IRMM-018	-1.62	0.15	0.023	-1.60	0.12	45
No outliers	BHVO-2	-0.28	0.02	0.003	-0.28	0.01	81
	Big batch	-10.57	0.13	0.017	-10.59	0.08	65
	Diatomite	+1.25	0.04	0.003	+1.25	0.02	146

computations as they are from a single laboratory.) For Big Batch, Diatomite and IRMM018, the original consensus value was established through analysis by several laboratories. In those cases, the original data on the histograms represent the mean value from each participating laboratory. Box-and-whisker plots of all data for each secondary standard are also presented.

The identification of outliers as recommended by ISO 13528 (ref. 14) and Ellison *et al.*¹⁵ is hampered by our use of published values as we cannot evaluate analytical issues with specific measurements. Statistical outliers were thus identified using three methods: (1) $\delta^{30}\text{Si}$ data whose absolute values were $> Q3 + 1.5 \times \text{IQR}$ or $< Q1 - 1.5 \times \text{IQR}$,¹⁷ (2) data where the absolute values of the modified Z -score exceeded 3.5,¹⁸ and (3) data whose Hampel estimator exceeds 3.0, *i.e.* $(\delta^{30}\text{Si} - \tilde{X})/\text{MAD} > 4.5$, where $\tilde{X}$ is the median and MAD is the median absolute deviation of all $\delta^{30}\text{Si}$ values under consideration.¹⁹ Data points were considered outliers if they met all three criteria. By this procedure the data for IRMM-018 did not contain any outliers, while those for Diatomite contained 8, those for BHVO-2 had 2 and those for Big Batch had 1. Outliers are indicated by the red symbols in the whisker plots presented in Figures 1–4.

Comparison across measures of central tendency show little effect of the presence of outliers (Table 2). The means and medians computed with and without outliers are identical to within two decimal points for all secondary standards. Removing outliers decreased σ_{SD} slightly. MAD showed a more varied response with the removal of outliers increasing slightly for Big Batch, decreasing slightly for BHVO-2 and remaining unchanged for Diatomite.

Table 3 Statistical results for secondary standards with weighted means (weighting factors $1/\sigma_{SD}^2$). Note change in N as not all studies reported uncertainty estimates

	Standard	Mean $\delta_{30}\text{Si}$	$1\sigma\text{SD}$	95% CI	N
With outliers	BHVO-2	-0.29	0.02	0.005	83
	Big batch	-10.57	0.13	0.03	66
	Diatomite	+1.25	0.04	0.006	154
	IRMM-018	-1.65	0.14	0.04	45
No outliers	BHVO-2	-0.29	0.02	0.004	81
	Big batch	-10.56	0.12	0.03	65
	Diatomite	+1.25	0.03	0.005	146

Table 4 Comparison of revised isotope values compared to the original consensus values

Standard	Revised				Original			
	Mean $\delta^{30}\text{Si}$ (‰)	$1\sigma_{\text{SD}}$	95% CI	N (reports)	Mean $\delta^{30}\text{Si}$ (‰)	$1\sigma_{\text{SD}}$	95% CI	N (labs)
BHVO-2	−0.29	0.02	0.004	81	−0.29	0.27	0.28	6
Big batch	−10.56	0.12	0.03	65	−10.48	0.27	0.25	7
Diatomite	+1.25	0.03	0.005	146	+1.26	0.10	0.10	6
IRMM-018	−1.65	0.14	0.04	45	−1.65	0.11	0.09	8

Final estimates with and without outliers are shown in Table 3. Estimates were computed as weighted means with weights $1/\sigma_{\text{SD}}^2$ (ref. 15), where σ_{SD} is the standard deviation of the mean value for a given secondary standard reported in each publication. Studies that did not report uncertainty values (see SI) were necessarily excluded from this analysis. The removal of outliers for Diatomite and BHVO-2 did not change the weighted means but improved the 95% confidence interval (95% CI) slightly. The removal of outliers shifted the weighted mean for Big Batch by 0.04‰ and decreased the 95% CI. The final consensus value estimates we report are weighted means excluding outliers, as recommended by Ellison *et al.*¹⁵

Comparison of the updated and original mean isotope values for these standards shows very small differences: 0.00‰ (0%) for BHVO-2 and IRMM-018, −0.01‰ (0.8%) for diatomite, and −0.05‰ (0.5%) for Big Batch (Table 4). Examining the distribution of the original data from ref. 5 and 7 relative to the literature compilation for each standard (Fig. 1–4), this level of agreement almost seems fortuitous in some cases. For Big Batch and IRMM-018, none of the original data establishing the original consensus values were considered outliers by our criteria. However, three of the six outlier values for Diatomite in the present analysis are from the publication establishing their original consensus value.⁵ For BHVO-2, two of the six values reported by Abraham *et al.*²⁰ would be considered outliers in the present analysis (Fig. 1). Outliers from the original studies include measurements by both MC-ICP-MS and IRMS. They occur for a basalt (BHVO-2) and a calcined diatomite (Diatomite), so it is not a function of the type of material analyzed. Inconsistencies across or within laboratories with regard to sample preparation or instrument performance (especially in the early years of method development) are among the factors that might be involved in producing this result, but these cannot be evaluated when analyzing data taken from the literature. Thus, we are not able to determine the reason(s) for original data being outliers in the present analysis.

All of the differences between the prior and our updated consensus values are in statistical agreement (average $2\sigma_{\text{SD}}$ for the studies used here is $\pm 0.06\%$). The biggest change for all standards was a significantly improved uncertainty estimate (95% CI) due to the larger sample size in this new compilation. Standard deviations also decreased for BHVO-2, Big Batch and Diatomite, while that for IRMM-018 increased somewhat compared to the results reported in Reynolds *et al.*⁵ This agrees

with the higher variability in reported values for IRMM-018 noted by Reynolds *et al.*⁵ compared to Big Batch and Diatomite.

Our analysis results in revised consensus values for the four secondary standards that are each very close to their original consensus values. Mao *et al.*¹⁰ found a similar result when re-evaluating Diatomite (1.240 ± 0.028 , 2SD, $N = 16$), BHVO-2 (0.287 ± 0.021 2SD, $N = 23$) and IRMM018 (-1.645 ± 0.040 2SD, $N = 13$) using a considerably smaller dataset available from the Geological and Environmental Reference Materials database (GeoReM), with deviations from original consensus values of 0‰ for BHVO-2 and IRMM-018 and −0.04‰ for Diatomite. The level of agreement seen by us and¹⁰ is reassuring, in that all previous evaluations of data quality using the original consensus values for all four secondary standard materials remain robust.

Reference material availability

IRMM-018 is no longer available and has been replaced with IRMM-018a.²¹ The revised values reported here will aid laboratories that still analyze IRMM-018 from their personal inventory. BHVO-2 can be purchased from the United States Geological Survey (<https://www.usgs.gov/labs/reston-stable-isotope-laboratory/reference-materials-and-calibration-services>). Big Batch and Diatomite are available for the price of shipping from co-author Jeffrey Krause at the Dauphin Island Sea Lab.

Author contributions

Mark Brzezinski (conceptualizing, data curation, methodology, formal analysis, investigation, methodology, visualization, writing-original draft), Colin Maden (conceptualization, methodology, writing – review and editing), Katharine Hendry, Gregory de Souza, Jeffrey Krause (conceptualization, writing – review and editing).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6ja00094k>.

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