




RESEARCH ARTICLE

New Ag_3PO_4 comparison material for stable oxygen isotope analysis

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Rationale: A silver phosphate reference material (Ag_3PO_4) for the measurement of stable oxygen isotope compositions is much needed; however, it is not available from the authorities distributing reference materials. This study aims to fill this gap by calibrating a new Ag_3PO_4 stable isotope comparison material produced by the University of Natural Resources and Life Sciences (BOKU).

Methods: Aliquots of Ag_3PO_4 were distributed to four laboratories who frequently measure the $\delta^{18}\text{O}$ value in Ag_3PO_4 ; the University of Natural Resources and Life Sciences (BOKU), the University of Western Australia (UWA), the University of Helsinki (UH), and the Helmholtz Centre for Environmental Research (UFZ). The instruments used to perform the measurements were high-temperature conversion elemental analysers coupled with continuous flow isotope ratio mass spectrometers. The working gas $\delta^{18}\text{O}$ value was set to 0‰ and the normalization was done by a three-point linear regression using the reference materials IAEA-601, IAEA-602, and NBS127.

Results: The mean $\delta^{18}\text{O}$ value of the new BOKU Ag_3PO_4 comparison material on the VSMOW-SLAP scale is 13.71‰ and the combined uncertainty is estimated as $\pm 0.34\%$. This estimated uncertainty is within the range typical for comparison materials of phosphates and sulphates. Consistent results from the different laboratories probably derived from similar instrumentation, and use of the same reference materials and normalization procedure. The matrix effect of the different reference materials used in this study was deemed negligible.

Conclusions: The BOKU Ag_3PO_4 can be used as an alternative comparison material for stable oxygen isotope analysis and is available for stable isotope research laboratories to facilitate calibration.

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1 | INTRODUCTION

Phosphorus (P) is one of the common elements in the Earth's crust and crucial for all life forms due to its abundance in several important biomolecules (DNA, RNA, biomembranes, ATP). Phosphorus has only one stable isotope, ^{31}P , and several radioactive isotopes. In nature, phosphorus is usually present as phosphate (PO_4^{3-}) and almost exclusively as the ^{31}P isotope. Oxygen in PO_4^{3-} can be represented by one or all of its stable isotopes (^{16}O , ^{17}O , and ^{18}O). These stable oxygen isotopes can be used to trace sources of PO_4 , because, in the absence of biological activity, the isotope exchange of oxygen with surrounding water molecules under common environmental conditions of the hydrosphere is negligible, even on geological time scales. However, in the presence of biological processes, the enzymatic activity will rapidly exchange the oxygen between phosphate and water. A temperature-dependent isotope equilibrium between oxygen in water and phosphate is observed which has been used in palaeoclimatology, palaeohydrology, palaeoseasonality and bioarcheology.^{1–6} Recently, the stable isotopic composition of oxygen in phosphate has been increasingly used in environmental studies to identify sources of phosphate pollution and to understand biological processes in aquatic and terrestrial ecosystems.^{7–9}

Over the last 50 years, extensive methodological development has been conducted to measure PO_4 in various environmental matrices. In the 1970s, early methods relied on fluorinating phosphates and conversion of the released oxygen into CO_2 for isotope measurements. Previous steps involved the precipitation of phosphate as BiPO_4 ,¹⁰ but BiPO_4 precipitate is hygroscopic, and great care was needed to avoid contamination with water. The most recent methods rely on the precipitation of PO_4 as silver phosphate (Ag_3PO_4), which is non-hygroscopic and does not incorporate water in its crystals during precipitation.¹¹ The high-temperature conversion of Ag_3PO_4 was first introduced by O'Neil et al.¹² Nowadays, measurement is commonly done using high-temperature conversion (HTC) in an elemental analyser (EA) coupled to a continuous flow isotope ratio mass spectrometer.^{13,14} In the majority of studies, the isotope ratio of $^{18}\text{O}/^{16}\text{O}$ is targeted and only a few studies have investigated $^{17}\text{O}/^{16}\text{O}$ in PO_4 precipitates.¹⁵

Accurate measurement of the stable oxygen isotope ratio requires certified calibration standards similar to the sample matrix. The suitability of a Ag_3PO_4 reference standard for the determination of the oxygen isotope composition has long been recognized and various Ag_3PO_4 in-house laboratory standards have been used.¹⁴ The Ag_3PO_4 stable oxygen isotope composition changes very little during storage (high stability and low hygroscopicity) and it is easy to handle. For these reasons, it has been proposed as a good candidate to become a reference material for the determination of the $^{18}\text{O}/^{16}\text{O}$ ratios of phosphate.^{13,14,16} In 2010, Ag_3PO_4 comparison materials (UMCS-1, UMCS-2, and AGPO-SCRI) were introduced¹⁷ but only small amounts of these materials are still available and the need for an alternative comparison material has been recognized. The National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) had produced a Rock phosphate standard known as SRM120c,

previously NBS120c, which was certified for the measurement of the concentrations of constituents, but it is also used widely as a stable oxygen isotope standard.^{14,18,19} Recently, the Reston Stable Isotope Laboratory of the U.S. Geological Survey (Reston, VA, USA) has introduced two Ag_3PO_4 reference materials, USGS80 and USGS81, but the values have not been published and the uncertainty of these materials is not as yet been provided. Elemental Microanalysis Ltd (Okehampton, UK) has also introduced an Ag_3PO_4 standard, but information on the analysis and evaluation procedure is not yet available. This study aimed to calibrate a new Ag_3PO_4 comparison material and test consistency between laboratories using exactly the same normalization method and standards in each laboratory.

2 | MATERIALS AND METHODS

The University of Natural Resources and Life Science (BOKU) prepared a silver phosphate comparison material (named BOKU Ag_3PO_4) for measurement of the stable oxygen isotope composition from a commercially available Ag_3PO_4 (98% purity, Sigma Aldrich, St Louis, MO, USA). This material was dried (105°C), ball-milled, and distributed to other stable isotope laboratories that frequently measure $\delta^{18}\text{O}$ values in Ag_3PO_4 . The contributing laboratories were the University of Natural Resources and Life Science (BOKU, Tulln, Austria), The University of Western Australia (UWA, Crawley, Australia), the University of Helsinki (UH, Helsinki, Finland), and the Helmholtz Centre for Environmental Research (UFZ, Halle, Germany).

All contributing laboratories stored the BOKU Ag_3PO_4 comparison material, the international reference materials, and laboratory standards in a desiccator filled with a drying agent to prevent moisture absorption. In addition, the UFZ ground and oven-dried (103°C) all the comparison and reference materials. Aliquots were weighed into silver capsules 1 day before analysis and stored in a desiccator. The UFZ added nickelized carbon to the Ag_3PO_4 and NBS127 standards before folding the capsules to improve the reaction between the oxygen in the samples and the carbon, enhancing the production of CO_2 .^{20,21} Detailed information on the sample preparation and storage can be found in Table 1.

Measurements for stable oxygen isotope analysis of bulk samples were done by continuous flow isotope ratio mass spectrometry (CF-IRMS). Oxygen in the sample was converted into carbon monoxide in an oxygen-free atmosphere via HTC. The produced gases were separated and entered a continuous flow gas management device needed to manage the introduction of carbon monoxide sample gas and working gas to a magnetic sector mass spectrometer. The instrumental and operational specifications of the participating laboratories are listed in Table 2. The samples packed in silver capsules were loaded into an autosampler and subsequently flushed with helium (He) to remove atmospheric air. The samples were then dropped into a graphite crucible positioned at the hottest zone of a pyrolysis reactor. The reactor consisted of an outer ceramic and inner glassy carbon tube filled with glassy carbon granules over a silver wool plug, and operated with reverse He flow. BOKU, UH, and UFZ

TABLE 1 Details on the sample preparation for oxygen stable isotope measurements

Laboratory	Sample information		Capsule specification producer, type
	Ag ₃ PO ₄ (mg)	Treatment, storage	
UWA, Australia	0.5–0.7	Desiccator with silica gel	IVA Analysentechnik, Meerbusch, Germany
BOKU, Austria	0.73–0.86	Desiccator with silica gel	IVA Analysentechnik, Ag (for solids), 3.3 × 5 mm
UH, Finland	0.44–0.46	Desiccator with silica gel and P ₂ O ₅	IVA Analysentechnik, Ag (for solids), 3.3 × 5 mm
UFZ, Germany	0.38–0.45	grinding, 103°C drying, desiccator storage, nickelized carbon additive ^a	HEKAtech, Wegberg, Germany, Ag (for solids), 4 × 6 mm

^a0.1–0.3 mg additives were added to Ag₃PO₄, BaSO₄ (NBS127), and laboratory standards, but not to the benzoic acid reference materials.

TABLE 2 Instrumental and operational specifications for the determination of the stable oxygen isotope composition ($\delta^{18}\text{O}$)

Laboratory	IRMS instrumentation producer, model	Continuous flow gas management device producer, model	High-temperature conversion elemental analyser				GC column, column temp.	Autosampler producer, model
			Producer, model	He carrier flow	Reactor filling, reaction temperature	Interconnected trap		
UWA, Australia	Thermo Finnigan, Bremen, Germany, Delta ^{Plus} XL	Thermo Finnigan, ConFlo III	Thermo Finnigan, TC/EA	80 mL/min (1.0 bar)	Outer ceramic -, inner glassy carbon tube, glassy carbon granules filling, 1450°C	None	5 Å mol. sieve, 80 °C	Thermo Finnigan, MAS 200R
BOKU, Austria	Thermo Finnigan, Delta ^{Plus} XP	Thermo Finnigan, ConFlo III	Thermo Finnigan, TC/EA	140 mL/min (1.3 bar)	Outer ceramic -, inner glassy carbon tube, glassy carbon granules filling, silver wool plug, 1440°C	Glassy carbon granules, NaOH-coated silica (Ascarite®), Mg(ClO ₄) ₂ (1/3 each)	5 Å mol. sieve, 75°C	Thermo Finnigan, MAS 200R
UH, Finland	Thermo Scientific, Bremen, Germany, Delta ^V Plus	Thermo Scientific, ConFlo IV	Thermo Scientific, CNSOH EA	80 mL/min	Outer ceramic -, inner glassy carbon tube, glassy carbon granules filling, silver wool plug, 1430 °C	Granulated activated carbon/anhydrous Mg(ClO ₄) ₂ (1/2 each)	5 Å mol. sieve, 50°C	Costech, Valencia, CA, USA, zero blank
UFZ, Germany	Finnigan, Bremen, Germany, Delta S	Thermo Finnigan, ConFlo II	HEKAtech, Wegberg, Germany, HTC	120 mL/min	Glassy carbon, 1450°C	Mg(ClO ₄) ₂ (HEKAtech GmbH)	5 Å mol. sieve, 65°C	EuroVector, Pavia, Italy, zero blank autosampler VECTOR SAS-01

purified the produced gases via a trap to remove traces of water and carbon dioxide. Gas separation was accomplished in a stainless steel gas chromatography column filled with 5 Å molecular sieve. After passing through a temperature conductivity detector (TCD) (at UH), part of the CO gas was then transferred to the isotope ratio mass spectrometer. After electron ionization, the abundance of the mass-to-charge (m/z) ratio of the masses 28, 29, and 30 were continuously measured in a collector array consisting of Faraday cups.

Each laboratory analysed the comparison material in a minimum of two independent measuring rounds (on different days) with a minimum of 10 individual measurements. The working gas $\delta^{18}\text{O}$ value was set to 0‰ and the normalization to the VSMOW-SLAP scale was done using the internationally certified reference materials IAEA-601 ($\delta^{18}\text{O}_{\text{VSMOW}} = +23.14 \pm 0.19\text{‰}$), IAEA-602 ($\delta^{18}\text{O}_{\text{VSMOW}} = +71.28 \pm 0.36\text{‰}$) (both benzoic acid), and NBS127 (barium sulphate)

($\delta^{18}\text{O}_{\text{VSMOW}} = +8.59 \pm 0.26\text{‰}$) for each measuring round.^{22,23} Benzoic acid reference materials were chosen because they convert quantitatively even at lower temperatures, while NBS127 was chosen because it requires close contact to the carbon for quantitative conversion and proved a reliable sulphate reference material.²² We expected close behaviour of NBS127 and Ag₃PO₄ with respect to peak shape and conversion efficiency. For each measurement round, the blank contribution was checked by blank capsule measurements (including additives, which were used at UFZ). The instrumental drift was monitored by using additional reference material measurements and the raw data was corrected if necessary (blank correction and linear drift correction) (Table S2, supporting information). At UWA, BOKU, and UFZ the instrument drift and blank were negligible and the need for linearity correction was avoided by adjusting the weights of all standards to generate the same level of CO signal. At UH the

results were corrected for instrumental drift determined from reference materials. Following drift correction all raw results were normalized to the VSMOW-SLAP international scale using a three-point linear regression constructed based on IAEA-601, IAEA602, and NBS127 measured and certified values.²⁴

3 | RESULTS AND DISCUSSION

The information on the instrumental drift, slope, intercept, and coefficient of determination of the linear regression as well as the number of measurements and standard deviation of the reference materials used to compute the regression line is summarized in Table S1 (supporting information). The analytical reproducibility of additional laboratory standards is presented in Table S2 (supporting information). All the participating laboratories had experienced lower reproducibility of the $\delta^{18}\text{O}$ value for IAEA-602 than for that of IAEA-601. The observation was that this was not due to storage (age) effects, as it was also observed for newly purchased batches of the reference standard (BOKU and UH). Low reproducibility has been previously noted by Brand et al,²² and inhomogeneity of the material was deemed responsible. Brand et al²² suggested regrinding of the reference material. In this way, inhomogeneity was minimized and not observed, at least with sample amounts of 5 mg. Regrinding of IAEA-602 was only done by UFZ. In addition, a 5-mg sample is less suitable for the presented analytical method using TC/EA.

The arithmetic mean (\bar{x}) and standard deviation (1σ) of the $\delta^{18}\text{O}$ value of the new BOKU Ag_3PO_4 comparison material from the single measurements was $13.74 \pm 0.33\text{‰}$ on the VSMOW-SLAP scale ($n = 100$), while the mean (\bar{x}) and standard deviation (1σ) of the laboratories was $13.71 \pm 0.19\text{‰}$ ($n = 4$) and the median value of the laboratories was 13.80‰ ($n = 4$) (Table 3).

$$\bar{x} = \frac{\sum_{i=1}^n \delta_i}{n}, \quad (1)$$

where δ_i is the δ value of the measurements and n is the number of independent measurements.

$$\sigma = \frac{\sum_{i=1}^n |\delta_i - \bar{x}|}{n-1}, \quad (2)$$

where δ_i is the δ value of the measurements, \bar{x} the mean value of n measurements, and n is the number of independent measurements.

The arithmetic means of single measuring rounds were all within two times the uncertainty as estimated below (0.34‰ , $k = 1$) and therefore all data was used for further calculations.

While the mean values from BOKU, UFZ, and UH are very close (range = 0.02‰), the mean value from UWA is about 0.4‰ lower, which explains the slight difference between the arithmetic mean of all single measurements and the median of the single laboratories (0.06‰). The arithmetic mean of the $\delta^{18}\text{O}$ value of the

laboratories, 13.71‰ , is defined as the mean value of the BOKU Ag_3PO_4 comparison material.

Calibrating with the organic standards (IAEA-601 and IAEA-602), excluding barium sulphate NBS127 from the normalization only slightly increased the mean $\delta^{18}\text{O}$ value to $13.77 \pm 0.36\text{‰}$ ($n = 100$) (Figure 1). The arithmetic mean of all measurement rounds was within the uncertainty ($k = 2$) when calibrating with IAEA-601 and IAEA-602. We discarded the bias associated with differences in the chemical matrices of the standards. We also used the two-point calibration to calculate NBS127 and used it as a quality control (Table S3, supporting information).

For uncertainty estimation, we ultimately adapted approaches presented by Skrzypek and Sadler²³ and Assonov et al²⁵ to the requirements of a laboratory comparison study, where raw data of the reference material might not be available and the referencing strategy was not consistent with respect to the number of measurements of reference material. Three major uncertainty sources were considered and combined into the uncertainty budget: (i) the uncertainty of the reference materials used for the normalization to the VSMOW-SLAP scale and their propagation during the normalization procedure; (ii) the uncertainty associated with the homogeneity of the BOKU comparison material and analytical reproducibility; and (iii) the uncertainty associated with the analytical scatter between participating laboratories.

(i) We estimated the uncertainty associated with the reference materials and normalization using a Monte Carlo approach for a limited number of 3 permutations with repetition. Linear regression models of 27 possible combinations considering the assigned value, assigned value plus uncertainty, and assigned value minus uncertainty of each of three reference materials (IAEA-601: $23.14 \pm 0.19\text{‰}$; IAEA-602: $71.28 \pm 0.36\text{‰}$; NBS127: $8.59 \pm 0.26\text{‰}$)²² were applied for normalization of the value determined for the BOKU standard (13.71‰). The standard deviation of the normalized Ag_3PO_4 comparison material gives the average uncertainty introduced by the reference material uncertainty ($u_{\text{calibration}} = 0.14\text{‰}$). The uncertainty is a conservative estimate as it is based on only two replicate measurements.

(ii) The uncertainty resulting from the heterogeneity of the distributed comparison material along with analytical reproducibility, reflecting the instrument precision, was estimated by calculating the arithmetic mean of the standard deviations of the single measurement rounds; $u_{\text{homogeneity}} = 0.26\text{‰}$.

(i) + (ii) The homogeneity uncertainty was included in the Monte Carlo simulation presented above (i) by repeating all calculations using all regression models for the determined BOKU value (13.71‰) plus and minus $u_{\text{homogeneity}}$; $u_{\text{calibration} + \text{homogeneity}} = 0.26\text{‰}$.

(iii) The analytical uncertainty reflecting the analytical scatter between participating laboratories might be estimated by calculating the standard deviation of the arithmetic mean of the single measurement rounds using either the BOKU Ag_3PO_4 comparison material or the reference material NBS127. For the latter case normalization was done with IAEA-601 and IAEA-602 only (refer to

TABLE 3 Single measurements, arithmetic mean (\bar{x}) and standard deviation (1σ) of the measurement rounds, the laboratories and the single measurements as well as the arithmetic mean (\bar{x}), standard deviation (1σ) and median of the laboratories results ($n = 4$) of the BOKU Ag_3PO_4 comparison material are presented. All $\delta^{18}\text{O}$ values on the VSMOW-SLAP scale were normalized using IAEA-601, IAEA-602, and NBS127

Replicate	$\delta^{18}\text{O}_{\text{VSMOW}} [\text{‰}]$							
	UWA	UWA	BOKU	BOKU	UH	UH	UFZ	UFZ
1	13.48	13.93	14.51	14.03	13.59	13.89	13.54	13.78
2	13.30	13.57	13.64	14.38	13.60	13.96	13.73	14.08
3	13.69	13.86	13.82	14.55	13.75	13.74	13.71	14.37
4	13.80	12.64	13.50	13.62	13.55	13.82	13.61	13.98
5	13.60	12.78	13.25	13.83	13.73	14.01	13.46	13.64
6	13.67	13.28	13.66	13.55	13.57	14.09	14.02	13.99
7	13.73	13.13	13.59	13.33	13.88	13.82	13.72	13.78
8	13.48	13.34	14.00	13.57	13.65	14.02	13.62	14.15
9	13.12	13.39	13.91	13.65	13.67	13.86	14.43	13.99
10		13.19	13.56	13.80	13.75	14.01	13.68	13.57
11				13.83	13.90	13.78	14.07	13.89
12					13.59	14.00	13.20	14.15
13					13.76	14.04	13.32	14.05
14					13.58	14.11	13.27	13.90
15					13.76	14.06	13.78	14.00
\bar{x}	13.54	13.31	13.74	13.83	13.69	13.95	13.68	13.95
σ	0.22	0.41	0.34	0.37	0.11	0.12	0.32	0.21
$\bar{x} \pm \sigma$	13.42 \pm 0.35 ($n = 19$)		13.79 \pm 0.35 ($n = 21$)		13.82 \pm 0.17 ($n = 30$)		13.82 \pm 0.30 ($n = 30$)	
$\bar{x} \pm \sigma$	13.74 \pm 0.33 ($n = 100$)							
$\bar{x} \pm \sigma$	13.71 \pm 0.19 ($n = 4$)							
Median	13.80 ($n = 4$)							

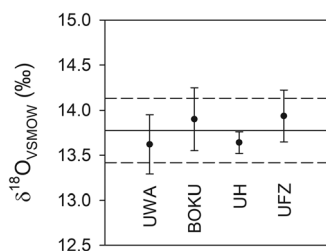


FIGURE 1 The arithmetic means and standard deviations (1σ) of the single labs normalized using IAEA-601 and IAEA-602 only. The arithmetic mean of the results from all laboratories' is given as a solid line with combined uncertainty ($k = 1$) as a dotted line

Figure 1). The analytical uncertainty ($u_{\text{analytical}}$) determined by the BOKU Ag_3PO_4 was 0.21‰, and determined using NBS127 was 0.24‰. The analytical uncertainty determined by the BOKU Ag_3PO_4 was used to calculate the combined uncertainty.

The uncertainty due to the matrix effect was deemed to be negligible. The uncertainty due to water condensation was estimated to be minor due to the identical treatment principle followed. The three uncertainty components were defined as independent and the combined uncertainty (u_{combined}) was calculated as the square

roots of the summarized variances. Using this approach, the uncertainty was estimated to be 0.34‰.

$$u_{\text{combined}} = \sqrt{u_{\text{analytical}}^2 + u_{\text{calibration+homogeneity}}^2} \quad (3)$$

The UH had additional Ag_3PO_4 comparison materials in the measurement rounds, whose $\delta^{18}\text{O}$ values had been published previously, namely $\text{AGPO-SCRI} = 14.58 \pm 0.13\text{‰}$ and Ag_3PO_4 extracted from $\text{NBS120c} = 21.79 \pm 0.15\text{‰}$,¹⁷ to check the quality of the data. These materials were normalized using IAEA-601, IAEA-602 and NBS127, as described above, and attained mean values of 14.6‰ (± 0.2) and 22.9‰ (± 0.2) for AGPO-SCRI and NBS120c ($n = 6$), respectively. The $\delta^{18}\text{O}$ value for AGPO-SCRI was well within the envelope of values reported by Halas et al,¹⁷ but the $\delta^{18}\text{O}$ value of NBS120c was 1.1‰ higher. While the generally accepted estimate for the “correct” $\delta^{18}\text{O}$ value for NBS120c, which is not certified as a stable isotope reference material, is 21.7‰,^{18,19} a range of values has been observed. For example, mean values reported for TC/EA-based analyses from different laboratories range from 21.6 to 22.3‰.¹⁹ The causes of the variability are not exactly known and might relate to e.g. material inhomogeneity, differences in extraction procedures, normalization, and IRMS analytical conditions.

4 | CONCLUSIONS

The mean $\delta^{18}\text{O}$ value and combined uncertainty of the new BOKU Ag_3PO_4 comparison material were determined as $13.71 \pm 0.34\text{‰}$ on the VSMOW-SLAP scale. The new material is available for stable isotope research laboratories to facilitate the calibration of their laboratory comparison material and requests can be sent to Andrea Watzinger (andrea.watzinger@boku.ac.at). The differences between uncertainties calculated using various methods should be taken into account when comparing analytical uncertainties from different laboratories and publications.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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