Synthesis of In-House Produced Calibrated Silver Phosphate with a Large Range of Oxygen Isotope Compositions

Christophe Lécuyer (1)*, François Fourel (2), Magali Seris (1), Romain Amiot (1), Jean Goedert (1, 3) and Laurent Simon (2)

(1) LGT-TPE, UMR 5276, CNRS, Université Claude Bernard Lyon 1, Villeurbanne, 69622, France
(2) LEHNA, UMR 5023, CNRS, Université Claude Bernard Lyon 1, ENITPE, Villeurbanne, 69622, France
(3) PACEA, UMR 5199, CNRS, Université de Bordeaux, Bâtiment B18, Allée Geoffroy Saint-Hilaire, CS 50023, Pessac, FR-33615, France
* Corresponding author. e-mail: christophe.lecuyer@univ-lyon1.fr

The large range of stable oxygen isotope values of phosphate-bearing minerals and dissolved phosphate of inorganic or organic origin requires the availability of in-house produced calibrated silver phosphate of which isotopic ratios must closely bracket those of studied samples. We propose a simple protocol to synthesise Ag₃PO₄ in a wide range of oxygen isotope compositions based on the equilibrium isotopic fractionation factor and the kinetics and temperature of isotopic exchange in the phosphate–water system. Ag₃PO₄ crystals were obtained from KH₂PO₄ that was dissolved in water of known oxygen isotope composition. Isotopic exchange between dissolved phosphate and water took place at a desired and constant temperature into PYREX™ tubes that were placed in a high precision oven for defined run-times. Samples were withdrawn at desired times, quenched in cold water and precipitated as Ag₃PO₄. We provide a calculation sheet that computes the δ¹⁸O of precipitated Ag₃PO₄ as a function of time, temperature and δ¹⁸O of both reactants KH₂PO₄ and H₂O at t = 0. Predicted oxygen isotope compositions of synthesised silver phosphate range from -7 to +31‰ VSMOW for a temperature range comprised between 110 and 130 °C and a range of water δ¹⁸O from -20 to +15‰ VSMOW.

Keywords: oxygen isotopes, isotopic fractionation, kinetics, silver phosphate, internal reference.

Received 08 Feb 19 – Accepted 12 Jun 19

During the past decades, the rise of automated devices coupled to mass spectrometers operating in continuous flow or in dual-inlet mode have resulted in an explosive growth of the number of data published in scientific fields exploiting the stable isotope ratios of organic and inorganic compounds. Consequently, there is an increasing use and need for developing in-house produced materials calibrated against certified reference materials. Moreover, a large range of isotopic compositions is highly desirable to bracket the expected compositions of the studied sample collection as well as to be able to perform a two-point calibration, which is required for the acquisition of high-quality data.

In Earth and Archaeological Sciences, to only mention the most concerned research fields, the $^{18}O/^{16}O$ ratio of the phosphate radical (PO₄³⁻) is now widely used to reconstruct the palaeoclimates of the Earth (Kolodny and Raab 1988, Fricke and O’Neil 1996, Amiot et al. 2004, Joachimski et al. 2012, Goedert et al. 2017), the thermophysiology and ecology of extinct vertebrates (Barrick and Showers 1994, Fricke and Rogers 2000, Amiot et al. 2006, Tütken and Vennemann 2009, Bernard et al. 2010, Rey et al. 2018), the source and recycling of dissolved phosphate in natural waters (Markel et al. 1994, McLaughlin et al. 2006, Pistocchi et al. 2017) as well as the diet and living environment of past human populations (White et al. 1998, Evans et al. 2006, Touzeau et al. 2013, Lightfoot and O’Connell 2016, Pellegrini et al. 2016). The most common way to determine the $^{18}O/^{16}O$ ratio of the phosphate radical is to isolate it as silver phosphate (Ag₃PO₄) crystals through a wet chemistry procedure (Crowson et al. 1991). Then, they are pyrolysed in the presence of graphite at high temperature to produce either CO₂ or CO measured either offline or online with an isotope ratio mass
spectrometer (O’Neil et al. 1994, Lécuyer et al. 1998, 2007, Fourel et al. 2011). Fluorination has also been proved to be a precise and accurate technique that provided the first determination value of the δ<sup>18</sup>O<sub>SMOW</sub> value of the Miocene Florida phosphate NIST SRM 120c (Lécuyer et al. 1993). Whatever the research field, the δ<sup>18</sup>O value of calcium phosphate minerals (e.g., biogenic, magmatic or hydrothermal apatite) and dissolved phosphate (H<sub>2</sub>PO<sub>4</sub>–, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>) range world-wide from about a few per mil up to values close to 30‰. Indeed, high-temperature apatites of magmatic or hydrothermal origin have δ<sup>18</sup>O ranging from 6‰ to 11‰ (Sun et al. 2016). With respect to soils and their connected aquatic environments (rivers, ponds and lakes), dissolved phosphate also displays a large range of oxygen isotope compositions between 8‰ and 25‰ (Markel et al. 1994, Grunau et al. 2005, Angert et al. 2012, Davies et al. 2014, Tamburini et al. 2014, Pistocchi et al. 2017, Granger et al. 2017, Baute et al. 2018). In the case of dissolved phosphate being isotopically equilibrated with ambient water through biological recycling (Longinelli et al. 1976, Liang and Blake 2009, Chang and Blake 2015, von Sperber et al. 2017), it is expected to have δ<sup>18</sup>O values that range from 6‰ (high-latitude freshwater environments) to ≈ 20‰ for seawater and to ≈ 22‰ for low-latitude freshwater environments in agreement with the available isotope fractionation equations (Kalodny et al. 1983, Lécuyer et al. 2013). In the case of biogenic apatites, their δ<sup>18</sup>O values range from a few ‰ for vertebrates drinking highly 18O-depleted waters (δ<sup>18</sup>O as low as −20‰) relative to SMOW (high-altitude or high-latitude environments; e.g., Rey et al. 2018) up to about 30‰ for vertebrates living in and environments (Lécuyer et al. 1999a).

To the present time researchers have used NIST SRM 120c for which an agreed δ<sup>18</sup>O<sub>SMOW</sub> value of 21.7 ± 0.2‰ (VSMOW) was only established in recent years. Indeed, Chenery et al. (2010) proposed a comparable value of 21.7 ± 0.7‰ after a 6-month period of repeated measurements of NIST SRM 120c calibrated against NBS 127 barium sulfate, which is consistent with the mean value of published data for NIST SRM 120c (21.5 ± 0.5‰) analysed in different laboratories (Chenery et al. 2010). Thereafter, Halas et al. (2011) confirmed the absence of any sizable isotope fractionation effect during the conversion of Ag<sub>3</sub>PO<sub>4</sub> into CO, and proposed a mean δ<sup>18</sup>O value of 21.8 ± 0.2‰ for NIST SRM 120c based on inter-laboratory calibrations. It is also worth noting that Vennemann et al. (2002) proposed a significantly higher value of 22.5‰ for NIST SRM 120c, although later Vennemann (2012) concluded that the most accurate value for NIST SRM 120c is likely close to 21.7‰. This value of 21.7 ± 0.2‰ for NIST SRM 120c is now widely accepted as exemplified by the recent study published by Huang et al. (2018). It has also to be pointed out that an isotopic ratio of 21.7 ± 0.16‰ for NIST SRM 120c was determined for the first time by using quantitative fluorination 25 years ago (Lécuyer et al. 1993). Nevertheless, it must be underlined that the Florida phosphate NIST SRM 120c is a compositional, not an isotopic international reference material, and hence, its oxygen isotope ratio has never been officially certified. In order to comply with the IUPAC recommendations (Brandt et al. 2014), a two-point calibration can also be performed with NBS 127, which is a barium sulfate calibrated reference material for oxygen isotopes (δ<sup>18</sup>O = 9.3‰ VSMOW), as was done by, for example, Rey et al. (2018) and Goedert et al. (2018). However, we underline that NBS 127 is a different matrix, (i.e., a barium sulfate instead of a silver phosphate) – a chemical difference that needs to be taken into account during calibration procedures even though the recently developed ‘purge-and-trap’ technology was able to overcome this pitfall as shown by Fourel et al. (2011). Moreover, the stock of NBS 127 provided by the IAEA is now exhausted, thus seriously reducing the possibility of calibrating the oxygen isotope composition of solid matrices. Therefore, the need for alternative calibrated material is becoming critical.

Here, we propose a simple and inexpensive protocol to synthesise silver phosphate in a wide range (±35‰) of oxygen isotope compositions based on the thermodynamic properties of the phosphate–water system, more specifically the equilibrium isotopic fractionation factor and the kinetics and temperature of isotopic exchange according to the data published by Lécuyer et al. (1999b). Beyond the theoretical considerations, an Excel calculation sheet is provided (Table S1), which allows the δ<sup>18</sup>O value of precipitated Ag<sub>3</sub>PO<sub>4</sub> to be predicted by tuning various parameters such as the temperature of oxygen isotope exchange, the duration of the reaction and the isotopic compositions of reactants.

**Theoretical background**

**First-order kinetics of isotopic exchange between dissolved phosphate and water**

The most common pH-dependent speciation of phosphorus in aqueous solutions of low ionic strength are (a) the dihydrogen phosphate ion (H<sub>2</sub>PO<sub>4</sub>–), (b) the hydrogen phosphate ion (HPO<sub>4</sub><sup>2-</sup>) and (c) the phosphate ion (PO<sub>4</sub><sup>3-</sup>) according to the three following chemical equilibria at 25 °C (Zeebe and Wolf-Gladrow 2001, Figure 1):
with \( A \) being the Arrhenius pre-exponential factor, \( E_a \) the activation energy (kJ mol\(^{-1}\)) of the isotopic reaction, \( R \) the universal gas constant, \( T \) the absolute temperature (K), \( t \) the time (s), \( \delta^{18}\text{O}(\text{PO}_4) \), the oxygen isotope composition of the reactant at \( t = 0 \), \( \delta^{18}\text{O}(\text{PO}_4) \), the oxygen isotope composition of \( \text{H}_2\text{PO}_4^- \) at any time \( t \) during the course of the isotopic reaction and \( \delta^{18}\text{O}(\text{PO}_4) \), the oxygen isotope composition of \( \text{H}_2\text{PO}_4^- \) at isotopic equilibrium with \( \text{H}_2\text{O} \).

Note that when \( t = 0, \ f = 0 \) and \( \delta^{18}\text{O}(\text{PO}_4) = \delta^{18}\text{O}(\text{PO}_4) \) while when \( t \rightarrow \infty, \ f \rightarrow 1 \) and \( \delta^{18}\text{O}(\text{PO}_4) = \delta^{18}\text{O}(\text{PO}_4) \).

### Experimental determination of thermodynamic variables (\( k, E_a \) and \( \alpha \))

The rate constant \( k \): Lécuyer et al. (1999b) performed a best fit of their data with the Arrhenius law and found a strong temperature dependence of the rate constant \( k \):

\[
\log(k) = 12.35 \pm 0.63 - 6.98 \pm 0.24(10^3T^{-1})
\]

A convenient way to report graphically the rate of isotopic exchange against time is to rewrite Equation (4) as follows:

\[
\ln(1 - f) = -kt
\]

The absolute value of the slope of the straight line for a given temperature \( T \) is the rate constant \( k \) of the reaction. Equation (7) also allows the half-time \( (t_{1/2}) \) of the isotopic reaction to be determined by solving for \( t = 0.5 \) as follows:

\[
t = \frac{0.693}{k}
\]

**The activation energy \( E_a \) of the reaction:** Due to the tetrahedral architecture and covalent bonds (P–O) of the phosphate ion, the activation energy \( E_a \) necessary to promote oxygen isotope exchange between phosphate and water molecules is very high, with a value of 133.6 ± 4.6 kJ mol\(^{-1}\) at pH = 5 (Lécuyer et al. 1999b). The activation energy \( E_a \) is calculated from the slope of the straight line defined by Equation (6) combined with Equation (5).

**The fractionation coefficient \( \alpha \) between \( \text{H}_2\text{PO}_4^- \) and \( \text{H}_2\text{O} \):** At thermodynamic equilibrium, and according to the Mass Action Law, we can write the following isotopic exchange equation:

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}
\]

Rearranging the terms in Equation (9), the equilibrium constant or isotopic fractionation factor called \( \alpha \) which is determined for a given temperature \( T \), is expressed as follows:

\[
\alpha = \frac{[\text{PO}_4^{3-}]}{[\text{H}_2\text{O}][\text{H}_2\text{PO}_4^-]}
\]

It is important to note that this temperature-dependent fractionation factor \( \alpha \) must be independent from the isotopic compositions of both reactants according to Northrop and Wolf-Gladrow (2001).
Clayton (1966). Lécuyer et al. (1999b) determined $\delta^{18}O(H_2PO_4 \rightarrow H_2O)$ experimentally in the temperature range 75–135 °C:

$$10^3 \ln \alpha(H_2PO_4 \rightarrow H_2O) = 18.35 \pm 0.37(10^3 T^{-1})$$

$$-32.29 \pm 1.01$$

(11)

**Application to the synthesis of silver phosphate of known oxygen isotope ratio**

**Experimental protocol of silver phosphate precipitation**

We present a protocol of silver phosphate precipitation from a highly soluble salt in water (solubility = 25 g 100 ml$^{-1}$ at 25 °C, Lide 2005) such as potassium dihydrogen phosphate KH$_2$PO$_4$ (Lécuyer et al. 1999b). An aliquot of 50 mg of pure high-grade (> 99.5% m/m) Sigma-Aldrich™ synthetic KH$_2$PO$_4$ was dissolved in 35 ml of de-ionised water of known oxygen isotope composition. The resulting aqueous solutions had a concentration of 1 g l$^{-1}$ (10.6 mmol l$^{-1}$) of phosphate ions with a pH of 5 at ambient temperature. It is important to note that the amount of oxygen in water is much higher than in the pool of dissolved phosphate (oxygen molar ratio between H$_2$O and KH$_2$PO$_4$ ~ 5000) and, consequently, the change in the oxygen isotope composition before and after equilibrium is not detectable with respect to the analytical uncertainties (1σ = 0.05‰ for the $\delta^{18}O$ value of H$_2$O). The solutions were transferred into Ace Glass™ PYREX tubes and sealed with threaded Teflon plugs. Each set of tubes for a given temperature was placed in a high precision oven for run-times defined by the user. Samples were withdrawn at desired times and quenched in cold water to room temperature within a few minutes. Each sample of dissolved phosphate was quantitatively precipitated as silver phosphate (chemical yields were close to 100%) according to the protocol determined by Firsching (1961), which means that all the dissolved phosphate species ($\approx$ H$_2$PO$_4$) were converted into Ag$_3$PO$_4$. For a chemical yield of 100%, the expected amount of silver phosphate is close to 150 mg. Running an experiment batch with ten Ace Glass™ PYREX tubes at the same time ensures the production of about 1.5 g of silver phosphate crystals of predicted oxygen isotope composition.

**Oxygen isotope analysis of silver phosphate**

Oxygen isotope compositions were measured using a high-temperature pyrolysis technique involving a VarioPYROcube™ elemental analyser (EA) interfaced in continuous flow (CF) mode to an Isoprime™ isotope ratio mass spectrometer (IRMS; EA-Py-CF-IRMS technique (Lécuyer et al. 2007, Fourel et al. 2011)) at the University Claude Bernard Lyon 1. For each sample, five aliquots of 300 μg of Ag$_3$PO$_4$ were mixed with 300 μg of pure carbon black powder and loaded in silver foil capsules. Pyrolysis was performed at a temperature of 1450 °C. Measurements were calibrated against NIST SRM 120c (natural Miocene phosphate from Florida) and NBS 127 (barium sulfate, BaSO$_4$, $\delta^{18}O = 9.3$‰ VSMOW). The $\delta^{18}O$ value of NIST SRM 120c is fixed at 21.7‰ (VSMOW) according to Lécuyer et al. (1993) who determined this value by fluorinating silver phosphate crystals ($n = 25, 1σ = 0.16$) at 600 °C for 12 h, and calibrated the oxygen isotope ratios with the certified reference material NBS 28 quartz (9.5 ± 0.2‰s), and measurement standards “Snowbird” quartz (16.1 ± 0.1‰s) and tholeiitic basaltic glass CIRCE 93 (5.6 ± 0.1‰s).

**Predicted oxygen isotope composition of synthesised silver phosphate**

According to Equation (4), for any temperature $T$, $k$ and $\delta^{18}O$(PO$_4$)$_2$ are calculated, $\delta^{18}O$(PO$_4$) is measured, which means that $\delta^{18}O$(PO$_4$) can be predicted as follows:

$$\delta^{18}O(PO_4) = \delta^{18}O(PO_4)_0 \cdot \left\{ \frac{\delta^{18}O(PO_4) - \delta^{18}O(PO_4)_0}{1 - \exp(-kt)} \right\}$$

(12)

We emphasise that the recommended working temperature range is 110–130 °C. Below a temperature of 110 °C, the reaction kinetics are so slow that significant isotopic exchange takes months, or even years when the temperature is < 100 °C. On the other hand, above a temperature of 130 °C, the Ace Glass™ PYREX tubes sealed with a threaded Teflon™ plug could start to leak, leading to a shift of the initial oxygen isotope ratio of water. Finally, we provide an ‘Excel calculation sheet’ (Table S1) that automatically computes the oxygen isotope composition of the precipitated silver phosphate depending on time $t$ and temperature $T$ of isotopic exchange as well as the oxygen isotope compositions of reactants KH$_2$PO$_4$ and H$_2$O at $t = 0$. Predicted oxygen isotope compositions of synthesised silver phosphate ranged from -7 to +31‰ VSMOW for a temperature range between 110 and 130 °C and a range of water $\delta^{18}O$ from -20 to +15‰ VSMOW (Figure 2). For example, Table S1 shows a possible tuning of the parameters described above to obtain silver phosphate crystals with a $\delta^{18}O$ value (%) VSMOW that mimics for the barium sulfate international reference material NBS 127.
To further demonstrate the efficiency of this method, we measured the oxygen isotope compositions of three silver phosphates with expected $\delta^{18}$O values ranging from about +10 to +22‰ VSOW (Table 1), which cover the most common range of documented $\delta^{18}$O values for natural dissolved phosphate and apatites. We report the measured $\delta^{18}$O values as a function of the expected ones, and obtained a strong linear correlation with a slope close to 1 ($a = 1.032 \pm 0.029$) and an intercept close to 0 ($b = -0.794 \pm 0.466$) (Figure 3). Within this isotopic variation range of 12‰, the calculated standard error is 0.24‰, which is comparable to the error associated with the established $\delta^{18}$O value of NIST SRM 120c. This shows that the method described is suitable to produce robust in-house produced calibrated $\text{Ag}_3\text{PO}_4$ for oxygen isotope measurements in phosphatic compounds.

### Potential application to the sulfate-water system

A similar protocol may be applied to the sulfate-water system to produce barium sulfate of known oxygen isotope composition. Indeed, the required thermodynamic properties such as the rate constant $k_a$, the activation $E_a$ and the T-dependent isotopic fractionation factor $\alpha$ have been determined by Chiba and Sakai (1985). The oxygen isotope measurement of sulfates, whatever their natural or anthropogenic origin, could be very useful in tracing their mechanisms of formation. For instance, sulfates may form in the atmosphere from the oxidation of sulfur dioxide by hydroxyl radicals, hydrogen peroxide or ozone. Sulfates may also result from a high-temperature oxidation to produce sulfur trioxide during combustion processes before being ultimately hydrated to form sulfuric acid. Various oxygen isotope fractionations could be associated with these chemical reactions, requiring the production of calibrated barium sulfate with different $\delta^{18}$O values.

### Table 1.

Comparison between measured ($\delta^{18}$O$_{\text{measured}}$) and predicted ($\delta^{18}$O$_{\text{predicted}}$) oxygen isotope compositions of silver phosphate samples

| Calibrated material | $\delta^{18}$O(water) VSMOW (%) | Equilibration (days) | $\delta^{18}$O($\text{Ag}_3\text{PO}_4$) predicted (%) VSMOW | $\delta^{18}$O($\text{Ag}_3\text{PO}_4$) measured (%) VSMOW | $\delta^{18}$O($\text{Ag}_3\text{PO}_4$) 1s | $\delta^{18}$O($\text{Ag}_3\text{PO}_4$) 1s | N |
|---------------------|-------------------------------|----------------------|-------------------------------------------------------------|-------------------------------------------------------------|--------------------------------|--------------------------------|----|
| CAL1                | 7.74                          | 37                   | 21.68                                                       | 21.66                                                       | 0.54                          | 0.10                          | 8  |
| CAL3                | -1.18                         | 44                   | 15.06                                                       | 14.55                                                       | 0.01                          | 0.35                          | 10 |
| CAL2                | -7.42                         | 44                   | 9.90                                                        | 9.53                                                        | 0.28                          | 0.28                          | 6  |

The $\delta^{18}$O$_{\text{predicted}}$ values were calculated by using Equations (6) and (12) knowing the temperature $T$ and duration $t$ of isotope exchange reaction along with the initial compositions of dissolved phosphate $\delta^{18}$O($\text{PO}_4$) and water $\delta^{18}$O($\text{H}_2\text{O}$) reactants. The $\delta^{18}$O$_{\text{measured}}$ values were obtained by using the analytical protocol presented in the sections ‘Experimental protocol of silver phosphate precipitation’ and ‘Oxygen isotope measurement of silver phosphate’.
continental vertebrates. Earth and Planetary Science Letters, 226, 255–272.

Amiot R., Lécuyer C., Buffetaut E., Escarguel G., Fluteau F. and Martineau F. (2006) Oxygen isotopes from biogenic apatites suggest widespread endothermy in Cretaceous dinosaurs. Earth and Planetary Science Letters, 246, 41–54.

Angert A., Weiner T., Mazzoh S. and Steennberg M. (2012) Soil phosphate stable oxygen isotopes across rainfall and bedrock gradients. Environmental Science and Technology, 46, 2156–2162.

Barrick R.E. and Showers W.J. (1994) Thermophysiology of Tyrannosaurus rex: Evidence from oxygen isotopes. Science, 265, 222–224.

Bauke S.L., von Sperber C., Tamburini F., Gocke M.J., Honermeier B., Schweitzer K., Baumlecker M., Don A., Sandhage-Hofmann A. and Amelung W. (2018) Subsoil phosphorus is affected by fertilization regime in long-term agricultural experimental trials. European Journal of Soil Science, 69, 103–112.

Bernard A., Lécuyer C., Vincent P., Amiot R., Bardet N., Buffetaut E., Cuny G., Fouloul F., Martineau F., Mazin J.-M. and Prieur A. (2010) Regulation of body temperature in some Mesozoic marine reptiles. Science, 328, 1379–1382.

Brandt W., Coplen T.B., Vogl J., Rosner M. and Prohaska T. (2014) Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure and Applied Chemistry, 86, 425–467.

Chang S.J. and Blake R.E. (2015) Precise calibration of equilibrium oxygen isotope fractionations between dissolved phosphate and water from 3 to 37°C. Geochimica et Cosmochimica Acta, 150, 314–329.

Chenery C., Meldner G., Evans J., Eckardt H. and Lewis M. (2010) Strontium and stable isotope evidence for diet and mobility in Roman Gloucester, UK. Journal of Archaeological Science, 37, 150–163.

Chiba H. and Sakai H. (1985) Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. Geochimica et Cosmochimica Acta, 49, 993–1000.

Crowson R.A., Showers W.J., Wright E.K. and Hoering T.C. (1991) A method for preparation of phosphate samples for oxygen isotope analysis. Analytical Chemistry, 63, 2397–2400.

Davies C.L., Surridge B.W. and Gooddy D.C. (2014) Phosphate oxygen isotopes within aquatic ecosystems: Global data synthesis and future research priorities. Science of the Total Environment, 496, 563–575.

Evans J.A., Cherny C.A. and Fitzpatrick A.P. (2006) Bronze age childhood migration of individuals near Stonehenge, revealed by strontium and oxygen isotope tooth enamel analysis. Archaeometry, 48, 309–321.

Figure 3. Linear regression between the oxygen isotope compositions of measured and predicted $\delta^{18}O$ values of three samples of synthesised silver phosphate. A slope of $1.032 \pm 0.029$ and an intercept of $-0.794 \pm 0.466$ with a $R^2$ of 0.999 indicate a good fit between these two variables. The standard error (0.24‰) measures the robustness of the isotopic composition of the precipitated silver phosphate that can be used as in-house produced calibrated material.

Conclusions

The protocol developed in this study is based on the equilibrium isotopic fractionation factor $\alpha$, the kinetics $k$ and temperature $T$ of isotopic exchange in the dissolved phosphate–water system. It offers the possibility to produce in a reasonable amount of time (a few days or a couple of weeks) about 1.5 g (the equivalent of 1000 measurements) of silver phosphate of known oxygen isotope composition. Moreover, the tuning of some parameters (time and temperature of isotopic exchange and the compositions of reactants) allows the synthesis of silver phosphate within a large range (1000 measurements) of oxygen isotope ratios that match the documented natural variability for both phosphate-bearing minerals and dissolved phosphate of organic or inorganic origin.

Acknowledgement

This study was funded by the CNRS and IUF (CL).

References

Amiot R., Lécuyer C., Buffetaut E., Fluteau F., Legendre S. and Martineau F. (2004) Latitudinal temperature gradient during the Cretaceous Upper Campanian-Middle Maastrichtian: $\delta^{18}O$ record of
references

Fisching F.H. (1961)
Precipitation of silver phosphate from homogeneous solution. Analytical Chemistry, 33, 873–874.

Fourel F., Martineau F., Lécuyer C., Kupka H.J., Lange L., Ojémi C. and Seed M. (2011)
$^{18}$O/$^{16}$O ratios measurements of inorganic and organic materials by EA-Pyrolysis–IRMS continuous flow techniques. Rapid Communications in Mass Spectrometry, 25, 2691–2696.

Fricke H.C. and O'Neil J.R. (1996)
Inter- and intra-tooth variation in the oxygen isotope composition of mammalian tooth enamel phosphate: Implications for palaeoclimatological and palaeobiological research. Palaeogeography, Palaeoclimatology, Palaeoecology, 126, 91–99.

Fricke H.C. and Rogers R.R. (2000)
Multiple taxon–multiple locality approach to providing oxygen isotope evidence for warm-blooded theropod dinosaurs. Geology, 28, 799–802.

Goedert J., Aminot R., Cuny G., Fourel F., Amaud Godet F., Henderson J.A., Pedreira-Segade U. and Lécuyer C. (2017)
Micceno (Burdigalian) seawater and air temperatures estimated from the geochemistry of vertebrate remains from the Aquitaine Basin, France. Palaeogeography, Palaeoclimatology, Palaeoecology, 481, 14–28.

Goedert J., Lécuyer C., Aminot R., Wang X., Cui L., Cuny G., Douay G., Fourel F., Simon L., Steyer S. and Zhu M. (2018)
Euxynilene ecology of early tetrapods revealed by stable isotopes. Nature, 558, 68–72.

Granger S.J., Harris P., Peukert S., Guo R., Tamburini F., Blackwell M.S., Howden N.J.K. and McGrath S. (2017)
Phosphate stable oxygen isotope variability within a temperate agricultural soil. Geoderma, 285, 64–75.

Gruau G., Legeas M., Rieu C., Gallacier E., Martineau F. and Hénin O. (2005)
The oxygen isotope composition of dissolved anthropogenic phosphates: A new tool for eutrophication research? Water Research, 39, 232–238.

Halas S., Skrzypek G., Meier-Augenstein W., Pelc A. and Kemp H.F. (2011)
Inter-laboratory calibration of new silver orthophosphate comparison materials for the stable oxygen isotope analysis of phosphates. Rapid Communications in Mass Spectrometry, 25, 579–584.

Huang C., Joachimski M.M. and Gong Y. (2018)
Did climate changes trigger the Late Devonian Kellwasser Crisis? Evidence from a high-resolution conodont $^{18}$O record from South China. Earth and Planetary Science Letters, 495, 174–184.

Joachimski M.M., Lai X., Shen S., Jiang H., Luo G., Chen B., Chen J. and Sun Y. (2012)
Climate warming in the latest Permian and the Permian–Triassic mass extinction. Geology, 40, 195–198.

Kolodny Y. and Raab M. (1988)
Oxygen isotopes in phosphatic fish remains from Israel. Paleothemometry of tropical Cretaceous and Tertiary shelf waters. Palaeogeography, Palaeoclimatology, Palaeoecology, 64, 59–67.

Kolodny Y., Luz B. and Navon O. (1983)
Oxygen isotope variations in phosphate of biogenic apatites. I. Fish bone apatite – Rechecking the rules of the game. Earth and Planetary Science Letters, 64, 398–404.

Lécuyer C., Grandjean P., O’Neil J.R., Cappetta H. and Martineau F. (1993)
Thermal excursions in the ocean at the Cretaceous-Tertiary boundary (northern Morocco): $^{18}$O record of phosphatic fish debris. Palaeogeography, Palaeoclimatology, Palaeoecology, 105, 235–243.

Lécuyer C., Grandjean P., Barrat J.-A., Nolvak J., Emig C.C., Paris F. and Robardet M. (1998)
$^{18}$O and REE contents of phosphatic brachiopods: A comparison between modern and lower Paleozoic populations. Geochimica et Cosmochimica Acta, 62, 2429–2436.

Lécuyer C., Grandjean P., Mazin J.-M. and De Buffrein V. (1999a)
Oxygen isotope compositions of reptile bones and teeth: A potential record of terrestrial and marine palaeoenvironments. In: Hoch E. and Brantsen A.K. (eds), Secondary adaptation to life in water II. Geologisk Museum, University of Copenhagen (Denmark), 33pp.

Lécuyer C., Grandjean P. and Sheppard S.M.F. (1999b)
Oxygen isotope exchange between dissolved phosphate and water at temperatures <135 °C: Inorganic versus biological fractionations. Geochimica et Cosmochimica Acta, 63, 855–862.

Lécuyer C., Fourel F., Martineau F., Aminot R., Bernard A., Daux Y., Escarguel G. and Morrison J. (2007)
High-precision determination of $^{18}$O/$^{16}$O ratios of silver phosphate by EA-pyrolysis–IRMS continuous flow technique. Journal of Mass Spectrometry, 42, 36–41.

Lécuyer C., Aminot R., Trotter J. and Touzeau A. (2013)
Calibration of the phosphate $^{18}$O paleothermometer with the calcium carbonate-water oxygen isotope fractionation equations. Chemical Geology, 347, 217–226.

Liang Y. and Blake R.E. (2009)
Compound- and enzyme-specific phosphodiester hydrolysis mechanisms revealed by $^{18}$O of dissolved inorganic phosphate: Implications for marine P cycling. Geochimica et Cosmochimica Acta, 73, 3792–3794.

Lide D.R. (2005)
CRC handbook of chemistry and physics (86th Edition 2005–2006). CRC Press, Taylor and Francis (Boca Raton, FL), 4–79.
references

Lightfoot E. and O’Connell T.C. (2016)
On the use of biomineral oxygen isotope data to identify human migrants in the archaeological record: Intra-sample variation, statistical methods and geographical considerations. PLoS ONE, 11, e0153850.

Longinelli A., Bartelloni M. and Cortesi G. (1976)
The isotopic cycle of oceanic phosphate. I. 1976. Earth and Planetary Science Letters, 32, 389–392.

Markel D., Kolodny Y., Luz B. and Nishi A. (1994)
Phosphorus cycling and phosphorus sources in Lake Kinneret. Tracing by oxygen isotopes in phosphate. Israeli Journal of Earth Sciences, 43, 165–178.

McLaughlin K., Kendall C., Silva S.R., Young M. and Paytan A. (2006)
Phosphate oxygen isotope ratios as a tracer for sources and cycling of phosphate in North San Francisco Bay, California. Journal of Geophysical Research, 111, GO3003.

Northrop D.A. and Clayton R.N. (1966)
Oxygen isotope fractionations in systems containing dolomite. Journal of Geology, 74, 174–196.

O’Neil J.R., Roe L.J., Reinhard E. and Blake R.E. (1994)
A rapid and precise method of oxygen isotope analysis of biogenic phosphate. Israeli Journal of Earth Sciences, 43, 203–212.

Pellegrini M., Pourcatt J., Jay M., Pearson M.P. and Richards M.P. (2016)
Tooth enamel oxygen “isoscapes” show a high degree of human mobility in prehistoric Britain. Scientific Reports, 6, 34986.

Pistocchi C., Tamburini F., Gruau G., Ferhi A., Trevisan D. and Dorazio J.-M. (2017)
Tracing the sources and cycling of phosphorus in river sediments using oxygen isotopes: Methodological adaptations and first results from a case study in France. Water Research, 111, 346–356.

Rey K., Day M.O., Amiot R., Goedert J., Lécuyer C., Sealy J. and Rubidge B.S. (2018)
Stable isotope record implicates aridification in late Capitanian mass extinction. Gondwana Research, 59, 1–8.

von Sperber C., Lewandowski H., Tamburini F., Bernasconi S.M., Amelung W. and Frossard E. (2017)
Kinetics of enzyme-catalysed oxygen isotope exchange between phosphate and water revealed by Raman spectroscopy. Journal of Raman Spectroscopy, 48, 368–373.

Sun Y., Wiedenbeck M., Joachimski M.M., Beier C., Kemner F. and Weinzierl C. (2016)
Chemical and oxygen isotope composition of gem-quality apatites: Implications for oxygen isotope reference materials for secondary ion mass spectrometry (SIMS). Chemical Geology, 440, 164–178.

Tamburini F., Pföhler V., von Sperber C., Frossard E. and Bernasconi S.M. (2014)
Oxygen isotopes for unraveling phosphorus transformations in the soil–plant system: A review. Soil Science Society of America Journal, 78, 38–46.

Touzeau A., Blichten-Toft J., Amiot R., Fourel F., Martineau F., Cockilt J., Hall K., Flandrois J.-P. and Lécuyer C. (2013)
Egyptian mummies record increasing aridity in the Nile valley from 5,500 to 1,500 B.P. Earth and Planetary Science Letters, 375, 92–100.

Tutken T. and Vennemann T. (2009)
Stable isotope ecology of Miocene large mammals from Sandelshausen, southern Germany. Palaeontologische Zeitschrift, 83, 207–226.

Vennemann T.W. (2012)
Further comparison of methods of oxygen isotope analysis of phosphates and standards used. IsöPhos 2012 Annual Meeting, 25–29 June (Ascona, Switzerland).

Vennemann T.W., Frick H.C., Blake R.E., O’Neil J.R. and Colman A. (2002)
Oxygen isotope analysis of phosphates: A comparison of techniques for analysis of $\text{Ag}_3$PO$_4$. Chemical Geology, 185, 321–336.

White C.D., Spence M.W., Stuart-Williams H.L.Q. and Schwarz H.P. (1998)
Oxygen isotopes and the identification of geographical origins: The Valley of Oaxaca versus the Valley of Mexico. Journal of Archaeological Science, 25, 643–655.

Zeebe R.E. and Wolf-Gladrow D. (2001)
CO$_2$ in seawater: Equilibrium, kinetics, isotopes. Elsevier Oceanography Series, 65, Elsevier (Amsterdam), 346pp.

Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Excel calculation sheet that computes the oxygen isotope composition of the precipitated silver phosphate depending on time $t$ and temperature $T$ of isotopic exchange along with the oxygen isotope compositions of reactants $\text{KH}_2\text{PO}_4$ and $\text{H}_2\text{O}$ at $t = 0$.

This material is available from: http://onlinelibrary.wiley.com/doi/10.1111/ggr.12285/abstract (This link will take you to the article abstract)