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**Synthesis of In-House Made Calibrated Silver Phosphate in a Large Range of Oxygen
Isotope Compositions**

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Abstract – 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 made calibrated silver phosphate of which isotopic ratios must closely bracket those of studied samples. We propose a simple protocol to synthesize Ag_3PO_4 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. Ag_3PO_4 crystals are obtained from KH_2PO_4 that is dissolved in water of known oxygen isotope composition. Isotopic exchange between dissolved phosphate and water takes place at a desired and constant temperature into pyrex tubes that are placed in a high precision oven for run-times defined by the user. Samples are withdrawn at desired times, quenched in cold water, and precipitated as Ag_3PO_4 . We provide a calculation sheet that computes the $\delta^{18}\text{O}$ of precipitated Ag_3PO_4 as a function of time, temperature and $\delta^{18}\text{O}$ of both reactants KH_2PO_4 and H_2O at $t = 0$. Predicted oxygen isotope compositions of synthesized silver phosphate range from -7 to +31‰ VSMOW for a temperature range comprised between 110°C and 130°C and a range of water $\delta^{18}\text{O}$ from -20 to +15‰ VSMOW.

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

41
42 Résumé – La large gamme de $\delta^{18}\text{O}$ des minéraux phosphatés et de phosphates dissous d'origine
43 inorganique ou organique nécessite l'existence d' Ag_3PO_4 calibré dont les rapports isotopiques
44 doivent encadrer les échantillons étudiés. Nous proposons un protocole simple pour synthétiser
45 Ag_3PO_4 dans une large gamme de compositions isotopiques. Ce protocole repose sur les
46 fractionnements isotopiques à l'équilibre et les températures et cinétiques d'échange isotopique
47 dans le système phosphate-eau. Les cristaux d' Ag_3PO_4 sont obtenus à partir de KH_2PO_4 dissous
48 dans une eau de $\delta^{18}\text{O}$ connu. Les échanges isotopiques entre le phosphate dissous et l'eau ont
49 lieu à une température constante dans des tubes en pyrex placés dans une étuve thermo-régulée
50 pour des durées de réactions définies par l'opérateur. Les échantillons sont retirés en temps
51 voulu, trempés dans de l'eau froide, et précipités sous la forme de cristaux de phosphate
52 d'argent. Nous fournissons une « feuille Excel » qui calcule le $\delta^{18}\text{O}$ d' Ag_3PO_4 précipité en
53 fonction du temps, de la température et des $\delta^{18}\text{O}$ de KH_2PO_4 et H_2O au temps $t = 0$. Les $\delta^{18}\text{O}$
54 prédits pour Ag_3PO_4 varient de -7 à +31‰ VSMOW pour une gamme de températures
55 comprises entre 110°C et 130°C et une gamme de $\delta^{18}\text{O}$ de l'eau de -20 to +15‰ VSMOW.

56
57 Mots-clés: isotopes de l'oxygène, fractionnement isotopique, cinétique, phosphate d'argent,
58 référence interne

59
60 **1. Introduction**

61 During the past decades, the rise of automated devices coupled to mass spectrometers
62 operating in continuous flow or in dual-inlet mode resulted in an explosive growth of the

number of data published in the scientific fields exploiting the stable isotope ratios of organic and inorganic compounds. Consequently, there is an increasing use and need for developing in-house made material 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 $^{18}\text{O}/^{16}\text{O}$ ratio of the phosphate radical (PO_4^{3-}) is now widely used to reconstruct the paleoclimates of the Earth (Fricke and O'Neil, 1996; Kolodny and Raab, 1988; 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 and Chenery, 2006; Touzeau et al., 2013; Lightfoot and O'Connell, 2016; Pellegrini et al., 2016). The most common way to determine the $^{18}\text{O}/^{16}\text{O}$ ratio of the phosphate radical is to isolate it as silver phosphate (Ag_3PO_4) crystals through a wet chemistry procedure (Crowson et al., 1991). Then they are pyrolyzed in the presence of graphite at high temperature to produce either CO_2 or CO analysed either off-line or on-line with an isotopic ratio mass spectrometer (O'Neil et al., 1994; Lécuyer et al., 1998; 2007; Fourel et al., 2011). Fluorination technique has also been proven to be a precise and accurate technique that allowed the first determination of the $\delta^{18}\text{O}_{\text{SMOW}}$ of the Miocene Florida phosphorite SRM 120c (Lécuyer et al., 1993). Whatever the considered research field, the $\delta^{18}\text{O}$ of calcium phosphate minerals (e.g.

biogenic, magmatic or hydrothermal apatite) and dissolved phosphate (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) range worldwide from about a few per mil up to values close to 30‰. Indeed, high-temperature apatites of magmatic or hydrothermal origin have $\delta^{18}\text{O}$ ranging from 6 to 11‰ (Sun et al., 2016). Concerning soils and their connected aquatic environments (rivers, ponds, lakes), dissolved phosphate also displays a large range of oxygen isotope compositions comprised between 8‰ and 25‰ (Markel et al., 1994; Gruau et al., 2005; Angert et al., 2012; Davies et al., 2014; Tamburini et al., 2014; Pistocchi et al., 2017; Granger et al., 2017; Bauke 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 $\delta^{18}\text{O}$ that range from 6‰ (high-latitude freshwater environments) to $\approx 20‰$ for seawater and to $\approx 22‰$ for low-latitude freshwater environments in agreement with the available isotopic fractionation equations (Kolodny et al., 1983; Lécuyer et al., 2013). In the case of biogenic apatites, their $\delta^{18}\text{O}$ values range from a few ‰ for vertebrates drinking highly ^{18}O -depleted waters ($\delta^{18}\text{O}$ 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 arid environments (Lécuyer et al., 1999a).

So far, researchers were using the Florida phosphorite SRM 120c, for which a consensual $\delta^{18}\text{O}_{\text{SMOW}}$ value of $21.7 \pm 0.2‰$ (VSMOW) was only admitted these last years. Indeed, Chenery et al. (2010) proposed a comparable value of $21.7 \pm 0.7‰$ after a 6-month period of repeated measurements of SRM 120c calibrated against NBS 127 barium sulfate, which is consistent with the average value of published data for SRM 120c ($21.5 \pm 0.5‰$) analyzed in different laboratories (Chenery et al., 2010). Thereafter, Halas et al. (2011) confirmed the absence of any sizable isotopic fractionation effect during the conversion of

Ag₃PO₄ into CO, and proposed a mean $\delta^{18}\text{O}$ value of $21.8 \pm 0.2\text{‰}$ for SRM 120c based on inter-laboratory calibrations. It is also worthy to note that Vennemann et al. (2002) proposed a significantly higher value of 22.5‰ for SRM 120c. But later on, in a communication given at ‘IsoPhos’ meeting in Ascona, Switzerland, Vennemann (2012) concluded that the most accurate value for SRM 120c is likely close to 21.7‰ . This value of $21.7 \pm 0.2\text{‰}$ for 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 $21.7 \pm 0.16\text{‰}$ for 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 phosphorite SRM 120c is a compositional, not an isotopic international reference, 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 ($\delta^{18}\text{O} = 9.3\text{‰}$ VSMOW), as we proceeded in some recent papers (e.g. Rey et al., 2018; 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 international reference hosted 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 cheap protocol to synthesize silver phosphate in a wide range ($\approx 35\text{‰}$) of oxygen isotope compositions based on 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 as a

supplementary material. This calculation sheet allows the $\delta^{18}\text{O}$ of precipitated Ag_3PO_4 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.

2. Theoretical background

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

The most common pH-dependent speciation of phosphorus in aqueous solution of low ionic strength are (1) the dihydrogen phosphate ion (H_2PO_4^-), (2) the hydrogen phosphate ion (HPO_4^{2-}), and (3) the phosphate ion (PO_4^{3-}) according to the three following chemical equilibria at 25°C (Zeebe and Wolf-Gladrow, 2001; Figure 1):

For seawater ($\text{pH} \approx 7.6$ to 8.4), the dominant species is HPO_4^{2-} while in the case of natural freshwater it is either H_2PO_4^- or HPO_4^{2-} . Lécuyer et al. (1999b) performed kinetics and isotopic experiments at a pH close to 5 for which H_2PO_4^- was almost the only species present in solution (Figure 1). During first-order kinetics of reaction, the rate of isotopic exchange can be quantified by considering f as follows,

$$f = 1 - \exp(-kt) = \frac{\delta^{18}\text{O}(\text{PO}_4)_i - \delta^{18}\text{O}(\text{PO}_4)_t}{\delta^{18}\text{O}(\text{PO}_4)_i - \delta^{18}\text{O}(\text{PO}_4)_e} \quad (4)$$

which is the mole fraction of exchanged isotopes between the phosphate ions and water molecules, while k is the rate constant (s^{-1}) of the isotopic reaction:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

with A being the Arrhenius pre-exponential factor, E_a the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$) of the isotopic reaction, R the universal gas constant, T the absolute temperature (K), t the time (s), $\delta^{18}\text{O}(\text{PO}_4)_i$ the oxygen isotope composition of the reactant at $t = 0$, $\delta^{18}\text{O}(\text{PO}_4)_t$ the oxygen isotope composition of H_2PO_4^- at any time t during the course of the isotopic reaction, and $\delta^{18}\text{O}(\text{PO}_4)_e$ the oxygen isotope composition of H_2PO_4^- at isotopic equilibrium with H_2O . Note that when $t = 0$; $f = 0$ and $\delta^{18}\text{O}(\text{PO}_4)_t = \delta^{18}\text{O}(\text{PO}_4)_i$ while when $t \rightarrow \infty$; $f \rightarrow 1$ and $\delta^{18}\text{O}(\text{PO}_4)_t = \delta^{18}\text{O}(\text{PO}_4)_e$.

2.2. Experimental determination of thermodynamic variables (k , E_a and α)

2.2.1. 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 :

$$\log(k) = 12.35 \pm 0.63 - 6.98 \pm 0.24(10^3 T^{-1}) \quad (6)$$

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

$$\ln(1 - f) = -kt \quad (7)$$

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 it for $f = 0.5$ as follows:

$$t = \frac{0.693}{k} \quad (8)$$

2.2.1. 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 the oxygen isotope exchange between phosphate and water molecules is very high with a value of $133.6 \pm 4.6 \text{ kJmol}^{-1}$ 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 to equation (5).

2.2.2. The fractionation coefficient α between H_2PO_4^- and H_2O

At thermodynamic equilibrium, and according to the Mass Action Law, we can write the following isotopic exchange equation:

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

$$\alpha_{(H_2PO_4^- - H_2O)} = \frac{\left[\frac{^{18}O}{^{16}O}\right]_{H_2PO_4^-}}{\left[\frac{^{18}O}{^{16}O}\right]_{H_2O}} \quad (10)$$

It is worthy to note that this temperature-dependent fractionation factor α must be independent from the isotopic compositions of both reactants according to Northrop and Clayton (1966). Lécuyer et al. (1999b) determined experimentally $\alpha(H_2PO_4^- - H_2O)$ in the temperature range 75 to 135°C:

$$10^3 \ln \alpha_{(H_2PO_4^- - H_2O)} = 18.35 \pm 0.37(10^3 T^{-1}) - 32.29 \pm 1.01 \quad (11)$$

3. Application to the synthesis of silver phosphate of known oxygen isotope ratio

3.1. 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 the potassium dihydrogen

phosphate KH_2PO_4 (Lécuyer et al., 1999b). An aliquot of 50 mg of pure high-grade (> 99.5 wt%) Sigma-Aldrich™ synthetic KH_2PO_4 is dissolved in 35 mL of deionized water of known oxygen isotope composition. The resulting aqueous solutions have 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_2O and $\text{KH}_2\text{PO}_4 \approx 5000$), consequently the change in the oxygen isotope composition before and after equilibrium is not detectable with respect to the analytical uncertainties ($1\sigma = 0.05\text{‰}$ for the $\delta^{18}\text{O}$ of H_2O). The solutions are transferred into Ace Glass™ pyrex tubes sealed with a threaded teflon plug. Each set of tubes for a given temperature is placed in a high precision oven for run-times defined by the user. Samples are withdrawn at desired times and quenched in cold water to room temperature within a few minutes. Each sample of dissolved phosphate is quantitatively precipitated as silver phosphate (chemical yields are close to 100%) according to the protocol determined by Firsching (1961), which means that all the dissolved phosphate species ($\approx \text{H}_2\text{PO}_4^-$), are converted into Ag_3PO_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.

3.2. Oxygen isotope analysis of silver phosphate

Oxygen isotope compositions are measured using a high-temperature pyrolysis technique involving a VarioPYROcube™ elemental analyzer (EA) interfaced in continuous flow (CF) mode to an Isoprime™ isotopic 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, 5 aliquots of 300 µg of Ag₃PO₄ are mixed with 300 µg of pure carbon black powder and loaded in silver foil capsules. Pyrolysis is performed at a temperature of 1450°C. Measurements are calibrated against the SRM 120c (natural Miocene phosphorite from Florida) and the NBS 127 (barium sulfate, BaSO₄: δ¹⁸O = 9.3‰ VSMOW). The δ¹⁸O of 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 hours and calibrated the oxygen isotope ratios with the calibrated reference material NBS 28 quartz (9.5±0.2‰), and measurement standards that are the “Snowbird” quartz (16.1±0.1‰) and the tholeiitic basaltic glass standard CIRCE 93 (5.6±0.1‰).

3.3. Predicted oxygen isotope composition of synthesized silver phosphate

According to equation (4), for any temperature T, k and δ¹⁸O(PO₄)_e are calculated, t and δ¹⁸O(PO₄)_i are measured, which means that δ¹⁸O(PO₄)_t can be predicted as follows:

$$\delta^{18}O(PO_4)_t = \delta^{18}O(PO_4)_i - \{\delta^{18}O(PO_4)_i - \delta^{18}O(PO_4)_e\}\{1 - \exp(-kt)\} \quad (12)$$

We emphasize that the recommended working range of temperature is from 110°C to 130°C. Indeed, below a temperature of 110°C, kinetics of reaction is so slow that significant isotopic exchange takes months, or even years when temperature is below 100°C. Then, 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” (Supplementary File) 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_2PO_4 and H_2O at $t = 0$. Predicted oxygen isotope compositions of synthesized silver phosphate range from -7 to +31‰ VSMOW for a temperature range comprised between 110°C and 130°C and a range of water $\delta^{18}\text{O}$ from -20 to +15‰ VSMOW (Figure 2). For example, we have provided a calculation table (Supplementary File) showing a possible tuning of the parameters described above to obtain silver phosphate crystals with a $\delta^{18}\text{O}$ value (‰ VSMOW) that mimics that certified for the NBS 127 barium sulfate international reference.

In order to further demonstrate the efficiency of this method, we analysed the oxygen isotope compositions of three silver phosphates with expected $\delta^{18}\text{O}$ values ranging from about +10 to +22 ‰ VSMOW (Table 1), which cover the most common range of documented $\delta^{18}\text{O}$ values for natural dissolved phosphate and apatites. We reported the measured $\delta^{18}\text{O}$ values as a function of the expected ones and we 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 admitted $\delta^{18}\text{O}$ value of SRM 120c. Therefore, we show that this method is suitable to produce robust in-house made calibrated Ag_3PO_4 for the oxygen isotope analysis of phosphatic compounds.

3.4. Potential application to the sulfate-water system

Furthermore, 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 , the activation E_a and the T -dependent isotopic fractionation factor α have been determined by Chiba and Sakai (1985). The oxygen isotope measurement of sulfates, whatever their natural or anthropogenic origin, could be very useful to trace the mechanisms of their 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 those chemical reactions, requiring the production of calibrated barium sulfate with different $\delta^{18}\text{O}_{\text{VSMOW}}$ values.

4. Conclusions

The protocol we developed in this study is based on the equilibrium isotopic fractionation factor α , 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 1,000 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 ($\approx 35\%$) of oxygen isotope ratios that match the documented natural variability for both phosphate-bearing minerals and dissolved phosphate of organic or inorganic origin.

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548

549 **Table captions:**

550

551 Table 1: Comparison between measured ($\delta^{18}\text{O}_{\text{measured}}$) and predicted ($\delta^{18}\text{O}_{\text{predicted}}$) oxygen
552 isotope compositions of silver phosphate samples. The $\delta^{18}\text{O}_{\text{predicted}}$ values have been calculated
553 by using equation (6) and (12) knowing the temperature T and duration t of isotope exchange
554 reaction along with the initial compositions of dissolved phosphate $\delta^{18}\text{O}(\text{PO}_4)_i$ and water
555 $\delta^{18}\text{O}(\text{H}_2\text{O})_i$ reactants. The $\delta^{18}\text{O}_{\text{measured}}$ values have been obtained by using the analytical
556 protocol presented in sections 3.1 and 3.2.

557

Figure captions:

Figure 1: pH-dependent speciation of dissolved phosphate in aqueous solution according to Zeebe and Wolf-Gladrow (2001).

Figure 2: Oxygen isotope composition of dissolved phosphate (or precipitated silver phosphate) as a function of time t (in days) of isotopic exchange for a temperature T of 110°C and a $\delta^{18}\text{O}$ of water of +15‰ (blue curve) and for a temperature T of 130°C and a $\delta^{18}\text{O}$ of water of -20‰ (red curve). After no more than 1 month of isotopic exchange between dissolved phosphate and water, the precipitated silver phosphate crystals reach the isotopic equilibrium with water and have $\delta^{18}\text{O}$ values close to +31‰ VSMOW (blue curve) and -7‰ VSMOW (red curve), respectively.

For instance, the $\delta^{18}\text{O}$ of $\text{H}_2\text{O}(\text{i})$ of +15‰ VSMOW can be obtained by collecting 1 L of residual water obtained by evaporation at ambient temperature ($\approx 20^\circ\text{C}$) under a laminar flow hood of 50 L of deionized water with an initial $\delta^{18}\text{O}$ of -10.5‰ of which the ultimate source is the Rhône river. The $\delta^{18}\text{O}$ of $\text{H}_2\text{O}(\text{i})$ of -20‰ VSMOW can be obtained in Lyon, France, by collecting frozen atmospheric vapour trapped inside a freezer working at a temperature of -80°C.

Figure 3: Linear regression between the oxygen isotope compositions of measured and predicted $\delta^{18}\text{O}$ values of three samples of synthesized silver phosphate. A slope of 1.032 ± 0.029 and an intercept of -0.794 ± 0.466 with a R^2 of 0.999 indicate a good fit between these two

581 variables. The standard error of 0.24‰ measures the robustness of the isotopic composition of
582 the precipitated silver phosphate that can be used as in-house made calibrated material.
583

584

585 **Supplementary File:**

586

587 Table: “Excel calculation sheet” that computes the oxygen isotope composition of the
588 precipitated silver phosphate depending on time t and temperature T of isotopic exchange along
589 with the oxygen isotope compositions of reactants KH_2PO_4 and H_2O at $t = 0$. The provided
590 example provided shows a possible tuning of the parameters described above to obtain silver
591 phosphate crystals with a $\delta^{18}\text{O}$ value (‰ VSMOW) similar to that certified for the NBS 127
592 barium sulfate international reference.

593 Description of column assignment: C0-C1 = temperature T ; C2-C3 = rate constant k ; C4-C5 =
594 time t ; C6 = fraction f of isotopic exchange; C7-C8 = oxygen isotope compositions of reactants
595 at $t = 0$; C9-C10 = isotopic fractionation factor α between dissolved phosphate and water; C11-
596 12 = oxygen isotope composition of dissolved phosphate at equilibrium at any time t .

597

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