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

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6 Christophe **Lécuyer**^{1,*}, François **Fourel**², Magali **Seris**¹, Romain **Amiot**¹, Jean **Goedert**^{1,3} and

7 Laurent **Simon**²

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11 ¹LGL-TPE, UMR 5276, CNRS, Université Claude Bernard Lyon 1, 69622 Villeurbanne,

12 France

13 ²LEHNA, UMR 5023, CNRS, Université Claude Bernard Lyon 1, ENTPE, 69622

14 Villeurbanne, France

15 ³PACEA, UMR 5199, CNRS, Université de Bordeaux, Bâtiment B18, Allée Geoffroy Saint-

16 Hilaire, CS 50023, FR-33615 Pessac, France

17

18 *corresponding author. E-mail : christophe.lecuyer@univ-lyon1.fr

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22

23 **Abstract** – The large range of stable oxygen isotope values of phosphate-bearing minerals and
24 dissolved phosphate of inorganic or organic origin requires the availability of in-house made
25 calibrated silver phosphate of which isotopic ratios must closely bracket those of studied
26 samples. We propose a simple protocol to synthesize Ag_3PO_4 in a wide range of oxygen isotope
27 compositions based on the equilibrium isotopic fractionation factor and the kinetics and
28 temperature of isotopic exchange in the phosphate-water system. Ag_3PO_4 crystals are obtained
29 from KH_2PO_4 that is dissolved in water of known oxygen isotope composition. Isotopic
30 exchange between dissolved phosphate and water takes place at a desired and constant
31 temperature into pyrex tubes that are placed in a high precision oven for run-times defined by
32 the user. Samples are withdrawn at desired times, quenched in cold water, and precipitated as
33 Ag_3PO_4 . We provide a calculation sheet that computes the $\delta^{18}\text{O}$ of precipitated Ag_3PO_4 as a
34 function of time, temperature and $\delta^{18}\text{O}$ of both reactants KH_2PO_4 and H_2O at $t = 0$. Predicted
35 oxygen isotope compositions of synthesized silver phosphate range from -7 to +31‰ VSMOW
36 for a temperature range comprised between 110°C and 130°C and a range of water $\delta^{18}\text{O}$ from
37 -20 to +15‰ VSMOW.

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

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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

63 number of data published in the scientific fields exploiting the stable isotope ratios of organic
64 and inorganic compounds. Consequently, there is an increasing use and need for developing in-
65 house made material calibrated against certified reference materials. Moreover, a large range
66 of isotopic compositions is highly desirable to bracket the expected compositions of the studied
67 sample collection as well as to be able to perform a two-point calibration, which is required for
68 the acquisition of high-quality data.

69 In Earth and Archaeological Sciences, to only mention the most concerned research
70 fields, the $^{18}\text{O}/^{16}\text{O}$ ratio of the phosphate radical (PO_4^{3-}) is now widely used to reconstruct the
71 paleoclimates of the Earth (Fricke and O'Neil, 1996; Kolodny and Raab, 1988; Amiot et al.,
72 2004; Joachimski et al., 2012; Goedert et al., 2017), the thermophysiology and ecology of
73 extinct vertebrates (Barrick and Showers, 1994; Fricke and Rogers, 2000; Amiot et al., 2006;
74 Tütken and Vennemann, 2009; Bernard et al., 2010; Rey et al., 2018), the source and recycling
75 of dissolved phosphate in natural waters (Markel et al., 1994; McLaughlin et al., 2006; Pistocchi
76 et al., 2017) as well as the diet and living environment of past human populations (White et al.,
77 1998; Evans and Chenery, 2006; Touzeau et al., 2013; Lightfoot and O'Connell, 2016;
78 Pellegrini et al., 2016). The most common way to determine the $^{18}\text{O}/^{16}\text{O}$ ratio of the phosphate
79 radical is to isolate it as silver phosphate (Ag_3PO_4) crystals through a wet chemistry procedure
80 (Crowson et al., 1991). Then they are pyrolyzed in the presence of graphite at high temperature
81 to produce either CO_2 or CO analysed either off-line or on-line with an isotopic ratio mass
82 spectrometer (O'Neil et al., 1994; Lécuyer et al., 1998; 2007; Fourel et al., 2011). Fluorination
83 technique has also been proven to be a precise and accurate technique that allowed the first
84 determination of the $\delta^{18}\text{O}_{\text{SMOW}}$ of the Miocene Florida phosphorite SRM 120c (Lécuyer et al.,
85 1993). Whatever the considered research field, the $\delta^{18}\text{O}$ of calcium phosphate minerals (e.g.

86 biogenic, magmatic or hydrothermal apatite) and dissolved phosphate (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}
87) range worldwide from about a few per mil up to values close to 30‰. Indeed, high-
88 temperature apatites of magmatic or hydrothermal origin have $\delta^{18}\text{O}$ ranging from 6 to 11‰
89 Sun et al., 2016). Concerning soils and their connected aquatic environments (rivers, ponds,
90 lakes), dissolved phosphate also displays a large range of oxygen isotope compositions
91 comprised between 8‰ and 25‰ (Markel et al., 1994; Gruau et al., 2005; Angert et al., 2012;
92 Davies et al., 2014; Tamburini et al., 2014; Pistocchi et al., 2017; Granger et al., 2017; Bauke
93 et al., 2018). In the case of dissolved phosphate being isotopically equilibrated with ambient
94 water through biological recycling (Longinelli et al., 1976; Liang and Blake, 2009; Chang and
95 Blake, 2015; von Sperber et al., 2017), it is expected to have $\delta^{18}\text{O}$ that range from 6‰ (high-
96 latitude freshwater environments) to $\approx 20\%$ for seawater and to $\approx 22\%$ for low-latitude
97 freshwater environments in agreement with the available isotopic fractionation equations
98 (Kolodny et al., 1983; Lécuyer et al., 2013). In the case of biogenic apatites, their $\delta^{18}\text{O}$ values
99 range from a few ‰ for vertebrates drinking highly ^{18}O -depleted waters ($\delta^{18}\text{O}$ as low as -20‰)
100 relative to SMOW (high-altitude or high-latitude environments; e.g. Rey et al., 2018) up to
101 about 30‰ for vertebrates living in arid environments (Lécuyer et al., 1999a).

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

109 Ag_3PO_4 into CO, and proposed a mean $\delta^{18}\text{O}$ value of $21.8 \pm 0.2\text{‰}$ for SRM 120c based on inter-
110 laboratory calibrations. It is also worthy to note that Vennemann et al. (2002) proposed a
111 significantly higher value of 22.5‰ for SRM 120c. But later on, in a communication given at
112 ‘IsoPhos’ meeting in Ascona, Switzerland, Vennemann (2012) concluded that the most accurate
113 value for SRM 120c is likely close to 21.7‰ . This value of $21.7 \pm 0.2\text{‰}$ for SRM 120c is now
114 widely accepted as exemplified by the recent study published by Huang et al. (2018). It has also
115 to be pointed out that an isotopic ratio of $21.7 \pm 0.16\text{‰}$ for SRM 120c was determined for the
116 first time by using quantitative fluorination 25 years ago (Lécuyer et al., 1993). Nevertheless,
117 it must be underlined that the Florida phosphorite SRM 120c is a compositional, not an isotopic
118 international reference, hence its oxygen isotope ratio has never been officially certified. In
119 order to comply with the IUPAC recommendations (Brandt et al., 2014), a two-point calibration
120 can also be performed with NBS 127, which is a barium sulfate calibrated reference material
121 for oxygen isotopes ($\delta^{18}\text{O} = 9.3\text{‰}$ VSMOW), as we proceeded in some recent papers (e.g. Rey
122 et al., 2018; Goedert et al., 2018). However, we underline that NBS 127 is a different matrix,
123 *i.e.* a barium sulfate instead of a silver phosphate, a chemical difference that needs to be taken
124 into account during calibration procedures even though the recently developed “purge-and-
125 trap” technology was able to overcome this pitfall as shown by Fourel et al. (2011). Moreover,
126 the stock of NBS 127 international reference hosted by the IAEA is now exhausted, thus
127 seriously reducing the possibility of calibrating the oxygen isotope composition of solid
128 matrices. Therefore, the need for alternative calibrated material is becoming critical.

129 Here, we propose a simple and cheap protocol to synthesize silver phosphate in a wide
130 range ($\approx 35\text{‰}$) of oxygen isotope compositions based on thermodynamic properties of the
131 phosphate-water system, more specifically the equilibrium isotopic fractionation factor and the
132 kinetics and temperature of isotopic exchange according to the data published by Lécuyer et al.
133 (1999b). Beyond the theoretical considerations, an “Excel calculation sheet” is provided as a

134 supplementary material. This calculation sheet allows the $\delta^{18}\text{O}$ of precipitated Ag_3PO_4 to be
135 predicted by tuning various parameters such as the temperature of oxygen isotope exchange,
136 the duration of the reaction and the isotopic compositions of reactants.

137

138 **2. Theoretical background**

139 **2.1. First-order kinetics of isotopic exchange between dissolved phosphate and water**

140

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

145



149

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

155

156
$$f = 1 - \exp(-kt) = \frac{\delta^{18}\text{O}(\text{PO}_4)_i - \delta^{18}\text{O}(\text{PO}_4)_t}{\delta^{18}\text{O}(\text{PO}_4)_i - \delta^{18}\text{O}(\text{PO}_4)_e} \quad (4)$$

157

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

160

161
$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

162

163 with A being the Arrhenius pre-exponential factor, E_a the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)
 164 of the isotopic reaction, R the universal gas constant, T the absolute temperature (K), t the time
 165 (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
 166 isotope composition of H_2PO_4^- at any time t during the course of the isotopic reaction, and
 167 $\delta^{18}\text{O}(\text{PO}_4)_e$ the oxygen isotope composition of H_2PO_4^- at isotopic equilibrium with H_2O . Note
 168 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 $\delta^{18}\text{O}(\text{PO}_4)_t =$
 169 $\delta^{18}\text{O}(\text{PO}_4)_e$.

170

171 **2.2. Experimental determination of thermodynamic variables (k, E_a and α)**

172 **2.2.1. The rate constant k**

173

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

176

177
$$\log(k) = 12.35 \pm 0.63 - 6.98 \pm 0.24(10^3 \text{T}^{-1}) \quad (6)$$

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

$$\ln(1 - f) = -kt \tag{7}$$

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:

$$t = \frac{0.693}{k} \tag{8}$$

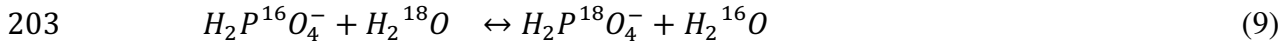
2.2.1. The activation energy E_a of the reaction

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 $\text{pH} = 5$ (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

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

202



204

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

207

$$208 \quad \alpha_{(H_2PO_4^- - H_2O)} = \frac{\left[\frac{^{18}O}{^{16}O}\right]_{H_2PO_4^-}}{\left[\frac{^{18}O}{^{16}O}\right]_{H_2O}} \quad (10)$$

209

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

214

$$215 \quad 10^3 \ln \alpha_{(H_2PO_4^- - H_2O)} = 18.35 \pm 0.37(10^3 T^{-1}) - 32.29 \pm 1.01 \quad (11)$$

216

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

218 **3.1. Experimental protocol of silver phosphate precipitation**

219

220 We present a protocol of silver phosphate precipitation from a highly soluble salt in
221 water (solubility = 25 g.100 mL⁻¹ at 25°C; Lide, 2005) such as the potassium dihydrogen

222 phosphate KH_2PO_4 (Lécuyer et al., 1999b). An aliquot of 50 mg of pure high-grade (> 99.5
223 wt%) Sigma-Aldrich™ synthetic KH_2PO_4 is dissolved in 35 mL of deionized water of known
224 oxygen isotope composition. The resulting aqueous solutions have a concentration of 1 g.L^{-1}
225 (10.6 mmol.l^{-1}) of phosphate ions with a pH of 5 at ambient temperature. It is important to note
226 that the amount of oxygen in water is much higher than in the pool of dissolved phosphate
227 (oxygen molar ratio between H_2O and $\text{KH}_2\text{PO}_4 \approx 5000$), consequently the change in the oxygen
228 isotope composition before and after equilibrium is not detectable with respect to the analytical
229 uncertainties ($1\sigma = 0.05\text{‰}$ for the $\delta^{18}\text{O}$ of H_2O). The solutions are transferred into Ace
230 Glass™ pyrex tubes sealed with a threaded teflon plug. Each set of tubes for a given temperature
231 is placed in a high precision oven for run-times defined by the user. Samples are withdrawn at
232 desired times and quenched in cold water to room temperature within a few minutes. Each
233 sample of dissolved phosphate is quantitatively precipitated as silver phosphate (chemical
234 yields are close to 100%) according to the protocol determined by Firsching (1961), which
235 means that all the dissolved phosphate species ($\approx \text{H}_2\text{PO}_4^-$), are converted into Ag_3PO_4 . For a
236 chemical yield of 100%, the expected amount of silver phosphate is close to 150 mg. Running
237 an experiment batch with ten Ace Glass™ pyrex tubes at the same time ensures the production
238 of about 1.5 g of silver phosphate crystals of predicted oxygen isotope composition.

239

240 **3.2. Oxygen isotope analysis of silver phosphate**

241

242 Oxygen isotope compositions are measured using a high-temperature pyrolysis
243 technique involving a VarioPYROcube™ elemental analyzer (EA) interfaced in continuous
244 flow (CF) mode to an Isoprime™ isotopic ratio mass spectrometer (IRMS) (EA-Py-CF-IRMS

245 technique (Lécuyer et al., 2007; Fourel et al., 2011) at the University Claude Bernard Lyon 1.
246 For each sample, 5 aliquots of 300 µg of Ag₃PO₄ are mixed with 300 µg of pure carbon black
247 powder and loaded in silver foil capsules. Pyrolysis is performed at a temperature of 1450°C.
248 Measurements are calibrated against the SRM 120c (natural Miocene phosphorite from Florida)
249 and the NBS 127 (barium sulfate, BaSO₄: δ¹⁸O = 9.3‰ VSMOW). The δ¹⁸O of SRM 120c is
250 fixed at 21.7‰ (VSMOW) according to Lécuyer et al. (1993) who determined this value by
251 fluorinating silver phosphate crystals (n = 25, 1σ = 0.16) at 600°C for 12 hours and calibrated
252 the oxygen isotope ratios with the calibrated reference material NBS 28 quartz (9.5±0.2‰), and
253 measurement standards that are the “Snowbird” quartz (16.1±0.1‰) and the tholeiitic basaltic
254 glass standard CIRCE 93 (5.6±0.1‰).

255

256 **3.3. Predicted oxygen isotope composition of synthesized silver phosphate**

257

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

260

$$261 \delta^{18}O(PO_4)_t = \delta^{18}O(PO_4)_i - \{\delta^{18}O(PO_4)_i - \delta^{18}O(PO_4)_e\} \{1 - \exp(-kt)\} \quad (12)$$

262

263 We emphasize that the recommended working range of temperature is from 110°C to
264 130°C. Indeed, below a temperature of 110°C, kinetics of reaction is so slow that significant
265 isotopic exchange takes months, or even years when temperature is below 100°C. Then, above
266 a temperature of 130°C, the Ace Glass™ pyrex tubes sealed with a threaded teflon plug could
267 start to leak, leading to a shift of the initial oxygen isotope ratio of water. Finally, we provide
268 an “Excel calculation sheet” (Supplementary File) that automatically computes the oxygen

269 isotope composition of the precipitated silver phosphate depending on time t and temperature
270 T of isotopic exchange as well as the oxygen isotope compositions of reactants KH_2PO_4 and
271 H_2O at $t = 0$. Predicted oxygen isotope compositions of synthesized silver phosphate range from
272 -7 to $+31\text{‰}$ VSMOW for a temperature range comprised between 110°C and 130°C and a range
273 of water $\delta^{18}\text{O}$ from -20 to $+15\text{‰}$ VSMOW (Figure 2). For example, we have provided a
274 calculation table (Supplementary File) showing a possible tuning of the parameters described
275 above to obtain silver phosphate crystals with a $\delta^{18}\text{O}$ value (‰ VSMOW) that mimics that
276 certified for the NBS 127 barium sulfate international reference.

277 In order to further demonstrate the efficiency of this method, we analysed the oxygen
278 isotope compositions of three silver phosphates with expected $\delta^{18}\text{O}$ values ranging from about
279 $+10$ to $+22\text{‰}$ VSMOW (Table 1), which cover the most common range of documented $\delta^{18}\text{O}$
280 values for natural dissolved phosphate and apatites. We reported the measured $\delta^{18}\text{O}$ values as
281 a function of the expected ones and we obtained a strong linear correlation with a slope close
282 to 1 ($a = 1.032 \pm 0.029$) and an intercept close to 0 ($b = -0.794 \pm 0.466$) (Figure 3). Within this
283 isotopic variation range of 12‰ , the calculated standard error is 0.24‰ , which is comparable
284 to the error associated with the admitted $\delta^{18}\text{O}$ value of SRM 120c. Therefore, we show that this
285 method is suitable to produce robust in-house made calibrated Ag_3PO_4 for the oxygen isotope
286 analysis of phosphatic compounds.

287

288 **3.4. Potential application to the sulfate-water system**

289

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

301

302 **4. Conclusions**

303

304 The protocol we developed in this study is based on the equilibrium isotopic
305 fractionation factor α , the kinetics k and temperature T of isotopic exchange in the dissolved
306 phosphate-water system. It offers the possibility to produce in a reasonable amount of time (a
307 few days or a couple of weeks) about 1.5 g (the equivalent of 1,000 measurements) of silver
308 phosphate of known oxygen isotope composition. Moreover, the tuning of some parameters
309 (time and temperature of isotopic exchange and the compositions of reactants) allows the
310 synthesis of silver phosphate within a large range ($\approx 35\text{‰}$) of oxygen isotope ratios that match
311 the documented natural variability for both phosphate-bearing minerals and dissolved
312 phosphate of organic or inorganic origin.

313

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547

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

558

559 **Figure captions:**

560

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

563

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

571 For instance, the $\delta^{18}\text{O}$ of $\text{H}_2\text{O}(\text{i})$ of $+15\text{‰}$ VSMOW can be obtained by collecting 1 L
572 of residual water obtained by evaporation at ambient temperature ($\approx 20^{\circ}\text{C}$) under a laminar flow
573 hood of 50 L of deionized water with an initial $\delta^{18}\text{O}$ of -10.5‰ of which the ultimate source is
574 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
575 collecting frozen atmospheric vapour trapped inside a freezer working at a temperature of -
576 80°C .

577

578 Figure 3: Linear regression between the oxygen isotope compositions of measured and
579 predicted $\delta^{18}\text{O}$ values of three samples of synthesized silver phosphate. A slope of 1.032 ± 0.029
580 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

