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1 **Temperature dependence of oxygen- and clumped isotope fractionation in carbonates: a**

2 **study of travertines and tufas in the 6-95ºC temperature range**

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18

19 **Abstract**

20

21 Conventional carbonate-water oxygen isotope thermometry and the more recently developed

22 clumped isotope thermometer have been widely used for the reconstruction of

23 paleotemperatures from a variety of carbonate materials. In spite of a large number of studies,

24 however, there are still large uncertainties in both $\delta^{18}O$- and Δ_{47}-based temperature

25 calibrations. For this reason there is a need to better understand the controls on isotope

26 fractionation especially on natural carbonates. In this study we analyzed oxygen, carbon and

27 clumped isotopes of a unique set of modern calcitic and aragonitic travertines, tufa and cave

28 deposits from natural springs and wells. Together these samples cover a temperature range

29 from 6 to 95°C. Travertine samples were collected close to the vents of the springs and from

30 pools, and tufa samples were collected from karstic creeks and a cave. The majority of our

31 vent and pool travertines and tufa samples show a carbonate-water oxygen isotope

32 fractionation comparable to the one of Tremaine et al. (2011) with some samples showing

33 higher fractionations. No significant difference between the calcite-water and aragonite-water

34 oxygen isotope fractionation could be observed. The Δ_{47} data from the travertines show a

35 strong relationship with temperature and define the regression $\Delta_{47} = (0.044\pm0.005 \times 10^6) / T^2$

36 $+ (0.205\pm0.05047)$. The pH of the parent solution, mineralogy and precipitation rate do not

37 appear to significantly affect the Δ_{47}–signature of carbonates, compared to the temperature

38 effect and the analytical error. The tufa samples and three biogenic calcites show an excellent

39 fit with the travertine calibration, indicating that this regression can be used for other

40 carbonates as well. This work extends the calibration range of the clumped isotope

41 thermometer to travertine and tufa deposits in the temperature range from 6ºC to 95ºC.

42

43

46

47 **1 Introduction**

48

49 Since the early times of stable isotope geochemistry, the oxygen isotope fractionation

50 between calcite and water is one of the most widely used methods to reconstruct the

51 temperature at which calcite has precipitated (McCrea, 1950; Epstein et al., 1953; Kim and

52 O'Neil, 1997; Coplen, 2007). More than 50 years of research have produced a number of

53 theoretical, empirical and laboratory-based calibrations, but significant discrepancies still

54 exist among them. Because laboratory calibrations are challenging, naturally precipitated

55 carbonates are an important source of calibration materials for the oxygen isotope

56 fractionation, provided that temperature and conditions of carbonate precipitation are well

57 known. In this paper we use an extensive set of travertine and tufa samples, precipitated under

58 very different geochemical conditions and in a large but well-constrained temperature range,

59 as a natural laboratory to better understand the dominant controls on the carbonate-water

60 isotope fractionation and on the recently developed carbonate clumped isotope thermometer.

61 Conventional carbonate-water paleothermometry requires knowledge of the oxygen isotope

62 composition of the water from which the carbonate precipitated, which is often impossible to

63 estimate. The carbonate clumped isotope thermometer (Ghosh et al., 2006a) circumvents this

64 problem because it requires no assumptions on the $\delta^{18}O$ of the precipitating water (Eiler,

65 2007). The theoretical basis of the clumped isotope paleothermometer is the proportionality

66 between observed excess abundance of $^{13}C^{18}O$-bonds in carbonate relative to its stochastic

67 distribution (defined as $\Delta_{47,}$ see below) and the carbonate precipitation temperature. This

68 excess abundance of $^{13}C^{18}O$-bonds is independent of the bulk carbonate isotopic composition.

69 Clumped isotope geochemistry has already been applied to a number of materials and

70 questions, for example to soil carbonates (Ghosh et al., 2006b; Snell et al., 2013), speleothems

71 and cryogenic cave carbonates (Affek et al., 2008; Daëron et al., 2011; Kluge et al., 2014a),

72 land snails (Zaarur et al., 2011), brachiopods (Came et al., 2007), and studies on diagenesis

73 and low grade metamorphism (Huntington et al., 2011; Ferry et al., 2011; Budd et al., 2013).

74   One of the open questions hampering a wider use of the carbonate clumped isotope

75   thermometer is the discrepancy between published temperature calibrations (Ghosh et al.,

76   2006a, 2007; Guo et al., 2009; Dennis and Schrag, 2010; Tripati et al., 2010; Eagle et al.,

77   2010; Thiagarajan et al., 2011; Henkes et al., 2013; Grauel et al., 2013; Zaarur et al., 2013;

78   Tang et al., 2014; Came et al., 2014; Fernandez et al., 2014). The reasons for these differences

79   remain largely unclear. Came et al. (2014) and Fernandez et al. (2014) suggested that the

80   different phosphoric acid reaction temperatures for the conversion of sample carbonate to CO_2

81   may be one of the main causes of discrepancies. However, Defliese et al. (2015) determined

82   the phosphoric acid fractionation factors for mass-47 CO_2 for a range of reaction temperatures

83   for calcite aragonite and dolomite, and suggested that mineralogical and acid fractionation

84   factor differences are not likely the cause of discrepant calibrations. Other differences in the

85   analytical procedures that could alternatively cause discrepancies are the use of common

86   versus individual reaction vessels or the amount of sample and acid used (Wacker et al.,

87   2013). Because with the Kiel IV- MAT 253 system operated at ETH the reaction occurs at

88   70°C and much less sample and acid is used compared to other setups, it is necessary to

89   evaluate the slope resulting from this analytical system.

90   In addition to the discrepancies, most calibrations based on natural samples are limited to

91   temperatures below 45°C. To improve applicability of this method it is vital to extend the

92   range of such calibrations to higher temperatures. Laboratory experiments are challenging,

93   and may not be representative for all naturally occurring carbonates (Henkes et al., 2013),

94   thus, in this study we focused on natural carbonates.

95   Among terrestrial carbonates, clumped isotopes have not yet been applied to travertines, as

96   they are typically considered to be non-equilibrium deposits. Indeed, deviations from the

97   expected oxygen isotope 'equilibrium', as defined from laboratory measurements (Kim and

98   O'Neil, 1997), have been observed in natural carbonates (Gonfiantini et al., 1968; Turi, 1986;

99   Friedman, 1970; Fouke et al., 2000; Coplen, 2007; Kele et al., 2008). However, it is currently

100 unclear which, if any, of the published calibrations represents true equilibrium.

101 The natural calcite from the Devils Hole vein which was analyzed by Coplen (2007), is often

102 argued to be very close to equilibrium due to the very slow growth rates in this subaqueous

103 setting. Travertines are continental carbonates composed mainly of calcium carbonate

104 produced from CO_2 degassing of supersaturated calcium bicarbonate-rich waters, typically

105 hydrothermal in origin. Previous case studies on travertines from Egerszalók (Kele et al.,

106 2008) and Pamukkale and Karahayit (Kele et al., 2011) have shown that travertines

107 precipitating very close to the vent of the springs show oxygen isotope compositions similar

108   to the values predicted by Coplen (2007). Significant deviations are only observed along the

109   flow path with increasing distance from the vents where the water first emerges from the

110   underground. Therefore, we hypothesize that a careful choice of samples collected close to

111   vents offers the possibility to establish a robust clumped isotope calibration to higher

112   temperatures than the range covered by the natural carbonate calibrations published so far.

113   We use calcitic and aragonitic travertines from natural springs and artificial thermal wells

114   covering a temperature range between 5.6 and 95°C. This is a unique sample set, because to

115   date there are no Δ_{47} data available for natural carbonates precipitated at the Earth surface

116   above 50°C. In addition, we analysed also a set of tufa and cave carbonate deposits from

117   karstic waters to evaluate if these deposits would show a similar isotope fractionation. The

118   term tufa refers to continental carbonates typical of karstic areas, composed dominantly of

119   calcite and produced from ambient temperature, calcium bicarbonate-rich waters, containing

120   abundant remains of micro- and macrophytes (Capezzuoli et al., 2014).

121   The main advantages using travertines for the calibration of the clumped isotope thermometer

122   are: 1) Travertines grow over a wide temperature range; 2) the temperature, pH, and

123   chemistry of the depositing water and rate of deposition can be measured in the field; 3) these

124   carbonates represent mainly inorganic deposits and show no biological vital effect; 4) they

125   can form different polymorphs of calcium carbonate (calcite, aragonite).

126   We propose a calibration equation based on vent and open air pool samples only, as they have

127   been shown to be the least likely to be affected by kinetic fractionation effects (Yan et al.,

128   2012; Wang et al., 2014). The carbonate formed close to the vents corresponds to only a small

129   fraction of the total available carbonate dissolved in the water because water rapidly flows

130   away from the vent. For this reason the carbonate closest to the vent orifice records

131   precipitation due to initial degassing of only a small fraction of the CO_2. This may be the

132   reason why the first precipitates may be closer to the equilibrium conditions corresponding to

133   the temperature of the fluid before its emergence. In the case of the pools the reason may be

134   that there is a very thick water layer, CO_2 degassing is very slow and the precipitation rate is

135   also very low. In this case, H_2O and HCO_3^- are more likely to reach equilibrium. We then

136   evaluate the effects of other factors besides temperature controlling clumped isotope values,

137   such as precipitation rate, CO_2 degassing (change in pH), and evaporation. Finally, we

138   compare the results of these inorganic samples with a set of biogenic carbonates to evaluate if

139   the temperature-Δ_{47} relationship based on travertines is applicable to biogenic samples. Our

140   results will help improve the confidence in paleotemperature reconstructions not only from

141   travertines, but also from cave carbonates, diagenetic cements and biogenic carbonates.

142

2 Description of the sampling sites

143

144

145 The sampling sites are presented in Figures 1, 2 and 3. A detailed description for most of the

146 sites is given in Chafetz and Lawrence (1994), Demény et al. (2010) and Yan et al. (2012).

147 Below we describe the newly sampled sites and sampling strategy. The characteristics of all

148 sampled sites are summarized in Table 1.

149

2.1 Travertines

150

151 *2.1.1 Central Italian travertines*

152

153 Central Italy is rich in travertine and tufa deposits (Capezzuoli et al., 2011). For this study, we

154 sampled nine of these sites. The thermal spring of Palagio is located in Piacenzian marine

155 clays about 50 km NW of Siena. Thermal water with a pH of 6.57, mean temperature of

156 22.7°C and a discharge of ~1 L/s (Minissale, 2004), forms a small pool with carbonate raft

157 precipitation (Fig. 1A).

158 Bagnoli is located in Piacenzian marine sandy deposits about 20 km NW of Siena. Water

159 chemistry suggests that the water circulates in an anhydrite-dolomite reservoir of Triassic age

160 (Casagli et al., 1990). The Bagnoli water (T_{mean} = 23.7°C, pH = 6.62) presently forms only a

161 thin travertine deposit around the vent but Pleistocene tufa deposits in the area suggest that

162 activity may have been higher in the past (Capezzuoli et al., 2008). Samples were taken at the

163 outlet of a pipe (Fig. 1B).

164 The spring of Acqua Borra is located ~15 km east of Siena in Zanclean marine clays. The

165 thermal water has a mean temperature of 36.1°C, a pH of 6.58 and a low discharge rate,

166 presently issuing from a small pipe (Fig. 1C), where the samples were taken. The water

167 differs from other Tuscan thermal springs for its high salt (>12 g/L, 75% NaCl) and high CO_2

168 content.

169 At Rapolano Terme located ~30 km east of Siena, two springs were sampled. *Terme San*

170 *Giovanni* was the most active travertine-depositing site in the area, until the water was

171 diverted for use in a spa in the 1990s. Calcite raft samples were taken from a small resurgence

172 at the NE termination of a fissure-ridge (Guo and Riding, 1999) (Fig. 1D). The water is rich in

173 calcium, bicarbonate and sulfate, with a pH of 6.53 and T = 41.2°C. The second spring,

174 *Madonna al Colle Well,* is an intermittent thermal spring (T = 28°C, pH = 6.62) outflowing

175 from a borehole drilled in the 1960s for geothermal exploration. Water flux is controlled by a

176 tap at the top of the borehole, but frequently overflows spontaneously due to fluid
177 overpressure (Fig. 1E). Carbonate encrustations were sampled directly at the well.

178 The Il Doccio spring is characterized by a high temperature (T = 48.3°C), relatively low
179 discharge (0.3 L/s; Minissale, 2004) and pH = 7.05. It is located ca. 10 km south of Siena on
180 the Northern Appennines orogenic deposits. Deposition rate is very low, forming a small
181 travertine mound (Fig. 1F).

182 The Bagni di Petriolo area is located 30 km south of Siena. Several active hot springs align
183 along a fault with a mean temperature of 42.5°C and a low-rate discharge of ca. 10 L/s
184 (Minissale, 2004). Travertine and thermal waters (T = 44.3°C, pH = 6.45) were taken at the
185 *Bagni di Petriolo* thermal spa (Fig. 1G).

186 The Bagni San Filippo travertine is located on the eastern side of the Middle Pleistocene
187 Monte Amiata volcano (Brogi et al., 2010). Several hot springs emerge at a maximum
188 temperature of 52°C. The *Fosso Bianco* spring (T = 44.6°C, pH: 6.53) located along the
189 homonymous creek, in the eastern and lower side of the same-fissured body, was sampled
190 (Fig. 1H).

191 The southern sampled area in the surrounding of Viterbo is located on Middle-to-Late
192 Pleistocene pyroclastics and lavas. The *Piscine Carletti* spring actively precipitates travertine
193 and it is characterized by T_{mean} = 57.9°C, pH = 5.67 and 3.7 L/s discharge (Pentecost, 1995;
194 Di Benedetto et al., 2011) (Fig. 2A).

195

196 *2.1.2 Carbonate deposits at Hungarian thermal wells*

197

198 Five travertine-depositing sites were sampled in Hungary. At Széchenyi thermal spa
199 (Budapest), groundwater is extracted from a 1257 m deep well from the top of the Triassic
200 aquifer. The sampled carbonate was formed in 2012 in the basement of the spa. Sample Sz.-
201 2/2 was taken directly at a fissure of the tube (Fig. 2B), while water with a temperature of
202 70.9°C and pH of 6.4 was sampled at a tap on the same tube several meters away. The 2092 m
203 deep Tura thermal well was drilled in 1963 as an oil-exploratory borehole and reached thermal
204 karst water discharging with 95°C and pH = 6.88. Deposited travertines cover the whole well-
205 head. The well was closed in 1998, but travertine and water samples were taken in 2000 at a
206 trial-operation of the well after the travertine cover was removed. The travertine sample
207 originates from the earliest deposition after 2000. Carbonate sample Bük-4 was collected
208 from the outflowing water (T = 54.9°C, pH = 6.88) of the 1282 m deep Bük-1 thermal well
209 (W Hungary), which supplies the Bük thermal spa with thermal water of 58°C since 1960.

210 The water originates from Miocene porous aquifers. Travertine and water were collected at

211 the standpipe of the well, where excess water is periodically overflowing (Fig. 2C). The spa

212 of Igal is supplied with thermal water (T = 75°C, pH = 6.89) of a Triassic and Cretaceous

213 aquifer via the 651 m deep well of Igal 1. Carbonate deposits were sampled from the wall of

214 the tube (Fig. 2D). The Köröm thermal well (NE Hungary) drilled in 1961 hit thermal water

215 (82°C) at 1880 m depth. Travertine and water were sampled directly at the well outlet (sample

216 Kör-13/0, T = 79.2°C, pH= 6.8) (Fig. 2E).

217

218 *2.1.3 Baishuitai travertine (China)*

219

220 The Baishuitai travertine, one of the largest travertine deposits in China, is located ~100 km

221 south of Shangri-La Town, Yunnan Province, China (Yan et al., 2012). Two travertine-

222 depositing systems are found here: a fast-flow channel system and slow-flow pool system.

223 The sample P5 (T_{summer} = 12°C, pH_{summer}= 8.14 and T_{winter} = 5.6°C, pH_{winter}= 8.19) was taken

224 about 300 m from the vent (spring S1-1) in the pool system (Fig. 2F).

225

226 *2.1.4 Narrow Gauge travertine (Yellowstone)*

227

228 The GeoBio-II spring (T_{vent} = 61.1°C, pH: 6.6) at Narrow Gauge Springs (Mammoth Hot

229 Springs, Yellowstone, USA, Chafetz and Lawrence, 1994) was sampled. Sample NG-2 is a

230 precipitate collected from a rope that was immersed in the water very close to the vent orifice

231 (T = 60.4°C, pH: 6.6; Fig. 2G) and represents the precipitation of a few hours.

232

233 *2.1.5 Madre del Agua (Tenerife, Spain)*

234

235 A 20 cm thick calcite encrustation sample and precipitating water were collected at the

236 discharge point of an artificial tunnel at Madre del Agua (Canarian Island) situated in the

237 south-eastern part of Tenerife. Water temperature at the sampling point was 33.8°C, with a

238 pH of 7.7 and a discharge rate 5.3 L/s (Demény et al., 2010).

239

240 **2.2 Tufa and cave tufa samples from Hungary and Italy**

241

242 Tufa samples were collected along a 2.4 km long section in the Szalajka-valley (Szilvásvárad,

243 Bükk Mts, Hungary) where supersaturated karstic springs (average runoff is 70 l/sec)

244   precipitate tufa terraces, dams and cascades, further promoting CO_2 degassing and tufa

245   precipitation. Starting from the Szalajka-spring (~8.6°C) three samples (Szal-2, Szal-6, Szal-

246   15; Fig. 3A,B,C; Table 1) were sampled in October along the flow path downstream 413 m (T

247   = 10.1°C, pH = 8.45), 773 m (T = 11°C, pH = 8.55) and 2462 m (T = 12.1°C, pH = 8.53)

248   from the spring, respectively.

249   Three tufa samples with temperatures ranging from 11°C to 20.7°C were collected from

250   Sarteano, Rapolano Terme (Canatoppa Creek) and La Pigna (all in Tuscany, Italy). The

251   Sarteano tufa is located along the Fosso dei Mulini Creek in Sarteano village. Water

252   originates from a private pool about 100 m upstream from the sampling point (T = 20.7°C, pH

253   =8.92) and the entire creek is carbonate-encrusted (Fig. 3D). The Canatoppa tufa (Rapolano

254   Terme) precipitate along the Canatoppa Creek (Fig. 3E) from water with a temperature of

255   11°C and pH of 8.94, north of the travertine fissure ridge at the Terme San Giovanni

256   described above. The La Pigna tufa is a perched spring tufa deposit formed from a small

257   resurgence south of Siena. We sampled the frontal portion of the system, about 20 m from the

258   spring point and below a 4 m-high cascade, where the temperature of the water is 12.5°C and

259   the pH is 8.61 (Fig. 3F). In order to represent different depositional environments, a recent

260   cave tufa (flowstone) sample precipitated from flowing water was additionally taken from the

261   Havasok tufa (Baradla cave, Aggtelek Karst, Hungary). The Havasok tufa dam (Fig. 3G)

262   forms from a thin, periodically flowing water film (~9.5°C).

263

264   **3 Methods**

265

266   *3.1 Sampling and in situ analyses*

267

268   In all cases only the uppermost surface of the recent travertine was sampled to ensure the

269   collection of freshly precipitated carbonates. Water samples were collected in 100 ml glass

270   bottles for stable oxygen isotope analyses. In situ measurements of temperature, pH and

271   electric conductivity (EC) of water were conducted at all sampling points using various

272   instruments: 1) At the Italian sites a Hanna HI 98130 meter was employed (precision: T =

273   ±0.1°C, pH = ±0.01). 2) The Yellowstone site was probed with a Hach HQ40d meter

274   (precision: T = ±0.1°C, pH = ±0.1). 3) At the Szalajka Creek a VWR EcoSense pH10

275   pH/Temperature Pen (precision: T = ±0.3°C, pH = ±0.02) was used, while conductivity was

276   measured with a Eutech Digital pH/EC Pen. 4) The Hungarian thermal wells were probed

277   with a WTW Multi 1970i meter with automatic temperature compensation to 20°C (precision:

278   T = ±0.1°C, pH = ±0.01).

279   At some sites the deposition rate could be calculated using the weight of carbonate deposited

280   on plexiglass substrates. The amount of modern travertine deposited on the plexiglass

281   substrates was determined by measuring the weight increase of the substrates. The detailed

282   description of the calculation can be found in Liu et al. (2010) and in Yan et al. (2012). In

283   cases where the placement of substrates was not possible the deposition rate (log R) was

284   estimated based on the size of the carbonate deposit. An annual change of the local carbonate

285   depositional morphology imply an intensive-to-moderate precipitation rate (cm/year), while a

286   slightly modified morphology implies a moderate-to-low precipitation rate (mm/year).

287   Considering the high deposition rates, the ages of sampled carbonates are estimated to be at

288   maximum several days for travertines or a few months for tufa.

289

290   *3.2 X–ray diffraction, electron microprobe, and stable isotope analyses*

291

292   The mineralogy of all carbonate samples was determined by X–ray powder diffraction (XRD)

293   using a Philips PW 1710 diffractometer (with CuKα radiation at 45 kV and 35 mA) at the

294   Institute for Geological and Geochemical Research, Hungarian Academy of Sciences (IGGR-

295   HAS, Budapest). Semi–quantitative phase analysis was made on randomly oriented samples

296   using the peak area of calcite 104 and aragonite 111 reflections (Bárdossy et al., 1980). The

297   relative error of the quantification is 5–10%. The mineralogy of some samples has been

298   determined at ETH Zürich using a Bruker AXS D8 Advance instrument. In order to determine

299   the size of individual crystals from the travertine deposits, electron microprobe analyses were

300   carried out at IGGR-HAS using a JEOL JXA-733 instrument.

301   All carbonate samples were powdered and homogenized using an agate mortar and pestle.

302   Carbon and oxygen isotope analyses of bulk carbonate samples were carried out as part of the

303   clumped isotope analyses with a Thermo Fisher Scientific Kiel IV preparation device coupled

304   to a Thermo Fisher Scientific MAT 253 isotope ratio mass spectrometer. For oxygen and

305   carbon isotopes the performance of the instrument was monitored with the 4 internal

306   standards ETH-1 ($\delta^{13}C$ = 2.14‰, $\delta^{18}O$ = −1.87‰), ETH-2 ($\delta^{13}C$ = −10.11‰, $\delta^{18}O$ =

307   −18.76‰), ETH-3 ($\delta^{13}C$ = 1.81‰, $\delta^{18}O$ = −1.77‰) and ETH-4 ($\delta^{13}C$ = −10.10‰, $\delta^{18}O$ =

308   −18.76‰), which are measured daily to carry out the corrections for clumped isotopes (see

309   below). The composition of these internal standards was determined using NBS 19 ($\delta^{13}C$ =

310   1.95‰ and $\delta^{18}O$ = −2.2‰) and NBS 18 ($\delta^{13}C$ = 5.05‰ and $\delta^{18}O$ = −23.1‰). The reference

311   gas used in the mass spectrometer is a commercial compressed gas tank, purity 99.99 % with

312   a $\delta^{13}C_{VPDB}$ value of −7.25‰ and a $\delta^{18}O_{VPDB}$ value of +1.65‰. $\delta^{18}O$ analyses of waters were

313   carried out at IGGR-HAS with a Thermo Fisher Scientific Delta Plus XP mass spectrometer

314   using the CO_2–water equilibration method (Epstein and Mayeda, 1953). In case of the water

315   samples, the in-house laboratory standards BWS-1, BWS-2 and BWS-3 were used, which are

316   calibrated against Vienna Standard Mean Ocean Water (V-SMOW) with International

317   Certification (SMOW, GISP and SLAP). Standard BWS-1 ($\delta^{18}O$ = −0.60±0.1‰) was made

318   from seawater and locally sampled lake water; BWS-2 ($\delta^{18}O$ = −10.50±0.1‰) was prepared

319   from tap water; and BWS-3 ($\delta^{18}O$ = −20.00±0.1‰) was made from snow from the Tatra

320   Mountains and Budapest (Kármán et al., 2014). Isotopic compositions are expressed in the

321   conventional δ notation in ‰ relative to V-PDB for carbonates and V-SMOW for water.

322   Reproducibility was better than ±0.1‰ for carbonate $\delta^{13}C$ and $\delta^{18}O$ and better than ±0.2‰ for

323     $\delta^{18}O$ of waters. The fractionation between carbonate and water are calculated from measured

324     $\delta^{18}O_{carbonate}$ and $\delta^{18}O_{water}$, where the fractionation factor is defined as α = (1 + $\delta^{18}O_{calcite}$/1000)

325   / (1 + $\delta^{18}O_{water}$/1000). $\delta^{18}O$ values of the three aragonitic travertines (Köröm, Széchenyi

326   thermal spa, Palagio) were corrected by −0.42‰, to account for the different phosphoric acid

327   digestion fractionation factor for aragonite (Kim et al., 2007).

328

329   *3.3 Clumped isotope analyses*

330

331   Carbonate isotopologue measurements were performed using a Thermo Fisher Kiel IV

332   preparation device coupled to a Thermo Fisher MAT 253 isotope ratio mass spectrometer as

333   described by Schmid and Bernasconi (2010), modified to include a Porapak trap eliminating

334   contaminants. The full procedure, including a new correction scheme, has been described by

335   Meckler et al. (2014). Briefly, per run 8-10 aliquots of 150-220 µg of two samples were

336   prepared and analysed in microvolume mode together with 8-10 aliquots each of 2 internal

337   carbonate standards. The $\delta^{13}C$, $\delta^{18}O$ and clumped isotope composition is calculated as the

338   average of the 8 to 10 analyses. Each analysis consisted of 6 cycles of 26 sec integration and

339   10 sec idle time after changeover valve switch. Initial m/z 44 beam intensities averaged

340   around 23 V, decreasing to around 13 V after 7 cycles. The temperature-dependent mass 47

341   anomaly is defined as (Ghosh et al., 2006a):

342     $$\Delta_{47}(‰) = \left[\left(\frac{R^{47}}{R^{47*}} - 1\right) - \left(\frac{R^{46}}{R^{46*}} - 1\right) - \left(\frac{R^{45}}{R^{45*}} - 1\right)\right] \times 1000 \, ,$$

343 where R^i is the abundance of the minor isotopologues relative to the most abundant

344 isotopologue with mass 44, and the expected stochastic ratios R^{i*} are calculated based on the

345 measured abundance of ^{13}C and ^{18}O in the sample.

346 The results for standards and samples were corrected offline for pressure baseline (PBL)

347 effects (Bernasconi et al., 2013, Meckler et al., 2014) and were transferred to the absolute

348 reference frame (Dennis et al., 2011) by means of an empirical transfer function (ETF) based

349 on heated and equilibrated gases measured during an earlier period (Meckler et al., 2014).

350 Afterwards, an acid fractionation correction of +0.064‰ was applied to the $\varDelta_{47}$, which results

351 from a linear scaling of the observed offset between 25°C and 90°C acid temperature (Henkes

352 et al., 2013) to our reaction temperature of 70°C. Subsequent correction steps for sample

353 results were based on carbonate standards only: The results were first corrected for offsets

354 between measured and accepted values of four in-house carbonate standards, averaged within

355 a moving window encompassing 11 standards (~5 days of measurements). Finally, small

356 differences in scale compression during the measurement periods compared to the initial ETF

357 period were monitored and corrected for with a transfer function based again on the four

358 standards, which strongly differ in bulk isotopic composition and ordering state. The

359 "accepted" $\varDelta_{47}$ of the standards used for these corrections are (in parenthesis the sample

360 names used in Meckler et al. 2014): ETH-1 (ISO A) = 0.267‰, ETH-2 (ISO B) = 0.269‰;

361 ETH-3 (ISO R) = 0.524‰ and ETH-4 (ISO C) = 0.705‰. Our internal Carrara marble (MS2)

362 standard has a $\varDelta_{47}$ value of 0.397‰ and NBS 19 yielded a $\varDelta_{47}$ value of 0.390‰ ± 0.005 (n =

363 3). Both these values are well in the range of published values for Carrara marbles and NBS

364 19 (Dennis et al., 2011). The four ETH carbonate samples are available as 1g aliquots upon

365 request from S. Bernasconi.

366 Each sample was measured at least three times on different days (with 8-10 aliquots

367 each). The reported results are the averages of the three or more measurements, and reported

368 errors are standard errors of these averages. The long-term reproducibility of the method

369 based on standards is ±0.012–0.016‰ (1 SD) (Meckler et al., 2014). The confidence intervals

370 of the regressions were calculated according to Sachs (1984).

371

372 **4 Results**

373

374 *4.1 Physico-chemical parameters, deposition rate and isotopic composition of thermal and*

375 *karstic waters*

376

377   The physico-chemical parameters of the spring waters are summarized in Table 1. For

378   travertines, temperatures ranged from 5.6°C to 95°C, pH ranged from 5.7 to 8.2, and

379   Electrical Conductivity (EC) varied from 1.38 to >20 mS cm^{-1}. $\delta^{18}O_{water}$ values ranged from

380   −17.9‰ to −4‰. Where deposition rates could be measured, they ranged from 0.05 and 28.5

381   mg cm^{-2}d^{-1} at the Italian Sites, and were determined as 0.44–2.5 mg cm^{-2}d^{-1} at Baishuitai (Yan

382   et al., 2012).

383   The three tufa samples from Italy were precipitated from waters of 11–20.7°C; the pH varied

384   between 8.61–8.94, while EC values ranged from 0.55 to 2.11 mS/cm. Karstic water samples

385   from the Szalajka Creek showed temperatures between 10.1 and 12.1ºC, pH between 8.45 and

386   8.55, EC between 0.473 and 0.503, and $\delta^{18}O_{water}$ values from −10.7 to −10.6‰.

387   The values reported here correspond to individual measurements at time of the sampling.

388   However, because the travertine depositing waters are old and derive from deep geothermal

389   circulation systems, their $\delta^{18}O$ values and physico-chemical parameters do not show seasonal

390   variations. In case of tufa sites minor seasonal changes might occur in both temperature and

391   $\delta^{18}O_{water}$, as these are more influenced by rainfall and seasonal change of ambient temperature

392   and insolation and they form further downstream, as in general there is no carbonate

393   deposition in the spring's orifice. However, due to the facts that sampling has been performed

394   mainly during dry season and that carbonate deposition is rapid (up to a few months for the

395   tufa samples), we can assume that the temperatures, measured during sampling campaigns,

396   adequately represent the growth temperatures of the samples.

397

398   *4.2 Mineralogy*

399

400   All samples are mainly composed of calcite, aragonite or their mixture (Table 1). Samples

401   containing elemental sulfur (Il Doccio, Bagni di Petriolo, Table 1) were excluded from

402   clumped isotope analysis as sulfur can affect the clumped isotope signal. Based on SEM

403   analyses, individual crystal size varies not only between samples but also within samples and

404   according to mineral phase. Travertine samples are composed mainly of complex calcite

405   crystals (~10–100 μm), with some exhibiting a dendritic morphology. Aragonite (~100 μm)

406   and gypsum crystals (100–150 μm) are also present in some samples (Fig. 4).

407

408   *4.3 Stable isotopic composition of travertine and tufa samples*

409

410 Carbon and oxygen isotope compositions of all travertine and tufa samples are reported in

411 Table 1. $\delta^{13}C$ and $\delta^{18}O$ values range between $-11.27‰$ and $+7.45‰$ and between $-24.51‰$

412 and $-5.43‰$, respectively. Tufa collected downstream from the karstic water of the Szalajka

413 Creek show a small increase in $\delta^{13}C_{tufa}$ (from $-10.2‰$ to $-9.43‰$) and decrease in $\delta^{18}O_{tufa}$

414 (from $-8.47‰$ to $-9.30‰$) (Table 1). The Havasok cave tufa shows similar $\delta^{13}C$ ($-10.95‰$)

415 and a bit higher $\delta^{18}O$ ($-7.73‰$) values compared to the Szalajka tufa samples taken from the

416 surface (Table 1). $\delta^{13}C$ values of the Italian tufa sites are similarly low (between $-11.27‰$

417 and $0.55‰$) and $\delta^{18}O_{tufa}$ values vary from $-7.39‰$ to $-5.66‰$. In Figure 5A we plotted the

418 carbonate–water $1000\ln\alpha$ values against temperature. The regression through the travertines

419 alone (diamonds and squares) shows a steeper slope than commonly observed in carbonates

420 (e.g. Kim and O'Neil, 1997; Tremaine et al., 2011). A regression through the entire dataset

421 including the tufa and cave carbonates (Triangles), however, defines a slope and intercept

422 much closer to the one of Tremaine et al. (2011) (see discussion below). No significant

423 difference is observed between aragonite and calcite samples (Fig. 5B).

424

425 *4.4 Δ_{47} values of travertine, tufa, and biogenic samples*

426

427 Δ_{47} values of travertine and tufa samples vary between $0.510\pm0.012‰$ and $0.760\pm0.008‰$

428 (Table 1). The three downstream tufa samples from the Szalajka Creek show no systematic

429 trend and Δ_{47} values are between $0.732\pm0.008‰$ and $0.760\pm0.008‰$ (Table 1). The Havasok

430 cave tufa shows a very similar Δ_{47} value ($0.756\pm0.01‰$). The Sarteano, Canatoppa and La

431 Pigna tufa samples yielded Δ_{47} values between $0.703\pm0.009‰$ and $0.742\pm0.008‰$ (Table 1).

432 When plotted against temperature (Fig. 6A, B), all samples show a very good fit in spite of

433 the different depositional environments. In addition, we did not observe a systematic

434 difference between calcite and aragonite samples (Fig. 6B). For comparison we also analyzed

435 three biogenic carbonates, which were previously analyzed for Δ_{47} and described in detail by

436 Wacker et al. (2014) (Table 2). All three samples fit very well on the regression defined by

437 the travertines. The Δ_{47} value of $0.648\pm0.014‰$ of the ostrich eggshell compares very well

438 with the $0.643\pm0.005‰$ obtained by Wacker et al. (2014). For *D. wyvillei* we obtained a Δ_{47}

439 value of $0.742\pm0.009‰$, which is 0.29 higher than the $0.713\pm0.009‰$ reported by Wacker et

440 al. (2014) and for *A. Islandica* we obtain a value of $0.759\pm0.004‰$, 0.035 higher than the

441 value reported in Wacker et al. (2014).

442

443 **5 Discussion**

444

5.1 Oxygen isotope fractionation

446

447 The temperature dependence of the oxygen isotope fractionation in our samples is compared
448 with that of other studies in Figure 7. The majority of our vent and pool travertines show a
449 higher mineral-water oxygen isotope fractionation than the Kim and O'Neil (1997) study, in
450 agreement with the results of Kele et al. (2008, 2011), and many of them fit well on the
451 curves published by Coplen (2007), Tremaine et al. (2011) and Affek and Zaarur (2014). Our
452 travertine data alone define a fractionation that can be expressed as $1000\ln\alpha = (20\pm2)$ x
453 $1000/T - (36\pm7)$ ($R^2 = 0.96$). This slope is steeper than the previously published curves and is
454 strongly influenced by 5 samples with very high fractionation. The cause of these very high
455 fractionations is not clear, and we could find no relationship with any physico-chemical
456 parameter we have measured, but similar high fractionations have also been reported by Kele
457 et al. (2011) in other travertines and seem to be a common feature that needs additional
458 studies. Possible causes for changes in isotope fractionation are pH variations (e.g. Zeebe,
459 1999), but we do not observe a systematic positive offsets with decreasing pH as it would be
460 expected if pH were a major controlling factor. A more comprehensive discussion of the
461 oxygen isotope fractionation based on a much larger dataset will be published elsewhere.
462 In case of the Szalajka spring section the $\delta^{18}O_{carbonate}$ show slight downstream increase (from
463 -10.2 to -9.44 ‰), while the $\delta^{18}O_{water}$ is nearly constant (-10.6‰) (Table 1). The water
464 temperature of the Szalajka Creek increases slightly downstream (from 10.1°C to 12.1°C,
465 Table 1) due to radiation and contact with the atmosphere, which is warmer than the cold
466 karstic water. This downstream temperature increase can cause the decreasing $\delta^{18}O_{carbonate}$
467 values along the flow path. If we include the tufa samples deposited from cold karstic waters,
468 the regression line becomes $1000\ln\alpha = (16.8\pm1.7)$ x $1000/T - (26\pm5.4)$ ($R^2 = 0.95$) (Fig. 5A),
469 which is indistinguishable from the regression line of Tremaine et al. (2011) and the results of
470 the surface precipitation experiments of Affek and Zaarur (2014), confirming that these
471 regression lines are valid to temperatures of up to 95°C. In spite of the fact that travertines
472 have generally very high precipitation rates (see below), which could lead to lower apparent
473 oxygen isotope fractionation, no significant difference between the calcite-water and
474 aragonite-water oxygen isotope fractionation is observed (Fig. 5B).

475

5.2 Temperature dependence of Δ_{47} in travertines and tufa

477

478 Figures 6A and 6B show the T-Δ_{47} relationship for the entire sample set defining an excellent
479 correlation of Δ_{47} with the temperature of deposition. If we only use the travertine samples
480 collected at temperatures between 5.6 and 95°C and exclude the tufa to avoid mixing of two
481 groups of samples that potentially have different characteristics to define the T-Δ_{47}
482 relationship, we obtain:

483

484 $$\Delta_{47} = (0.044 \pm 0.005 \times 10^{6}) / T^{2} + (0.205 \pm 0.047) \qquad R^{2} = 0.96 \qquad (eq.\ 1)$$

485

486 The tufa samples and the three biogenic samples fit well within the error of the regression,
487 supporting the validity of the travertine calibration also for tufa formed in karstic
488 environments.
489 The Δ_{47} value of the calcite raft sample collected from the Terme San Giovanni fissure ridge
490 (Table 1, Fig. 6B) shows a positive offset compared to the empirical calibration line. If this
491 outlier is discarded from the calibration data set, the r^{2} increases to 0.99, while *eq. 1* does not
492 change significantly. This positive offset cannot be explained by enhanced disequilibrium at
493 the surface of the solution (Affek and Zaarur, 2014), as this would produce Δ_{47} values below
494 the calibration line. For this sample, the water temperature was measured below the water
495 surface, while the raft sample could record slightly lower water temperature at the water-air
496 interface, potentially explaining a small part of the 10°C offset. Affek et al. (2014) similarly
497 found enriched Δ_{47} in a surface raft sample from a cave pool and speculated that the reason
498 could be reduced super-saturation of the precipitating water compared to other speleothem
499 formation sites due to prior calcite precipitation.
500 For the karstic Szalajka Creek, tufa deposition only starts 400 m further downstream of the
501 spring. Δ_{47} values of tufa deposits collected downstream show no systematic trend with
502 distance from the discharge point and the samples scatter around the travertine regression
503 (Fig. 6A). The lack of any systematic downstream effect on Δ_{47} may be explained by the
504 relatively constant water temperatures along the stream and relatively low precipitation rates.
505 This shows that there is no significant influence of kinetic fractionation effects on Δ_{47} in these
506 tufa samples. It is also noteworthy that the three biogenic samples analyzed fit very well on
507 the calibration line (Fig. 6A), indicating that this calibration is potentially useful also for
508 biogenic materials.
509 Comparison with other published T-Δ_{47} calibrations (Fig. 8) shows that the slope of our
510 regression line is intermediate between a group of steeper ones, derived from 25°C acid
511 digestions (Ghosh et al., 2006a; Tripati et al., 2010; Zaarur et al., 2013; Came et al., 2014)

512   and a group of shallower slopes, produced with 90°C acid digestions (Dennis and Schrag,

513   2010; Henkes et al., 2013; Eagle et al., 2013; Wacker et al., 2014; Kluge et al., 2015). The

514   difference between our calibration and the one of Wacker et al. (2014) is due to the higher

515   values we obtain for the samples grown at cold temperatures, whereas for the Ostrich eggshell

516   formed at 38°C we obtained the same Δ_{47} value. This could be seen as further evidence for the

517   supposed relationship between calibration slopes and carbonate acid digestion temperature of

518   carbonates (Fernandez et al., 2014), with a stronger influence on samples with high Δ_{47} values.

519   However, this explanation has recently been questioned by the experiments of Defliese et al.

520   (2015). It must furthermore be noted that other effects can influence the slope of the T-Δ_{47}

521   relationship, exemplified by two recent studies reporting shallow slopes, despite acid

522   digestions at 25°C: The surface precipitate calibration of Affek and Zaarur (2014) and the

523   recent calibration of Petrizzo et al. (2014). In view of these unknowns, it is important to

524   increase the efforts to understand the origin of these differences including interlaboratory

525   calibration exercises and studies of other possible causes for discrepancies such as the sample

526   to acid ratio and/or factors influencing the re-equilibration of CO_2 with water during the

527   digestion (Defliese et al., 2015). Considering the systematic differences in the slopes of the

528   calibrations obtained with different analytical setups it is important that the calibration used to

529   calculate temperatures was produced with a similar system as used for the samples. One

530   advantage of the high-temperature digestions at 70 and 90°C is the increased reaction rate that

531   improves the sample throughput and allows an automatisation of the extraction system (e.g.

532   Passey et al., 2010; Meckler et al., 2014) which is not possible for reactions at 25°C.

533

534   *5.3. Effects of depositional environment on the Δ_{47} values: places of equilibrium and*

535   *disequilibrium*

536

537   The data presented in this study are derived from samples that were carefully chosen to

538   minimize kinetic fractionation effects. We chose only vent and pool samples, which have

539   been shown to be least affected by kinetic fractionation due to progressive degassing (Yan et

540   al., 2012; Wang et al., 2014). The 1000lnα values for most of the samples in this study are

541   close to the original regression line of Kele et al. (2011) and the one of Tremaine et al. (2011),

542   but some samples show higher $\delta^{18}O$ values. As already noted by Affek and Zaarur (2014),

543   rapid degassing may induce additional fractionation in $\delta^{18}O$, leading to higher carbonate $\delta^{18}O$.

544   We observe here an even larger extent of fractionation in carbonate $\delta^{18}O$ than what has been

545   observed by Affek and Zaarur (2014). At present it is unclear what the cause of this

546 divergence is, but our data confirms the observations of Affek and Zaarur (2014) that these

547 higher fractionations in $\delta^{18}O$ do not seem to be reflected in the clumped isotope data.

548 The depositional environments for the different samples in this study are very diverse. Where

549 CO_2 degassing rate is fast and the dissolved carbonate and calcium contents of the water are

550 high enough, travertine deposition starts directly at the spring orifice (e.g. Fig. 2D).

551 Sometimes, however, deposition begins only further downstream: e.g., at Pamukkale,

552 carbonate precipitation only starts 155 m downstream from the spring (Kele et al., 2011). If

553 the spring discharges inside a pool, deposition can take place on the surface of the pool in

554 form of calcite rafts (Fig. 1A). Deposition can also occur at the bottom or at the pool rim.

555 Although the mechanism and rate of precipitation in the pools is different from vents (much

556 lower precipitation rate in the pools), Δ_{47} data of pool travertine agree well with the vent

557 travertine calibration curve (Fig. 1A). In pools, with slow carbonate deposition, oxygen

558 isotope exchange between dissolved bicarbonate and H_2O drives oxygen and clumped isotope

559 values towards equilibrium. In cases of limited degassing and very slow carbonate

560 precipitation, the DIC can approach full oxygen isotope exchange with water, leading to

561 equilibrium $\delta^{18}O$ and Δ_{47} values (Affek et al., 2008). At artificial wells, the chosen deposits

562 are mainly carbonate encrustations on tubes (e.g. Rapolano Terme, Fig. 1E) and these fit the

563 vent and pool data very well.

564 Disequilibrium growth conditions can cause significant changes in both $\delta^{18}O$ and Δ_{47}. Kinetic

565 isotope effects during rapid CO_2 degassing can lead to higher $\delta^{18}O$ (and $\delta^{13}C$), but lower Δ_{47}

566 values (Guo et al., 2008; Affek, 2013). This inverse correlation was observed in modern

567 speleothems (Daëron et al., 2011; Wainer et al., 2011; Kluge and Affek, 2012; Kluge et al.,

568 2013), which are potentially more susceptible to kinetic isotope effects than carbonates

569 precipitated in bulk solution (Affek et al., 2008). Theoretical calculations of Guo (2008)

570 indicated that for each 1‰ increase in $\delta^{18}O$ a reduction of 0.0175-0.029‰ in Δ_{47} should

571 occur. Guo (2008) explained the kinetic effects as a consequence of irreversible dehydration

572 or dehydroxylation of carbonic acid or bicarbonate (respectively), followed by outgassing of

573 dissolved CO_2. In Figure 9B we cross-plot the deviation of 1000lnα and Δ_{47} from the

574 respective regression curves to evaluate if positive offsets in $\delta^{18}O$ are systematically

575 correlated with negative offsets in Δ_{47}. We point out that calculating the deviation from the

576 regression line does not necessarily imply that the observed correlation represents isotopic

577 equilibrium. However the excellent correlation with temperature strongly suggests that

578 temperature is the dominant control on both Δ_{47} and $\delta^{18}O$ in our dataset. No correlation is

579 observed if the deviation in 1000lnα is calculated with respect to the published curves of Kim

580   and O'Neil (1997) and Tremaine et al. (2011). The lack of correlation suggests that no

581   significant kinetic isotope effect related to degassing in our sample set. The average Δ_{47} offset

582   (0.009‰, $\approx$ 3.7°C) is lower than the standard error of the Δ_{47} values (0.011‰ on average;

583   Table 1, Fig. 9B), and the average 1000lnα offset of travertines is 0.647‰ ($\approx$ 3.5°C).

584   The mean Δ_{47} value of the slowly precipitating subaqueous Devils Hole vein calcite, which

585   has been assumed to grow under isotopic equilibrium conditions (Coplen, 2007; Kluge et al.,

586   2014b), locates slightly above (but within the confidence limits of) the empirical travertine

587   curve (Fig. 6A). This offset is in line with initial results from a laboratory inter-comparison

588   study using the four carbonate standards that suggest that Δ_{47} results at Yale University tend

589   to be higher than at ETH (by 0.007 - 0.045‰; average = 0.025 ‰). Considering the current

590   uncertainties in interlaboratory data comparability, these data suggest that vent and pool

591   travertines, which are the least likely to be affected by kinetic fractionation based on previous

592   stable isotope studies (Kele et al., 2008; Kele et al., 2011; Yan et al., 2012; Wang et al.,

593   2014), in relation to their clumped isotope composition probably represent close to

594   equilibrium precipitation in the entire 5.6-95°C temperature range.

595

596   *5.4 Effect of mineralogy (calcite-aragonite) on the Δ_{47} values*

597

598   Travertine and tufa are mostly composed of inorganic calcite and aragonite and can be used to

599   assess the effect of CaCO$_3$ polymorphism. Theoretical models of Schauble et al. (2006)

600   suggested that the calcite and aragonite crystal structure and cation substitution (Mg vs. Ca)

601   should have a modest influence of the abundance of ^{13}C-^{18}O bonds, and theoretical

602   calculations of Guo et al. (2009) similarly predicted different Δ_{47}-T calibration lines for

603   calcite and aragonite for the 260-1500 (K) temperature range. The predicted difference in Δ_{47}

604   between aragonite and calcite is between 0.017‰ (278 K) and 0.0095‰ (363 K) for the

605   temperature range covered in our study. Our sample set contains pure calcitic, almost pure

606   aragonitic and mixed calcitic-aragonitic samples (Table 1). The aragonite-rich samples from

607   Palagio (22.7°C, 99% aragonite) and the other samples with aragonite contents above 80%

608   which were precipitated at temperatures >56°C, all fit within analytical error onto the

609   regression line from all samples (Fig. 6B). A mixed sample with low (<35%) aragonite

610   content (Rapolano Terme, T=28°C) is also on the calibration line. Therefore, our results

611   suggest that aragonite and calcite exhibit a very similar Δ_{47}-T relationship. Similarly, many

612   other studies on biogenic and synthetic carbonates did not resolve any clear mineralogical

613   effects (Tripati et al., 2010; Thiagarajan et al., 2011; Zaarur et al., 2013; Henkes et al., 2013;

614   Defliese et al., 2015; Kluge and John, 2015).

615

616   *5.5 Effect of pH*

617

618   pH can have an important effect on the oxygen isotopic composition of $CaCO_3$ since it

619   controls the dissolved carbonate species in the travertine precipitating water, hence the $\delta^{18}O$

620   and Δ_{47} of the mineral (Usdowski et al., 1991; Zeebe 1999, 2007; Beck et al., 2005; Dietzel et

621   al., 2009; Hill et al., 2014). The dominant DIC species at low pH (<6) is CO_2 (aq), at

622   intermediate pH (6-9.5) HCO_3^-, while at high pH (>10.5) CO_3^{2-} becomes dominant. The $\delta^{18}O$

623   and the Δ_{47} of the DIC species decrease in this sequence (Zeebe, 1999; Hill et al., 2014).

624   Therefore, carbonates precipitated at higher pH may result in lower $\delta^{18}O$ and lower Δ_{47} values

625   due to higher proportion of CO_3^{2-} in the DIC (McCrea, 1950; Usdowski et al., 1991; Hill et

626   al., 2014). Based on theoretical calculations of Guo (2008) CO_3^{2-} is estimated to be ~0.018‰

627   lower in Δ_{47} than HCO_3^-, while the $\delta^{18}O$ value of the CO_3^{2-} is ~7‰ lower at 25ºC (Beck et al.,

628   2005; Kim et al., 2006).

629   It is somewhat difficult to assess the effect of pH on our sample set, because changes in pH

630   cannot be isolated from other parameters such as T, degassing rate, and ionic strength. The pH

631   for the travertines varies between 5.6 and 7.7, which is lower than the pH typically used for

632   laboratory-based calibrations (Ghosh et al., 2006a; Zaarur et al., 2013), and two travertine

633   pool samples were precipitated at a pH of 8.1. In Figure 10 we grouped the samples by pH,

634   and the lack of systematic offsets suggests that pH has no major influence on Δ_{47} in our

635   sample set. The experimental study of Tang et al. (2014) ($8.3 \leq pH \leq 10.5$ at 5°C, 25°C and

636   40°C) concluded that there are no clear effects of variable pH, ionic strength and growth rate

637   on the measured Δ_{47} values.

638

639   *5.6 Effect of precipitation rate*

640

641   Recent studies by Dietzel et al. (2009), Day and Henderson (2010) and Gabitov et al. (2012)

642   emphasized the fact that oxygen isotope fractionation between calcite and water can be

643   affected by the precipitation rate of calcite. Their experiments showed that high carbonate

644   precipitation rates drive $\delta^{18}O_{carbonate}$ to lower values. Deposition rate might affect the Δ_{47}

645   values, too. Saenger et al. (2012) studied rapidly calcifying hermatypic corals and suggested

646   that their higher than expected Δ_{47} values might be caused by fast calcification, while slowly

647   calcifying corals are close to or within the range of data from inorganic experiments (Ghosh

648   et al., 2006a). Based on theoretical calculations and precipitation experiments, Tripati and Hill

649   (2014) suggested that the crystal may inherit the Δ_{47} value of the DIC species and thus record

650   a disequilibrium mineral composition, when the growth rate is high, while DIC speciation

651   effects are likely to be negligible for slow-growing crystals.

652   In case of the studied travertines the precipitation rate (log R) is variable. At places where log

653   R was measured directly, it varied between 0.06 and 28.5 mg/cm^2/day. The highest

654   precipitation rate was measured at the Terme San Giovanni fissure ridge (28.5 mg/cm^2/day)

655   coinciding with the highest positive offset from our empirical calibration curve (Table 1, Figs.

656   6A, 11A). At other places (e.g. Bük, Narrow Gauge springs, Szalajka Creek) precipitation

657   rates are high and Δ_{47} shows also higher values relative to the calibration line (Fig. 6A) but

658   other samples with high precipitation rates (e.g. Tura, Köröm, Igal) plot below the calibration

659   line. Δ_{47} offsets of all travertine and tufa samples calculated relative to water temperature

660   using *eq. 1* show no correlation with precipitation rate (Fig. 8B). Where direct measurements

661   were not possible we qualitatively differentiate sites with low, moderate, high, and very high

662   (cm-to-m/year, comparable to surface corals) deposition. As can be seen in Figure 11B there

663   is no clear correlation between the offset from the calibration regression and the precipitation

664   rates. The morphology of deposited crystals can be affected by their precipitation rate and

665   potentially be used to estimate precipitation rate in case of inactive travertines. However,

666   crystal size can also vary due to several other influencing factors, such as water flow rates or

667   solution chemistry, which can vary through time. To conclude, our data suggest that

668   precipitation rate has no detectable or only minor effects on the Δ_{47} values of these carbonates.

669

670   Conclusions

671

672   Recent calcitic and aragonitic travertines and tufa samples precipitating from natural

673   thermal springs and wells, as well as one cave tufa sample, were studied for oxygen and

674   clumped isotopes. Our samples represent a wide temperature and pH range, diverse

675   mineralogy and depositional environments with various precipitation rates from

676   geographically different regions. The majority of our vent and pool travertine data show an

677   oxygen isotope fractionation between the mineral-phase and water compatible with the

678   Tremaine et al. (2011) relationship. No significant difference between the calcite-water and

679   aragonite-water oxygen isotope fractionation could be observed.

680 $\mathit{\Delta}_{47}$ data of vent and pool travertines and tufa samples show an excellent correlation

681 with temperature ($r^2>0.96$) which is described by the following equation: $\mathit{\Delta}_{47} = (0.044\pm0.005$

682 x 10^6) / T^2 + (0.205 ± 0.047). The slope of the $\mathit{\Delta}_{47}$–T travertine relationship is intermediate

683 compared to previously published ones, and seems to support the hypothesis that a

684 relationship exists between calibration slopes and acid digestion temperature. The $\mathit{\Delta}_{47}$ –T

685 correlation is strong, indicating that factors other than temperature (pH, mineralogy,

686 precipitation rate) have no or only minor effects on the $\mathit{\Delta}_{47}$–signal of carbonates. Our

687 calibration is the most robust available calibration from naturally precipitated inorganic

688 carbonates and it can be used to derive the deposition temperature of ancient carbonate

689 deposits (vent travertine, tufa, cave pool carbonate). Consistent data from three biogenic

690 samples furthermore suggests that the calibration might also be applicable to biogenic

691 carbonates. Using the travertine-based, empirically determined calcite-water oxygen isotope

692 fractionation factor, the $\delta^{18}O$ values of the travertine and tufa depositing waters can be

693 calculated with more confidence.

694

695 **AUTHOR CONTRIBUTION STATEMENT**

696

697 S. K. and S. M. B. designed the project. S. K. prepared and measured most of the samples at

698 ETH Zürich, interpreted the data and wrote the manuscript. S. M. B., I. M. M., A. N. M., M.

699 Z., S. F. M. B. developed the method at ETH Zürich and wrote parts of the manuscript. I. M.

700 M. prepared and measured some samples. The figures were prepared by S. F. M. B. and S.K..

701 T. K. and C. M. J. provided input to the analysis of the data. E. C., K. H., Z. L., H. Y. and D.

702 J. provided samples for clumped isotope analyses and contributed to the descriptions of the

703 sites. All co-authors contributed to discussions of this work.

704

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706

726

727   **Appendix A. Supplementary material**

728

729   Supplementary material related to this article can be found online at http://..

730

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Figure and table captions

Fig. 1

Field photos of the travertine sites with the sampling points:

A) Recent travertine deposits and thermal pool of Palagio.
B) Sampling point at Bagnoli thermal spring (precipitation at the tube outlet).
C) Reddish–brownish recent travertine at the discharge point of the Acqua Borra spring.
D) Recently active part of the Terme San Giovanni fissure–ridge.
E) Tap of the Madonna al Colle Well drilled for geothermal exploration.
F) Small and actively forming travertine mounds indicate the discharge points of the Il Doccio spring located on the riverbank.
G) Opened thermal spa with recent travertine deposition directly on the riverbank at Bagni di Petriolo.
H) The outlet of the Fosso Bianco spring (Bagni San Filippo).

Fig. 2

Travertine sites with the sampling points:

A) Vent pool at Piscine Carletti (Viterbo, Italy).
B) Carbonate deposits in the cellar of the Széchenyi thermal spa.
C) The Bük thermal well with its recent carbonate deposit.
D) Carbonate encrustation within the tube of the Igal thermal well.
E) Recent aragonitic travertine deposition at the Köröm thermal well.
F) Terraced slope travertine deposit (P5) at Baishuitai (China).
G) Vent pool outlet (sample NG-2) at Narrow Gauge Springs (Mammoth Hot Springs, Yellowstone, USA).

Fig. 3

Tufa deposits from karstic creeks and caves. The scale bars represents 20 cm.

A-C) Calcareous tufa encrustations and dams (samples Szal-2, Szal-6, Szal-15) in Szalajka Creek (Hungary).
D) Creek bed tufa encrustation at Sarteano (Italy) and at Canatoppa (E).
F) Perched spring tufa deposit at La Pigna (Italy).
G) Recent, periodically forming tufa deposit (Havasok tufa) from Baradla cave (Hungary).

Fig. 4

SEM photomicrographs of some selected travertine samples (**Table 1**) showing the variety of crystal shapes and sizes:

A) Calcite crystals and extracellular polymeric substances (EPS) produced by microorganisms (Bagni San Filippo, Fosso Bianco).
B) Dendritic structures resembling calcite "feather-like" crystals (Il Doccio).
C) Gypsum crystals within the calcite (Bagni di Petriolo).
D) Calcite and goethite (Acqua Borra).
E) Diatoms within the calcitic-aragonitic travertine (well deposit) of Rapolano Terme.

52   F) Dendritic calcite with gypsum crystal (Terme San Giovanni).
53   G) EPS filaments and diatom like structures within calcite (Bagnoli).
54   H) EPS filaments within aragonitic travertine of Palagio.
55
56   **Fig. 5**
57
58   A) Observed $1000ln\alpha_{CaCO_3-water}$ values versus precipitation temperatures. The Devils Hole data
59   point from Coplen (2007) is plotted for comparison. B) Same as A, but coded according to
60   mineralogy. The error bars for $1000ln\alpha_{CaCO_3-water}$ values are smaller than the size of the
61   symbols.
62
63   **Fig. 6**
64
65   A) Correlation between precipitation temperature and Δ_{47} of all analyzed recent travertine,
66   tufa and cave carbonates and three biogenic samples. The empirical Δ_{47} - T calibration is
67   based on vent and pool travertine samples. Tufa samples are also shown, together with the Δ_{47}
68   value of recent calcite raft and vein calcite sample from Devils Hole (Kluge et al., 2014b).
69
70   B) Δ_{47} values of vent and pool samples with different calcite/aragonite ratio versus
71   temperature.
72
73   **Fig. 7**
74
75   Comparison of the $1000ln\alpha_{CaCO_3-water}$ values determined in this study with those from Kim and
76   O'Neil (1997), Affek and Zaarur (2014), Coplen (2007) based on Devils Hole calcite and the
77   cave-specific calibration line of Tremaine et al. (2011).
78
79   **Fig. 8**
80
81   Comparison of the temperature dependence of Δ_{47} of travertines with other published studies.
82   Note the steeper slopes obtained with acid reaction temperature of 25°C (Zaarur et al., 2013),
83   and the lower slope for carbonates reacted at 90°C (Wacker et al., 2014). For comparison we
84   also show the theoretical relationship of Guo et al. (2009) and the surface precipitates from
85   Affek and Zaarur (2014).
86
87   **Fig. 9**
88
89   A) Observed $1000ln\alpha$ values versus Δ_{47} values.
90
91   B) Offsets in Δ_{47} versus offsets in $1000ln\alpha_{CaCO_3-water}$ from the respective calibration lines
92   determined in this study do not show any significant correlation. The error bar represents the
93   average analytical error in Δ_{47}, the analytical error in $1000ln\alpha$ is smaller than the size of the
94   symbols.
95
96   **Fig. 10**
97
98   A) Temperature dependence of Δ_{47} of travertines and tufa grouped according to pH. B) Δ_{47}
99   offsets from the calibration line (*eq. 1*) versus pH. The error bar represents the average
100   analytical error in Δ_{47}.
101
102   **Fig. 11**

103

104   A) Temperature dependence of Δ_{47} of travertines and tufa grouped by precipitation rate.

105

106   B) Δ_{47} offsets from the calibration line (*eq. 1*) versus precipitation rate (arbitrary scale). The
107   error bar represents the average analytical error in Δ_{47}.

108

109   **Table 1**

110

111   Mineralogy, facies types, physico-chemical parameters T, pH and EC, TDS, precipitation
112   rate, crystal size and isotopic composition ($\delta^{13}C_{travertine}$, $\delta^{18}O_{travertine}$, δ^{47}, Δ_{47}, $\delta^{18}O_{water}$) of the
113   studied samples. Δ_{47} data are reported in the absolute reference frame. "N" is the number of
114   analyzed aliquots of the sample. The Δ_{47} offset is calculated with regard to Δ_{47} obtained using
115   *eq. 1*. $T_{expected}$ shows temperatures calculated using measured Δ_{47} data and *eq. 1*. The $1000\ln\alpha$
116   offset refers to the difference between the observed calcite-water oxygen isotope fractionation
117   factor and the fractionation factors calculated using the travertine equation of this study. T
118   and pH values of the Madre del Agua sample are from Demény et al. (2010). Data of the
119   Baishuitai travertine samples are taken from Yan et al. (2012). $\delta^{18}O$ values of three aragonitic
120   travertines (Köröm, Széchenyi thermal spa, Palagio) were corrected by –0.42‰, according to
121   the aragonite acid digestion fractionation factor of Kim et al. (2007).

122

123   **Table 2**

124

125   Mineralogy and isotopic composition ($\delta^{13}C$, $\delta^{18}O$, δ^{47}, Δ_{47}) of the biogenic samples. Δ_{47} data
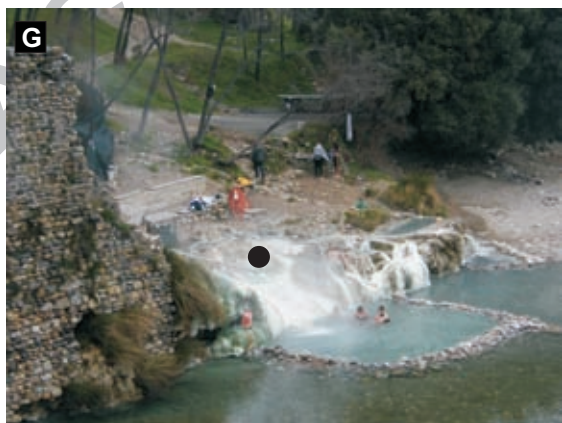126   are reported in the absolute reference frame. "N" is the number of analyzed aliquots for each
127   sample.

128
129

Table 1

Site name	GPS coordinates	Sample name	material	mineralogy	origin	facies	T	pH	EC	log R	crystal size and shape
	(degree, min, sec)			(%)			(°C)		(mS/cm)	(mg/cm²/d)	(μm)
Tura	N47°36'36", E19°34'17"	Tu-4 well/2000	travertine	97 % cc, 3% ar	thermal well	vent	95.0	6.88	3.04	intensive	
Igal	N46°32'37", E17°56'42"	B-1/2011	travertine	100 % cc	thermal well	vent (tube encrustation)	75.0	6.89	12.24	intensive	
Bük	N47°22'25", E16°46'35"	Bük-4	travertine	98 % cc, 1% ar	thermal well	vent (tube outlet)	54.9	6.88	12.90	intensive	
Szèchenyi Spa, Budapest*	N47°31'07", E19°05'03"	SZ-2/2	travertine	20% cc, 80 % ar	thermal well	tube encrustation	70.9	6.40	1.57	intensive	
Köröm*	N47°59'49", E20°59'14"	Kör 13/0	travertine	97 % ar., 3 % cc	thermal well	vent	79.2	6.80	1.38	intensive	
Madre del Agua, Tenerife	N28°10'57'', W16°35'40"	Canarian	travertine	100 % cc	natural spring	channel discharge	33.8	7.70	n.d.	moderate	
Acqua Borra	N43°18'28", E11°25'41"	Acqua Borra	travertine	85% cc, 15% goethite	natural spring	tube outlet	36.1	6.58	> 20	2.14 (moderate)	no crystal shape
Bagni di Petriolo	N43°04'45", E11°17'32"	BP	travertine	75% cc, 12% gypsum, 10% S	natural spring	tube outlet	44.3	6.45	4.54	moderate	70 (rhomb.), gypsum (100-200),
Bagnoli	N43°26'39", E11°03'15"	Bagnoli	travertine	95% cc, 2% gypsum, 3% Q	natural spring	tube outlet	23.7	6.62	2.98	0.06 (very low)	30-50 (rhomb.), microbial mats
Bagni San Filippo, Fosso Bianco	N42°55'39", E11°42'10"	BSF- FB	travertine	99% cc, 1%>ar, 1%>gypsum	natural spring	spring outlet	44.6	6.53	3.54	1 (moderate)	50 (dendritic)
Il Doccio	N43° 09'27", E11°17'08"	Il Doccio	travertine	60% cc, 35% gypsum, 3-5% S	natural spring	vent	48.3	7.05	8.7	0.1 (low)	50-70 (dendritic)
Palagio*	N43°29'51", E10°52'18"	Palagio	travertine	99% ar, 1% Q	natural spring	pool (raft)	22.7	6.57	6.36	0.61 (moderate)	no crystal shape, microbial mats
Rapolano Terme	N43°17'58", E11°36'11"	R T-1	travertine	80% cc, 20% ar	thermal well	water leak of a thermal well	28	6.62	5.72	low	50 (rhomb.), diatoms (10)
Terme San Giovanni	N43°16'43", E11°35'34"	TSG	travertine	90% cc, 2 % ar, 8% gypsum	natural spring	small pool on a fissure ridge (raft)	41.2	6.53	6.29	28.5 (very intensive)	20-50 (dendritic), gypsum (100)
Piscine Carletti, Viterbo	N42°25'18", E12°03'53"	P. Carletti-8.1	travertine	98% cc, 1%> ar.	natural spring	closest to vent channel sample	57.9	5.67	2.95	low	
Baishuitai	N27°30', E100°02'	P5 summer	travertine	100 % cc	natural spring	pool	12.0	8.14	0.76	0.66 (moderate)	
Baishuitai	N27°30', E100°02'	P5 winter	travertine	100 % cc	natural spring	pool	5.6	8.19	0.802	0.44 (moderate)	
Narrow Gauge (M.H.S., Yellowstone)	N44°34'52", W110°25'24''	NG-2	travertine	95 % cc, 5% ar, S	natural spring	vent pool outlet	60.4	6.6	1.38	intensive	
Sarteano	N42°59'52", E11°53'00"	SAR	tufa	100 % cc	karstic spring	downstream (100 m)	20.7	8.92	2.11	moderate	
Canatoppa	N43°16'41", E11°35'20"	CAN	tufa	100 % cc	karstic spring	downstream sample	11	8.94	1.65	moderate	
La Pigna	N43°06'38", E11°15'43"	LAP	tufa	100 % cc	karstic spring	downstream (20 m, below a cascade)	12.5	8.61	0.55	moderate	
Szalajka	N48°05'27", E20°24'09''	Szal-2	tufa	95 %cc, 5 % detrital min.	karstic spring	downstream tufa dam	10.1	8.45	0.503	intensive	
Szalajka	N48°05'27", E20°24'09''	Szal-6	tufa	96 %cc, 5 % detrital min.	karstic spring	downstream tufa dam	11.0	8.55	0.473	intensive	
Szalajka	N48°05'27", E20°24'09''	Szal-15	tufa	97 %cc, 5 % detrital min.	karstic spring	downstream tufa dam	12.1	8.53	0.484	intensive	
Havasok	N48°28'17'', E20°29'44''	Havasok	cave tufa	100 % cc	cave karst water	cascade/pool rim	9.5	n.d.	n.d.	very low	

Table 1 contd.

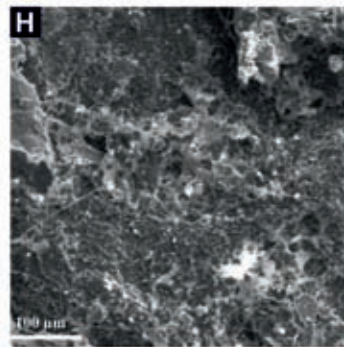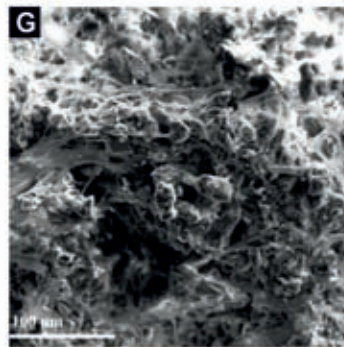| Site name	$\delta^{13}C_{trav}$	$\delta^{18}O_{trav}$	$\delta^{18}O_w$	δ^{47}	Δ_{47}	S.E.	N	Δ_{47} calculated	Δ_{47} offset	$T_{expected}$	1000 lnα obs.	1000 lnα calculated	1000 lnα offset
	(‰, PDB)	(‰, SMOW)	(‰ SMOW)	(‰)	(‰)	±		(using *eq.1* ; ‰)	(from *eq.1* ; ‰)	(using *eq.1*)	(‰)	(using *empirical eq* ; ‰)	(from emp. *eq* ; ‰)
Tura	3.78	6.89	-12.4	-6.648	0.51	0.012	30	0.525	-0.015	104	19.3	18.33	1.02
Igal	0.75	16.84	-4.0	0.474	0.555	0.013	30	0.563	-0.008	79	20.7	21.45	-0.74
Bük	2.34	15.27	-9.9	0.507	0.625	0.016	27	0.609	0.016	49	25.1	24.97	0.14
Szèchenyi Spa, Budapest*	2.9	9.33	-12.6	-4.562	0.567	0.011	30	0.572	-0.005	73	22.0	22.13	-0.16
Köröm*	3.62	7.84	-11.5	-5.399	0.545	0.004	37	0.554	-0.009	84	19.4	20.76	-1.39
Madre del Agua, Tenerife	0.24	20.14	-8.1	3.384	0.656	0.012	29	0.667	-0.011	37	28.1	29.16	-1.09
Acqua Borra	2.99	22.98	-5.2	8.884	0.655	0.025	30	0.660	-0.005	38	27.9	28.67	-0.74
Bagni di Petriolo	3.3	21.23	-6.4	n.d.	n.d.	n.d.	n.d.	n.d.		n.d.	27.4	27.00	0.43
Bagnoli	5.64	25.36	-7.0	13.859	0.695	0.010	22	0.699	-0.004	25	32.1	31.37	0.70
Bagni San Filippo, Fosso Bianco	7.45	20.74	-7.9	10.931	0.644	0.004	30	0.636	0.008	42	28.5	26.94	1.52
Il Doccio	2.4	19.99	-5.9	n.d.	n.d.	n.d.	n.d.	0.626		n.d.	25.7	26.22	-0.51
Palagio*	2.47	24.63	-7.0	10.09	0.696	0.018	30	0.703	-0.007	25	31.4	31.60	-0.24
Rapolano Terme	3.8	23.15	-6.9	9.851	0.68	0.016	33	0.685	-0.005	30	29.8	30.41	-0.61
Terme San Giovanni	2.58	21.73	-6.9	7.254	0.678	0.012	28	0.645	0.033	30	28.4	27.62	0.80
Piscine Carletti, Viterbo	7.25	18.18	-6.5	8.109	0.603	0.007	30	0.601	0.002	57	24.5	24.41	0.12
Baishuitai	5.63	16.14	n.d.	4.615	0.741	0.013	37	0.741	0.000	12	n.d.	34.14	n.d.
Baishuitai	5.28	17.66	n.d.	5.809	0.749	0.013	38	0.766	-0.017	10	n.d.	35.75	n.d.
Narrow Gauge (M.H.S., Yellowstone)	3.98	5.65	-17.9	-7.658	0.601	0.009	29	0.595	0.006	58	23.7	23.96	-0.27
Sarteano	0.55	23.3	-7.8	6.844	0.703	0.009	29	0.710	-0.007	23	30.8	32.06	-1.22
Canatoppa	-3.97	25.32	-6.5	4.517	0.742	0.008	29	0.745	-0.003	12	31.6	34.39	-2.82
La Pigna	-11.27	25.08	-6.8	-2.806	0.73	0.021	31	0.739	-0.009	15	31.6	34.02	-2.43
Szalajka	-10.2	22.19	-10.6	-4.616	0.755	0.006	27	0.748	0.007	8	32.6	34.61	-2.01
Szalajka	-9.86	21.94	-10.6	-4.553	0.732	0.008	29	0.745	-0.013	14	32.4	34.39	-2.03
Szalajka	-9.44	21.33	-10.7	-4.719	0.76	0.008	23	0.741	0.019	7	31.9	34.11	-2.25
Havasok	-10.95	22.95	-9.7	-4.586	0.756	0.01	30	0.751	0.005	8	32.4	34.76	-2.32

Table 2

Sample name	material	mineralogy	T (∘C)	$\delta^{13}C$ (‰, PDB)	$\delta^{18}Occ$ (‰, PDB)	δ^{47} (‰)	$\Delta_{47 \text{ (weighted average)}}$ (‰)	SE ±	N
Arctica Islandica	bivalve	aragonite	6	1.67	3.48	19.30	**0.759**	**0.004**	40
Dyscolia wyvillei	brachiopod	calcite	10	2.51	2.47	19.06	**0.742**	**0.018**	36
Eggshell of an Ostrich	eggshell	calcite	38	-12.68	-3.84	-2.34	**0.648**	**0.014**	36

Sample name	material	mineralogy	T (∘C)	$\delta^{13}C$ (‰, PDB)	$\delta^{18}Occ$ (‰, PDB)	δ^{47} (‰)	$\Delta_{47 \text{ (weighted average)}}$ (‰)	SE ±	N
Arctica Islandica	bivalve	aragonite		1.67	3.48	19.30	**0.759**	**0.004**	40
Dyscolia wyvillei	brachiopod	calcite		2.51	2.47	19.06	**0.742**	**0.018**	36
Eggshell of an Ostrich	eggshell	calcite	38	-12.68	-3.84	-2.34	**0.648**	**0.014**	36

A

$y = (20\pm2)x-(36\pm7)$
$N = 16$; $R^2= 0.96$

$y = (17\pm1.7)x-(26\pm5.4)$
$N = 23$; $R^2= 0.95$

$10^3/T$ [K]

$1000\ln\alpha$ [‰]

◇ Travertines
◇ Szechenyi Spa, Budapest
◆ Köröm
◆ Bagni San Filippo, Fosso Bianco
◆ Rapolano Terme
◆ Madre del Agua, Tenerife
◆ Bagni di Petriolo
◆ Igal
◇ Il Doccio
◆ Acqua Borra
◆ Bük
◆ Tura
◆ Piscine Carletti, Viterbo
◆ Terme San Giovanni
◆ Bagnoli

□ Pool travertines
■ Palagio
■ Narrow Gauge, Yellowstone

△ Tufa
▲ Sarteano
▲ Canatoppa
▲ La Pigna
△ Szalajka

▽ Cave tufa
▼ Havasok

■ Devils Hole (calcite mean)
- - - 95% conf. int., all
— 95% conf. int., travertines

B

$y = (20\pm2)x-(36\pm7)$
$N = 16$; $R^2= 0.96$

○ Calcite (>95%)
◐ Aragonite-Calcite mix
● Aragonite (>80%)

$10^3/T$ [K]

$1000\ln\alpha$ [‰]

A

$y = (0.044\pm0.005)x+(0.205\pm0.047)$
$R^2 = 0.96$

Δ_{47} [‰]

10^6T^{-2} [K]

B

$y = (0.044\pm0.005)x+(0.205\pm0.047)$
$R^2 = 0.96$

Δ_{47} [‰]

10^6T^{-2} [K]

○ Calcite (>95%)
◑ Aragonite-Calcite mix
● Aragonite (>80%)

◇ Travertines
◇ Szechenyi Spa, Budapest
◇ Köröm
◆ Bagni San Filippo, Fosso Bianco
◆ Rapolano Terme
◆ Madre del Agua, Tenerife
◆ Igal
◆ Acqua Borra
◆ Bük
◆ Tura
◆ Piscine Carletti, Viterbo
◆ Terme San Giovanni
◆ Bagnoli
□ Pool travertines
■ Palagio
■ Narrow Gauge, Yellowstone
■ Baishuitai
△ Tufa
▲ Sarteano
▲ Canatoppa
▲ La Pigna
△ Szalajka
▽ Cave tufa
▼ Havasok
⊗ Biogenic carbonates
⊗ Arctica Islandica
⊗ Dyscolia wyvillei
⊗ Ostrich egg
■ Devils Hole (calcite mean)
■ Devils Hole (modern rafts)
░ 95% conf. int., travertines

Kim & O'Neil (1997)
Coplen (2007)
Tremaine et al. (2011)
Affek & Zaarur (2014)
Vent calcite
Vent aragonite
Pool calcite
Pool aragonite
Tufa calcite
Cave calcite
95% conf. int. (travertines)

$y = (20 \pm 2.2)x - (36 \pm 6.8)$
$R^2 = 0.96$; $N = 16$

Legend:
- This study (red solid line)
- Guo et al. (2009) (orange dashed line)
- Zaarur et al. (2013) (green solid line)
- Affek & Zaarur (2014) (blue dotted line)
- Wacker et al. (2014) (purple dashed line)
- ◆ Vent calcite
- ◆ Vent aragonite
- □ Pool calcite
- ■ Pool aragonite
- ▲ Cave calcite
- 95% conf. int.

$y = (0.044\pm0.005)x - (0.205\pm0.047)$
$R^2 = 0.96; N = 16$

Axis labels: Δ_{47} [‰] (y-axis), $10^6/T$ [K] (x-axis)

A

1000lnα [‰]

Δ₄₇ [‰]

Vent calcite
Vent aragonite
Pool aragonite
Pool calcite
Tufa calcite
Cave calcite

B

1000lnα offset [‰]

Δ₄₇ offset [‰]