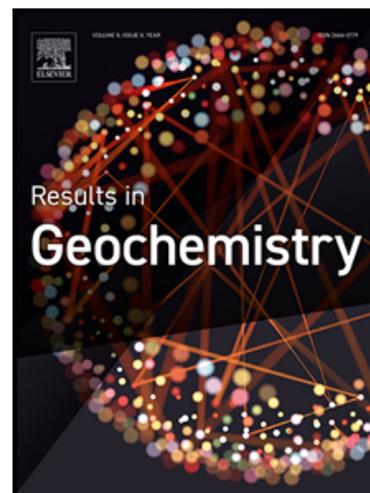# Journal Pre-proof

Condensation corrosion alters the oxygen and carbon isotope ratios of speleothem and limestone surfaces

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Please cite this article as: Jackson H. White , David Domínguez-Villar , Adam Hartland , Condensation corrosion alters the oxygen and carbon isotope ratios of speleothem and limestone surfaces, *Results in Geochemistry* (2021), doi: https://doi.org/10.1016/j.ringeo.2021.100008

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Highlights

Condensation corrosion is detected using stable isotope analysis of calcite surfaces

Dissolution and recrystallization cause distinct changes in C and O isotope ratios

Negative isotope correlation from degassing (higher ^{13}C) and condensation (lower ^{18}O)

Results are consistent with high-resolution studies of speleothem hiatuses

A new approach to the detection of condensation corrosion in managed caves

1

Condensation corrosion alters the oxygen and carbon isotope ratios of speleothem and limestone surfaces

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Abstract

Condensation corrosion is a natural process which enhances the chemical weathering of limestone cave chambers and speleothems. We evaluated the use of carbonate tablets for detecting condensation corrosion in Glowworm Cave, New Zealand, using local limestone and speleothem as experimental substrates (herein tablets). Evidence for condensation corrosion was assessed via three methods: gravimetric (mass wasting), microscopic (surface pitting, recrystallization) and isotopic (^{13}C and ^{18}O changes). Our results show little evidence of tablet mass loss throughout a 6-month deployment period. However, SEM imaging and isotope analysis (^{13}C and ^{18}\

suggest that condensation corrosion operates in the cave, especially in sectors affected by large diurnal microclimate variations.

Most notably, condensation water altered the tablet surface ^{13}C and ^{18}O values. Small, positive shifts in surface ^{13}C and ^{18}O values are considered to reflect pure dissolution (where dissolution favours the removal of lighter isotopologues). In contrast, tablets that exhibited large positive shifts in ^{13}C in tandem with large negative shifts in ^{18}O values, are interpreted as showing calcite recrystallization and the inheritance of higher DIC ^{13}C values (^{13}C fractionation by CO_2 degassing), lighter water ^{18}O values and/or kinetic fractionation of ^{18}O. This study therefore demonstrates that stable isotopes could be applied to detect paleoclimatic episodes of condensation corrosion in speleothems.

Graphical abstract
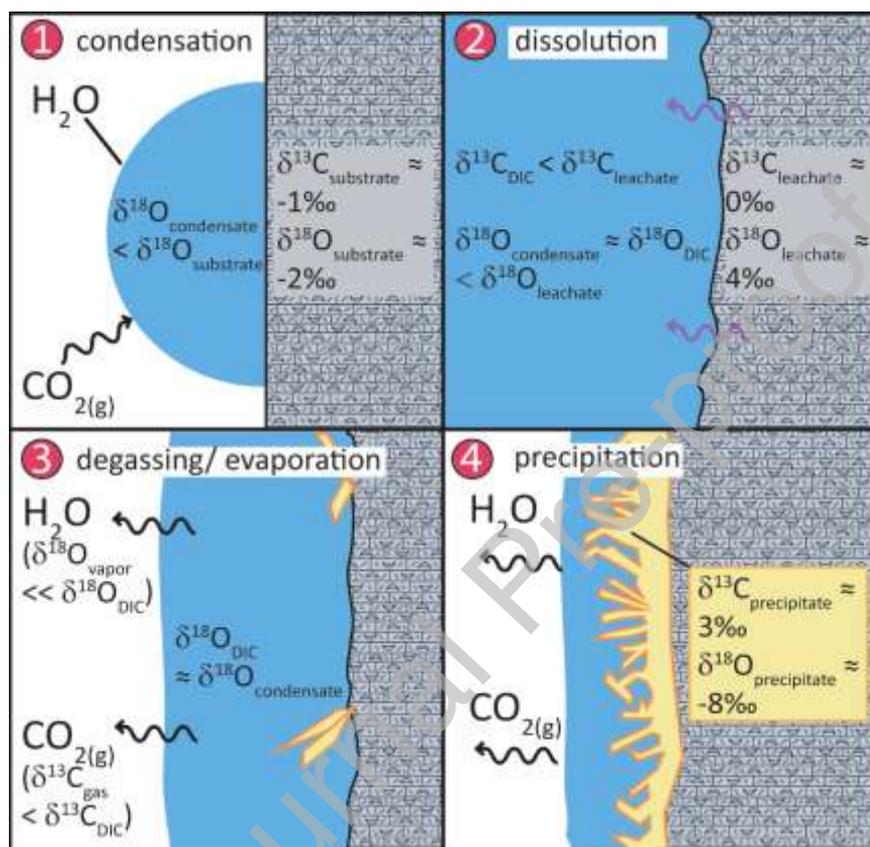
1. Introduction

Condensation corrosion is a chemical weathering process that enlarges limestone cave chambers through the dissolution of walls covered in condensation (Figure 1) [1-3]. Condensation corrosion occurs when $CaCO_3$ dissolves due to the action of atmospheric CO_2 diffusing into a water film on the bedrock surface [2,4]. This process also occurs in gypsum caves ($CaSO_4\ 2H_2O$), where it is known as condensation-solution [5], resulting in gypsum dissolution. In heavily trafficked tourist caves, condensation corrosion can potentially accelerate the degradation of cave formations, and cave art in some cases, because of more extreme microclimate variability.
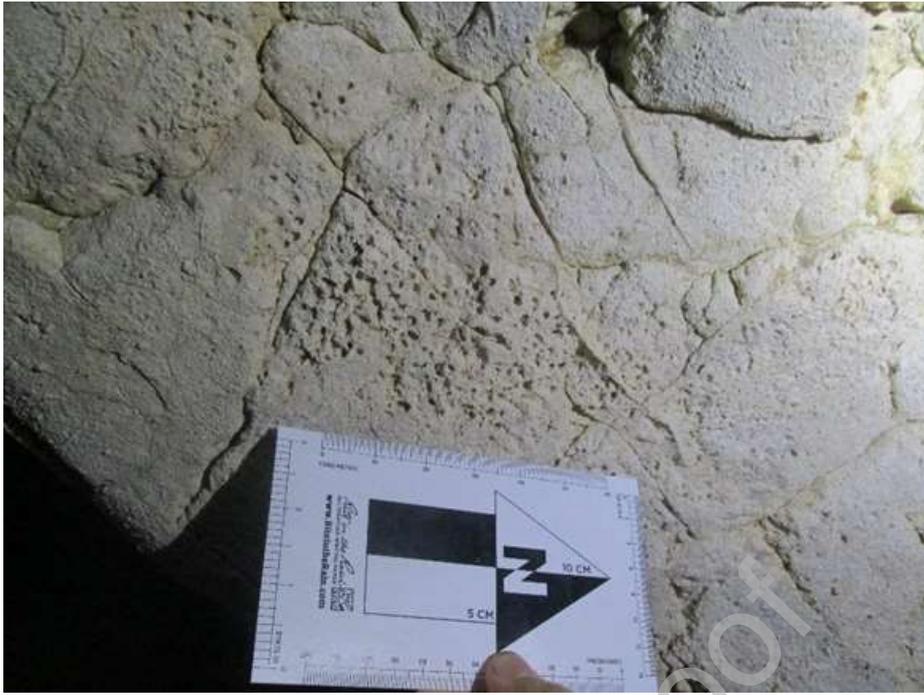
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Figure 1: Condensation corrosion dissolution features on the limestone ceiling in Tomo Passage, Waitomo Glowworm Cave. Photo from Ingrid Lindeman.

The Waitomo Caves, including Glowworm Cave, attracted over half a million tourists in 2016 and generated $71 million New Zealand dollars [6]. Tourism in these caves causes major changes in cave air temperature, relative humidity and CO_2 concentration, with potential to increase the rate of condensation corrosion. This is of concern because tourism has resulted in permanent deterioration of speleothems in other settings [7]. While the importance of condensation corrosion in each setting will vary with the local conservation values, it is important to understand how tourism may impact cave microclimate, cave formations and ecosystems. [8]

Previous studies in the Glowworm Cave have focused on conservation of cave formations through understanding cave air $p CO_2$ dynamics, including examination of the non-anthropogenic sources of carbon dioxide (CO_2) (i.e. stream $p CO_2$) [9] and chamber microclimate and ventilation [10]. In this study, we investigated condensation corrosion [8] with the aim of developing an empirical method to detect condensation corrosion in a cave setting where the ongoing impacts of visitation are ambiguous.

4

1.1 Geochemistry of condensation corrosion

The condensation corrosion process begins from dew deposition as a thin film on cave walls. Cave walls can be composed of a mix of soluble minerals such as calcite, dolomite, halite or gypsum. Dissolution of these minerals then occurs at the interface between the condensation water and rock surface [2]. The dissolution rate depends on the amount of condensation water on the rock surface over time and the concentration of atmospheric CO_2 [11]. The temperature gradient between the condensation water and rock surface only plays a minor role in corroding the rock surface, since the condensation water rapidly reaches thermal equilibrium. Condensation water becomes corrosive when CO_2 diffuses from the atmosphere into the water droplets, or water film (equation 1) forming carbonic acid (equation 2). Carbonic acid can dissociate by the reactions shown in equations 3 and 4 depending on the temperature, thereby changing the pH of the water [2].

$$\text{(1)}$$

$$\text{(2)}$$

$$\text{(3)}$$

$$\text{(4)}$$

The sum of all carbonate species in solution is known as dissolved inorganic carbon (DIC). DIC is largely composed of HCO_3^- at pH values typical of limestone caves [12].

1.2 Phase change and isotope exchange

Cave climate is responsive to the thermodynamic interaction between external air and cave air [13]. These interactions result in changes in condensation and evaporation rates. Condensation takes place when the air temperature decreasesand condensate forms on cooler surfaces, such as cave walls and speleothems. Evaporation is the opposite process and occurs when the cave air increases in temperature leading to a condensate losing water to the atmosphere [14,15].

1.2.1 Condensation

In caves, condensation occurs because of the sudden temperature change at the interface of the cave wall and air [16]. Initially, the wall temperature increases due to the latent heat release from the water vapour. During the deposition of condensation, atmospheric CO_2 dissolves into the condensation water lowering the pH and dissolving some $CaCO_3$. If the atmospheric CO_2 concentration lowers, or relative humidity drops, then CO_2 in the condensation water will degas, causing calcite precipitation. During the lifetime of a condensation film, dissolution and possible grain detachment of less-soluble bedrock caused by dissolution may also occur. Features of these processes were observed in our initial surveys of the Tomo Passage, Glowworm Cave (Figure 1): a proposed mechanism of formation is illustrated in Figure 2. Note the microcrystalline calcite depicted in the photograph (Figure 1) can formed by condensation, re-evaporation cycles, or by evaporation of water flowing along the seepage network. Microcrystalline calcite has been observed around the world in different cave climates, carbonate lithologies [16,19-25], and sulphate lithologies [5,26-28].
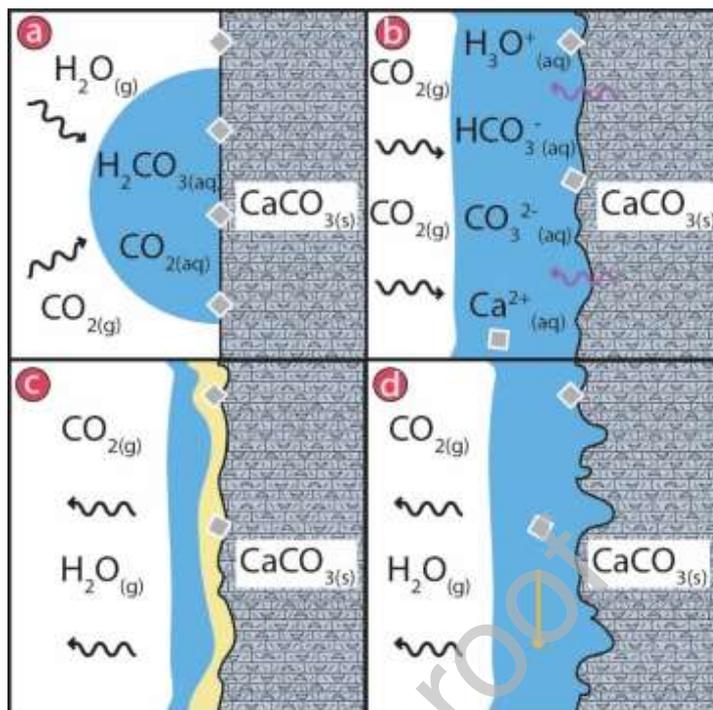
Figure 2: Formation of microcrystalline calcite. a) The formation of microcrystaline calcite begins with the nucleation of water on the cave wall surface and subsequent diffusion of atmospheric CO_2 into the condensate ($CO_{2(aq)}$). $CO_{2(aq)}$ hydrates forming carbonic acid ($H_2CO_{3(aq)}$). b) $H_2CO_{3(aq)}$ then dissociates releasing H^+, which instantly forms hydroxonium ions ($H_3O^+_{(aq)}$). $H_3O^+_{(aq)}$ enhances limestone dissolution (purple arrows), ionizing the calcite components into $Ca^{2+}_{(aq)}$ and $CO_3^{2-}_{(aq)}$, and releasing less soluble grains from the bedrock (grey diamonds). All ions in solution will move along with the water film. Removal of the more-soluble matrix will loosen less-soluble grains, which eventually detach from the cave wall. Grain detachment is the mechanism where most of the mass is lost from the cave wall. c) When evaporation of condensate takes place, the solution supersaturates leading to the precipitation of microcrystaline calcite (yellow layer). d) However, if the water flows down the wall (orange arrow representing the direction of flow), the bulk mass transport of the dissolved ions will result in dissolution features as those of (Figure 1).

1.2.2 Evaporation

Evaporation takes place when the relative humidity is less than 100%, and the atmosphere is undersaturated in water vapour. Evaporation is considered a kinetic process [30,31], where the lighter H_2O isotopologues preferentially evaporate from solution. Likewise lighter $CO_{2(g)}$ molecules degas [32,33] in response to a lowering of CO_2 partial pressure of the cave atmosphere (typical of touristic caves). Therefore, the residual heavier isotopologues of H_2O and CO_2 accumulate in solution resulting in exchange of heavier isotopes between H_2O, CO_2 and the DIC species. Calcite precipitated under these conditions is expected to have more positive ^{13}C values

[20,32-35]. However, heavier (more positive) ^{18}O values may not be identified due .... caused by the much greater abundance of H_2O (relative to DIC) in solution [36,37]. It can be the case that evaporation of H_2O can lead to high ^{13}C and ^{18}O values in precipitated calcite (Deininger *et al.*, (2012)), when relative humidity is sufficiently low and wind velocity is high. Deininger *et al.*, (2012) concluded that high evaporation rates are conducive to high calcite precipitation rates, because of the increased concentration of Ca^{2+} and HCO_3^-.

2. Study site

The Waitomo Glowworm Cave is located at latitude 38°15 o' .... -; in Waitomo, New Zealand, in a temperate oceanic climate (Köppen climate classification). The cave is located in the northeast-trending Waipa Fault [38,39], which focusses water flow under the karst landscape. The cave is developed in Otorohanga Limestone, a shallow marine grain-dominated packstone formed between 37.8 and 28.1 million years ago. [40].

2.1. Study locations within Glowworm Cave

The Glowworm Cave consists of 1300 m of interconnected passageways and has an estimated volume of 4000 m^3 [1]. The cave has an upper and a lower entrance, which are 14 m apart vertically and its main passage is 39 m long with an elliptical cross-section varying between 3-7 m^2 [1]. The Waitomo Stream passes through the lower entrance of the cave. Five sites were selected to study the effects of corrosion on tablets: the Upper Entrance, the Blanket Chamber, Tomo Passage, Organ Loft and Cathedral Chamber (Figure 3). Microcrystalline calcite is common on the cave walls and speleothem of the Blanket Chamber, lower parts of the Cathedral Chamber and speleothem in the Entrance Chamber. In contrast, the Tomo Passage and Organ Loft had very little of this texture present which is confined to fractures in the bedrock.

[5]   7˙8   ˙KU˙#   ˙V h˙-   ˙)˙˙˙= ˙y˙   ˙   ˙   ˙   \˙ \˙   ˙) of gypsum hydration water to ascertain the role of water condensation in the formation of subaerial gypsum speleothems, Chem. Geol., 2017, 452, 34-46. https://doi.org/10.1016/j.chemgeo.2017.01.021.

[6]   O. Carville, 2017, 5 May. The Great Tourism Squeeze: Small town tourist destinations buckle under weight of New Zealand's tourism boom, The New Zealand Herald. https://www.nzherald.co.nz/nz/news/article.cfm?c_id=1&objectid=11828398   (accessed May 2020).

[7]   D. Dragovich, J. Grose, Impact of tourists on carbon dioxide levels at Jenolan Caves, Australia: an examination of microclimatic constraints on tourist cave management, Geoforum, 1990, 21, 111-120. https://doi.org/10.1016/0016-7185(90)90009-U.

[8]   K. Krklec, D. Dominguez-Villar, R.M. Carrasco, J. Pedraza, Current denundation rates in dolostone karst from central Spain: Implications for the formation of unroofed caves, Geomorphology, 2016, 264, 1-11. https://doi.org/10.1016/j.geomorph.2016.04.007.

[9]   N.M. Miedema, 2009. Non-Anthropogenic Sources of Carbon Dioxide in the Glowworm Cave, Waitomo. MSc thesis, University of Waikato, Hamilton, New Zealand.

[10]   M.J. Gillies, 2011. Microclimate and Effects of Visitor Numbers and Ventilation on Carbon Dioxide Concentration in the Waitomo Glowworm Cave, New Zealand. BSc Hon. thesis, University of Auckland, Auckland, New Zealand.

[11]   ‡˙)   ˙7˙8   ˙U˙h   ˙#   ˙#   ˙˙˙   ˙ approach, Acta Carsologica, 2005, 34, 317-348. https://doi.org/10.3986/ac.v34i2.262.

[12]   M. Hansen, D. Scholz, B.R. Schöne, C. Spötl, Simulating speleothem growth in the ˙)   ˙   ˙   ˙ ^{13}#˙   ˙^{18}O) between H_2O, DIC and $CaCO_3$, Chem. Geol., 2019, 509, 20-44. https://doi.org/10.1016/j.chemgeo.2018.12.012.

[13]   C.R. de Freitas, R.N. Littlejohn, Cave climate: assessment of heat and moisture exchange, J. Climatol., 1987, 7, 553-569. https://doi.org/10.1002/joc.3370070604.

[14]   G. Badino, Clouds in caves, Speleogenesis and Evolution of Karst Aquifers, 2004, 2, 1-8.

[15]   J. Wallace, P. Hobbs, Atmospheric science: An introduction survey, 2nd ed., Elsevier USA, Boston, 2006.

[16]   C.R. de Freitas, A. Schmekal, Studies of condensation/evaporation processes in the Glowworm   Cave,   New   Zealand,   Int.   J.   Speleol.,   2006,   35,   75-81. http://dx.doi.org/10.5038/1827-806X.35.2.3.

[17]   R.D. Deshpande, A.S. Maurya, B. Kumar, A. Sarkar, S.K. Gupta, Kinetic fractionation of water isotopes during liquid condensation under super-saturated condition, Geochim. Cosmochim. Acta, 2013, 100. https://doi.org/10.1016/j.gca.2012.10.009.

[18] S.-T. Kim, T.B. Coplen, J. Horita, Normalization of stable isotope data for carbonate minerals: Implementation of IUPAC guidelines, Geochim. Cosmochim. Acta, 2015, 158, 276-289. https://doi.org/10.1016/j.gca.2015.02.011.

[19] S. Sánchez-Moral, V. Soler, J.C. Cañaveras, E. Sanz-Rubio, R. Van Grieken, K. Gysels, Inorganic deterioration affection the Altamira Cave, N Spain: quantitative approach to wall-corrosion (solutional etching) processes induced by visitors, Sci. Total Environ., 1999, 243, 67-84. https://doi.org/10.1016/S0048-9697(99)00348-4.

[20] C. Hendy, The isotopic geochemistry of speleothems   I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators, Geochim. Cosmochim. Acta, 1971, 35, 801-824. https://doi.org/10.1016/0016-7037(71)90127-X.

[21] A.A. Schmekal, C.R. de Freitas, 2001. Condensation in Glow-worm Cave, Waitomo, New Zealand. Department of Conservation Science Internal Series 15, Wellington, New Zealand. 11p.

[22] A.S. Auler, P.L. Smart, Rates of condensation corrosion in speleothems of semi-arid northeastern Brazil, Speleogenesis and Evolution of Karst Aquifers, 2004, 2, 1-2.

[23] S. Galdenzi, Corrosion of limestone tablets in sulfidic ground-water: measurements and speleogenetic implications, Int. J. Speleol., 2012, 41, 3. http://dx.doi.org/10.5038/1827-806X.41.2.3.

[24] M. Vattano, P. Audra, F. Benvenuto, J.Y. Bigot, J. De Waele, E. Galli, G. Madonia, J. Nobécourt, Hypogenic caves of Sicily (southern Italy), in: Proceedings of the 16th international congress of speleology, Vol. 3, 2013, pp. 144-149.

[25] F. Bourges, P. Genthon, D. Genty, M. Lorblanchet, E. Maunduit, D. D'Hulst, Conservation of prehistoric caves and stability of their inner climate: lessons from Chauvet and other French caves, Sci. Total Environ., 2014, 493, 79-91. https://doi.org/10.1016/j.scitotenv.2014.05.137.

[26] P. Audra, F. Hoblea, J.Y. Bigot, J.C. Nobécourt, The Role of Condensation Corrosion in Thermal Speleogenesis. Study of a Hypogenic Cave in Aix-les-Bains, France, Acta Carsologica, 2007, 36. https://doi.org/10.3986/ac.v36i2.186.

[27] P. Forti, S. Galdezi, S.M. Sarbu, The hypogenic caves: a powerful tool for the study of seeps and their environmental effects, Cont. Shelf Res., 2002, 22, 2373-2386. https://doi.org/10.1016/S0278-4343(02)00062-6.

[28] F. Gázquez, J.M. Calaforrab, P. Fortic, J. De Waelec, L. Sannad, The role of condensation in the evolution of dissolutional forms in gypsum caves: Study case in the karst of Sorbas (SE Spain), Geomorphology, 2015, 229, 100-111. https://doi.org/10.1016/j.geomorph.2014.07.006.

[29] G.A. Caddeo, L.B. Railsback, J. De Waele, F. Frau, Stable isotope data as constraints on models for the origin of coralloid and massive speleothems: the interplay of substrate, water supply, degassing, and evaporation, Sediment. Geol., 2015, 318, 130-141. https://doi.org/10.1016/j.sedgeo.2014.12.008.

[30]   Z. Sharp, Principles of stable isotope geochemistry, Pearson/Prentice Hall, Upper Saddle River, N.J., 2007.

[31]   J. Galewsky, H.C. Steen-Larsen, R.D. Field, J. Worden, C. Risi, M. Schneider, Stable isotopes in atmospheric water vapor and applications to the hydrologic cycle, Rev. Geophys., 2016, 54, 809-865. https://doi.org/10.1002/2015RG000512.

[32]   T.W. Horton, W.F. Defliese, A.K. Tripati, C. Oze, Evaporation induced ^{18}O and ^{13}C enrichment in lake systems: A global perspective on hydrologic balance effects, Quat. Sci. Rev., 2016, 131, 365-379. https://doi.org/10.1016/j.quascirev.2015.06.030.

[33]   W. Dreybrodt, M. Hansen, D. Scholz, Processes affecting the stable isotope composition of calcite during precipitation in the surface of stalagmites: Laboratory experiments investigating the isotope exchange between DIC in the solution layer on top of a speleothem and the CO2 of the cave atmosphere., Geochim. Cosmochim. Acta, 2016, 174, 247-262. https://doi.org/10.1016/j.gca.2015.11.012.

[34]   D.F. Ufnar, D.R. Gröcke, P.A. Beddows, Assessing pedogenic calcite stable-isotope values: Can positive linear covariant trends be used to quantify palaeo-evaporation rates?, Chem. Geol., 2008, 256, 46-51. https://doi.org/10.1016/j.chemgeo.2008.07.022.

[35]   D.M. Tremaine, P.N. Froelich, Y. Wang, Speleothem calcite farmed *in situ*: Modern ^{18} ^{13}C paleoclimate proxies in a continuously-monitored natural cave system, Geochim. Cosmochim. Acta, 2011, 75, 4929-4950. https://doi.org/10.1016/j.gca.2011.06.005.

[36]   W. Dreybrodt, Evolution of the isotopic composition of carbon ad oxygen in a calcite precipitating H_2O CO_2 $CaCO_3$ solution and the related isotopic composition of calcite in stalagmites, Geochim. Cosmochim. Acta, 2008, 72, 4712-4724. https://doi.org/10.1016/j.gca.2008.07.022.

[37]   M. Deininger, J. Fohlmeister, D. Scholz, A. Mangini, Isotope disequilibrium effects: The influence of evaporation and ventilation effects on the carbon and oxygen isotope composition of speleothems   A model approach., Geochim. Cosmochim. Acta, 2012, 96, 57-79. https://doi.org/10.1016/j.gca.2012.08.013.

[38]   Institute of Geological & Nuclear Sciences, S.W. Edbrooke, Geology of the Waikato area, Vol. 1, Institute of Geological & Nuclear Sciences, 2005.

[39]   C.S. Nelson, 1973. Stratigraphy and sedimentology of the Te Kuiti Group in Waitomo County, South Auckland. PhD thesis, University of Auckland, Auckland, New Zealand.

[40]   A.S. Anastas, R.W. Dalrymple, N.P. James, C.S. Nelson, Lithofacies and dynamics of a cool-water carbonate seaway: mid-Tertiary, Te Kuiti Group, New Zealand, Geol. Soc. Spec. Publ., 2006, 255, 245-268. https://doi.org/10.1144/GSL.SP.2006.255.01.15.

[41]   S.M. Mentzer, Micro XRF, Archaeological soil and sediment micromorphology, 2017, 431-440.

[42]   A.R. Pearson, A. Hartland, S. Frisia, B.R. Fox, Formation of calcite in the presence of dissolved organic matter: Partitioning, fabrics and fluorescence., Chem. Geol., 2020, 539, 119492. https://doi.org/10.1016/j.chemgeo.2020.119492.

[43]   S.L.L. Barker, G.M. Dipple, F. Dong, S. Baer, Use of Laser Spectrometry To Measure the 13C/12C and 18O/16O Compositions of Carbonate Minerals, Anal. Chem., 2011, 83, 2220-2226. https://doi.org/10.1021/ac103111y.

[44]   A. Beinlich, S.L. B   8 U)   U 8   ) o   "   o   #
        \   -bearing carbonate samples using laser absorption spectrometry., Econ. Geol., 2017, 112, 693-700. https://doi.org/10.2113/econgeo.112.3.693.

[45]   D. Freedman, R. Pisani, R. Purves, Statistics, W.W. Norton & Company, New York, NY, 2007.

[46]   J.M. Utts, Seeing Through Statistics, 4th ed., Cengage Learning, Stamford, CT, 2015.

[47]   K.F. Weaver, V. Morales, S.L. Dunn, K. Godde, P.F. Weaver, t-Test, in: An Introduction to Statitical Analysis in Research: With Applications in the Biological and Life Sciences, John Wiley & Sons, Hoboken, NJ, 2017, pp. 195-225.

[48]   J. Fohlmeister, N.R.G. Voarintsoac, F.A. Lechleitner, M. Boyd, S. Brandtstätter, M.J. Jacobson, J.L. Oster, Main controls on the stable carbon isotope composition of speleothems

Geochim. Cosmochim. Acta, 2020, 279, 67-87. https://doi.org/10.1016/j.gca.2020.03.042.

[49]   C. Nava-Fernandez, A. Hartland, F. Gázquez, O. Kwiecien, N. Marwan, B. Fox, J. Hellstrom, A. Pearson, B. Ward, A. French, D.A. Hodell, A. Immenhauser, S.F.M. Breitenbach, Pacific climate reflected in Waipuna Cave dripwater hydrochemistry, Hydrol. Earth Syst. Sci. Discuss., 2020. http://doi.org/10.5194/hess-2019-647.

[50]   E. Porca, V. Jurado, P.M. Martin-Snachez, B. Hermosin, F. Bastian, C. Alabouvette, C. Saiz-Jimenez, Aerobiology: An ecological indiator for early detection and control of fungal outbreaks   in   caves,   Ecol.   Indic.,   2011,   11,   1594-1598. https://doi.org/10.1016/j.ecolind.2011.04.003.

[51]   M. Hansen, D. Scholz, M.-L. Froeshmann, B.R. Schöne, C. Spötl, Carbon isotope exchange between gaseous CO2 and thin solution films: Artificial cave experiments and a complete diffusion-reaction model, Geochim. Cosmochim. Acta, 2017, 211, 28-47. https://doi.org/10.1016/j.gca.2017.05.005.

[52]   ) o   # U   " U   U   13#   18O in the solution layer on   stalagmite   surfaces,   Geochim.   Cosmochim.   Acta,   2009,   73,   2592-2602. https://doi.org/10.1016/j.gca.2009.02.015.

[53]   C. Mühlinghaus, D. Scholz, A. Mangini, Modelling fractionation of stable isotopes in stalagmites,   Geochim.   Cosmochim.   Acta,   2009,   73,   7275-7289. https://doi.org/10.1016/j.gca.2009.09.010.

[54]   S.-T. Kim, J.R. O'Neil, Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates, Geochim. Cosmochim. Acta, 1997, 61, 3461-3475. https://doi.org/10.1016/S0016-7037(97)00169-5.

[55]   T.B. Coplen, Calibration of the calcite water oxygen-isotope geothermometer at DEvils Hole, Nevada, a natural laboratory, Geochim. Cosmochim. Acta, 2007, 71, 3948-3957. https://doi.org/10.1016/j.gca.2007.05.028.

[56]   F. McDermott, Palaeo-climate reconstruction from stable isotope variation in speleothems: a review, Quat. Sci. Rev., 2004, 23, 901-918. https://doi.org/10.1016/j.quascirev.2003.06.021.

[57]   M. Skidmore, M. Sharp, M. Tranter, Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: implicatinos for detection of microbial CO2 signatures #-DIC., Geochim. Cosmochim. Acta, 2004, 68, 4309-4317. https://doi.org/10.1016/j.gca.2003.09.024.

[58]   E.H. Oelkers, P.A.P. von Strandmann, V. Mavromatis, The rapid resetting of the Ca isotopic signatures of calcite at ambient temperature during its congruent dissolution, precipitation, and at equilibrium, Chem. Geol., 2019, 512, 1-10. https://doi.org/10.1016/j.chemgeo.2019.02.035.

[59]   E.H. Oelkers, U.N. Berninger, A. Pérez-Fernandez, J. Chmeleff, V. Mavromatis, The temporal evolution of magnesium isotope fractionation during hydromagnesite dissolution, precipitation, and at equilibrium, Geochim. Cosmochim. Acta, 2018, 226, 36-49. https://doi.org/10.1016/j.gca.2017.11.004.

[60]   M. Dietzel, J. Tang, A. Leis, S.J. Köhler, Oxygen isotopic fractionation during inorganic calcite precipitation   Effects of temperature, precipiation rate and pH, Chem. Geol., 2009, 268, 107-115. https://doi.org/10.1016/j.chemgeo.2009.07.015.

[61]   C.C. Day, G.M. Henderson, Oxygen isotopes in calcite grown under cave-analogue conditions, Geochim. Cosmochim. Acta, 2011, 75, 3956-3972. https://doi.org/10.1016/j.gca.2011.04.026.

[62]   F.A. Lechleitner, A.J. Mason, S.F.M. Breitenbach, A. Vaks, N. Haghipour, G.M. Henderson, Permafrost-related hiatuses in stalagmite: Evaluating the potential for reconstruction of carbon cycle dynamics, Quat. Geochronol., 2020, 56, 101037. https://doi.org/10.1016/j.quageo.2019.101037.