# CaveCalc: A New Model for Speleothem Chemistry & Isotopes

Robert Owen[a], Christopher C. Day[a,*], Gideon M. Henderson[a]

[a]*Department of Earth Sciences, South Parks Road, Oxford, OX1 3AN*

**Abstract**

CaveCalc is a PHREEQC-based numerical model for cave dripwater and speleothem chemistry, designed to aid in the interpretation of speleothem palaeoclimate records and cave monitoring datasets.

CaveCalc forward-models dripwater and carbonate chemistry and isotopes through a variety of soil, karst and cave processes. Such processes include soil water & gas equilibration, carbonate bedrock dissolution, secondary carbonate precipitation and $CO_2$ degassing. CaveCalc is able to quantitatively model bedrock dissolution under semi-open conditions — a feature necessary to accurately simulate the gas chemistry occurring in real cave environments.

The model allows coupled modelling of multiple proxy systems, including $\delta^{18}O$, $\delta^{13}C$, $a^{14}C$, $\delta^{44/40}Ca$ and trace-elements (Mg/Ca, Sr/Ca, Ba/Ca), within a single framework. Additional proxy systems, chemical processes and calibration data may be added to the model as required.

*Keywords:* speleothems, isotopes, trace metals, geochemical modelling, palaeoclimatology

## 1. Introduction

Climate reconstructions based on the cave carbonate (speleothem) archive are an important source of information about continental palaeoclimate. A wide

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*Corresponding author
Email address:* `chris.day@earth.ox.ac.uk` (Christopher C. Day)

range of analytical methods have been used to extract such information; proxies include C and O isotope ratios [e.g. 1], radiocarbon [e.g. 2], trace metals [e.g. 3], and metal isotope ratios [4, 5, 6]. These proxies record information about cave hydrology and local climate on a variety of timescales; however, precise interpretation is rarely straightforward due to the complex set of soil, karst and cave processes that influence dripwater chemistry [7]. Understanding these controls and their effects requires accurate models for dripwater chemistry and stalagmite growth.

Several models for dripwater and speleothem chemistry have been developed previously, typically focusing on single components of dripwater and/or speleothem chemistry. These include models for dripwater Ca concentrations [8], DIC stable isotope evolution [9, 10, 11, 12], radiocarbon content [13, 14, 15], trace metal ratios [16, 17, 18] and metal isotope ratios [6]. Such models have proved highly informative, but they typically focus on single proxy systems, which limits their use in modelling multi-proxy datasets. Furthermore, with the exception of Fohlmeister et al. [13], these models either do not simulate bedrock dissolution, or are limited to simulating bedrock dissolution under fully open- or closed-system conditions. In reality, bedrock dissolution conditions fall between these two end members, in what we refer to as semi-open conditions. The 'openness' of bedrock dissolution is an important control on dripwater Ca concentrations and C isotope budgets [9, 13] and it is desirable that speleothem geochemical models are able to simulate these intermediate conditions.

In this paper we describe CaveCalc, a new numerical model for cave dripwater and speleothem chemistry and isotopes. CaveCalc provides a unified framework for forward-modelling the various chemical and isotopic systems frequently studied at cave sites, for example $\delta^{18}O$, $\delta^{13}C$, $a^{14}C$, Mg/Ca, Sr/Ca and $\delta^{44/40}Ca$. The model is able to simulate a range of processes thought to control

these proxy systems, including soil respiration, pyrite oxidation, calcite dissolution, dolomite dissolution, $CO_2$ degassing/equilibration and calcite precipitation. Other processes important to speleothem chemistry, such as weathering of minerals in the soil, are not replicated by the model, but the user can prescribe values for the chemical variables, such as fluid trace element composition, that are controlled by these processes. Perhaps most importantly, CaveCalc allows direct quantitative modelling of semi-open dissolution conditions, addressing the limitation of many previously published models. This paper describes the model, its capabilities, limitations and operational details.

## 2. Model Design

The purpose of CaveCalc is to forward-model the evolution of soil water chemistry (and any carbonate precipitated) as water moves downwards from the soil into the unsaturated zone overlying a cave, and finally emerges into a cave, potentially precipitating speleothems. Along this flow path many processes may modify water chemistry, including $CO_2$ exchange with gas phases (e.g. atmosphere, soil gas, cave air), carbonate dissolution and carbonate precipitation reactions.

CaveCalc is an open-source model written and distributed as a Python module. The model performs a user-defined sequence of chemical reactions upon an initial solution to simulate the chemical and isotopic evolution of water moving through the soil-karst-cave system. Individual reaction steps are calculated numerically using PHREEQC (see Section 2.1), while the Python code controls model flow and provides a user interface. This approach leverages the computational power of PHREEQC, while providing a flexible, cross-platform wrapper with additional functionality tailored to the specific requirements of cave geochemical modelling.

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## 2.1. PHREEQC

PHREEQC is a computer program for numerical modelling of aqueous solution chemistry [19]. It is designed to calculate chemical equilibrium between solutions, minerals, gases and ion exchangers, and over time has been expanded to include processes such as kinetics, isotope fractionation and one-dimensional transport [20]. CaveCalc uses PHREEQC to perform many isotope-enabled geochemical calculations including DIC speciation, calcite precipitation and bedrock dissolution. CaveCalc interacts with PHREEQC via the IPhreeqc interface [21].
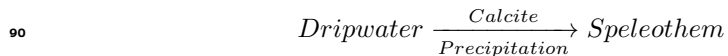
CaveCalc uses a custom PHREEQC database (oxotope.dat) to define the chemical and isotopic reactions, and thermodynamic data, necessary to describe a cave system. This database file is a modified version of iso.dat, a standard database distributed with PHREEQC 3.0. Modifications include the addition of Ca isotope systematics for aqueous ions and calcite (using the fractionation factor between calcite and water of Owen et al. [6]), and an update of the equilibrium C & O isotope fractionation factors associated with $CO_2$–DIC–calcite system, based on the calibration data of O'Neil and Adami [22], Romanek et al. [23], Zhang et al. [24], Beck et al. [25] and Coplen [26]. Oxotope.dat also includes reactions for the partitioning of Mg, Sr and Ba into calcite, using the temperature-dependent partition coefficients of Day and Henderson [27]. Key fractionation factors are summarised in Table 1. The full details of all reactions implemented in oxotope.dat are too extensive to list here — the reader is referred to the database file itself for an exhaustive description. Due to the modular nature of PHREEQC databases, oxotope.dat may be expanded as required to include new chemical species, reactions or isotope systems. It may even be replaced by another database entirely, provided that the replacement database includes the species and reactions used internally by CaveCalc.

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Table 1: Stable isotope fractionation factors used for key parts of the $CO_2$-DIC-Calcite system. Data are taken from the 'oxotope.dat' database used by CaveCalc. $^{14}C/^{12}C$ fractionation factors are double those given for $^{13}C/^{12}C$, in agreement with the findings of [28]. Full details of these and all other fractionation factors and equilibrium constants used can be found in the database file used by CaveCalc.

| $^{13}C/^{12}C$ | Value at 25 °C ($1000ln(\alpha)$) | Source |
|---|---|---|
| $\alpha_{CO2(aq)-CO2(g)}$ | -1.43 | Zhang et al. [24] |
| $\alpha_{HCO3-(aq)-CO2(g)}$ | 7.24 | Zhang et al. [24] |
| $\alpha_{CO3-2(aq)-CO2(g)}$ | 5.91 | Zhang et al. [24] |
| $\alpha_{Calcite-CO2(g)}$ | 8.95 | Romanek et al. [23] |
| $^{18}O/^{16}O$ | | |
| $\alpha_{Calcite-H2O}$ | 29.76 | Coplen [26] |
| $\alpha_{CO2(g)-H2O}$ | 40.0 | O'Neil and Adami [22] |
| $^{44}Ca/^{40}Ca$ | | |
| $\alpha_{Calcite-H2O}$ | -1.27 | Owen et al. [6] |

## 2.2. Supported Reactions

The sequence of reactions calculated by CaveCalc may be specified by the user to simulate a variety of soil, karst & cave processes. For example, a very simple dripwater evolution path could be described as follows:

$$Rain\,Water \xrightarrow[Respiration]{Soil} Soil\,Water$$

$$Soil\,Water \xrightarrow[Dissolution]{Bedrock} Dripwater$$

$$Dripwater \xrightarrow[Precipitation]{Calcite} Speleothem$$

where the labelled arrows represent reactions, and the names (e.g. Soil Water) represent states of the solution and/or calcite precipitate between reactions. This captures the essence of how CaveCalc works; an initial solution is defined and acted upon, in sequence, by a variety of chemical reactions. The state of the system is recorded after every reaction, allowing users to visualise how dripwater and carbonate chemistry evolve as the model progresses.

CaveCalc can model a set of chemical reactions that, when linked together, simulate various aspects of the soil-karst-cave system. CaveCalc may be expanded by users to include new reactions and isotope systems as needed. The chemical reactions available in the version described here are:

- $CO_2$ equilibration between DIC and $CO_{2(g)}$

- Calcite dissolution

- Dolomite dissolution

- Pyrite oxidation

- Calcite precipitation

- Equilibrium $CO_2$ degassing

- Kinetic $CO_2$ degassing

Internally, each of these reactions generates a block of PHREEQC input that is executed by IPhreeqc. CaveCalc allows users to save, view and edit these PHREEQC input blocks by selecting 'Log PHREEQC input' and choosing an 'Output Directory' in the CaveCalc input GUI. These input files can be run by PHREEQC to generate detailed calculation output by PHREEQC. Some other processes, such as oxygen-isotope disequilibrium between water and DIC species are not presently incorporated, but it is also possible for users to write their own PHREEQC input that specifies any possible reaction and use this as part of CaveCalc.

These basic reactions may be combined or run in sequence to describe and simulate a variety of soil and karst processes of interest to speleothem researchers, including some examples given below. Through all these reactions, full solution chemistry is tracked (including DIC speciation, pH & alkalinity),

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121 along with C, O and Ca isotopes. Mg, Sr and Ba partitioning into calcite are
122 also included.

123    A brief overview of the chemical processes included in CaveCalc is given here,
124 and details of their implementation in the model provided in the next section.

125 **Equilibration of soil gas and soil water** Most measurements of soil condi-
126    tions (e.g. $pCO_2$, $\delta^{13}C$, radiocarbon) relate to soil gas as it is easier to
127    sample than any liquid phase present. However, it is soil water chem-
128    istry that is the relevant starting point for dripwater evolution. Given gas
129    phase data, CaveCalc can calculate the chemical and isotopic composition
130    of the solution at equilibrium with it. This is used as the initial solution
131    composition for most CaveCalc model runs.

132 **Bedrock dissolution (in the presence of a gas phase)** CaveCalc can cal-
133    culate stoichiometric carbonate bedrock dissolution in any solution (e.g.
134    soil water) using the calcite or dolomite dissolution reactions. Bedrock
135    chemistry and isotopes may be specified by the user. This simulates closed-
136    system dissolution.

137 **Open system soil gas equilibration** If desired, CaveCalc can simulate open
138    or semi-open gas exchange in the soil during dissolution of carbonate rock.
139    In these simulations, dissolution occurs in the presence of an additional
140    (user defined) volume of gas. This process can be particularly important
141    for C isotopes ($\delta^{13}C$ and $a^{14}C$).

142 **Pyrite-oxidation-driven bedrock dissolution** In some caves, water acidity
143    (and hence bedrock dissolution) may be driven by pyrite oxidation, rather
144    than respiration of organic matter [e.g. 29]. The CaveCalc database in-
145    cludes the aqueous Fe and S chemistry necessary to model pyrite oxidation.
146    CaveCalc allows users to specify the amount (if any) of pyrite present in

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bedrock, and the oxygen concentration of soil water, to investigate the effects this may have on bedrock dissolution.

**Incongruent carbonate bedrock dissolution** Incongruent dissolution may be modelled by coupling a dissolution reaction (e.g. dolomite) with a synchronous precipitation reaction (e.g. calcite). CaveCalc will give the final, equilibrium solution chemistry. Such processes are often inferred in dolomite cave systems and may affect dripwater trace metal signatures.

**$CO_2$ degassing and PCP** $CO_2$ degassing and prior calcite precipitation (PCP) are important processes that may modify dripwater chemistry and isotopes prior to calcite growth. CaveCalc can model $CO_2$ degassing from dripwater, and the subsequent $CaCO_3$ precipitation, in a number of ways. For example, the solution may be allowed to fully equilibrate with a specified gas phase (e.g. cave air) in a single model step. Alternatively, $CO_2$ may be incrementally removed from solution to resolve a degassing evolution pathway. The user may allow calcite precipitation to occur during or after $CO_2$ degassing, not at all, or only once a specified saturation index is reached. CaveCalc does not distinguish between PCP calcite and speleothem calcite as they are precipitated by the same chemical process. It is up to the user to decide how the two are best divided, depending on the specific nature of the cave site they are interested in.

The model inputs used to fully define these reactions are described in Section 3, and the model output is discussed in Section 4.

There are a number of processes that CaveCalc does not presently seek to model. Notable examples that may be of interest to some researchers include water mass mixing, aragonite precipitation, silicate weathering in the soil and the effects of chemical and isotope kinetics on calcite precipitation, including growth rate-dependent partition coefficients and isotope fractionation factors.

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174  CaveCalc may be expanded to include new reactions, or additional isotope sys-

175  tems, as needed in the future.

## 3. Model Inputs

177  This section discusses the geochemical inputs available to determine how

178  the reactions described in Section 2.2 are performed, and provides more detail

179  about the operation of the model.

180  CaveCalc also has a range of input options that control model scripting and

181  the handling of model output. These operational details are discussed in the

182  user manual distributed with CaveCalc.

183  Most geochemical inputs are self-explanatory. Note that radiocarbon inputs

184  ('Atmospheric R14C' etc.) are age- and $\delta^{13}$C- corrected values expressed in per-

185  cent modern carbon (following Stuiver and Polach [30]). CaveCalc radiocarbon

186  outputs are expressed in the same units. When inputting oxygen, carbon and

187  calcium isotopes, users should ensure consistency relative to the chosen refer-

188  ence scale (e.g. VSMOW, VPDB, SRM 915a), based on recommended guidelines

189  [31, 32, 33].

### 3.1. Soil Gas & Water

191  CaveCalc models begin by calculating a soil water chemistry. This is used

192  as the starting point for a series of reactions defined either manually by the

193  user, or specified by the Degassing/Precipitation mode (see Section 3.6). To

194  calculate soil water chemistry, the user inputs the gas composition from which

195  CaveCalc calculates the equilibrium aqueous solution. Inputs for defining soil

196  gas chemistry are summarised in Table 2. CaveCalc provides two methods for

197  defining soil gas:

198  1. Explicitly define the initial gas chemistry ($O_2$, $pCO_2$, $\delta^{13}$C, $a^{14}$C)

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Table 2: CaveCalc inputs for specifying soil carbon & oxygen chemistry. 'Parameter' gives the user-friendly name of the input, while 'Model Name' gives the name used internally by CaveCalc. These inputs are discussed in Section 3.1.

| Parameter | Model Name | Default Value |
|---|---|---|
| Atmospheric Gas End-member | | |
| Atmospheric $O_2$ (%) | atm_O2 | 0.21 |
| Atmospheric $pCO_2$ (ppmv) | atm_pCO2 | 270 |
| Atmospheric $\delta^{13}C$ (‰) | atm_d13C | -7 |
| Atmospheric $R^{14}C$ (pmc) | atm_R14C | 100 |
| Soil Gas End-member | | |
| Soil Gas $O_2$ (%) | soil_O2 | 0 |
| Soil Gas $pCO_2$ (ppmv) | soil_pCO2 | 20000 |
| Soil Gas $\delta^{13}C$ (‰) | soil_d13C | -25 |
| Soil $R^{14}C$ (pmc) | soil_R14C | 100 |
| Initial Gas Chemistry | | |
| Atmospheric Gas Exchange (0-1) | atmo_exchange | 0 |
| Initial $O_2$ (%) | init_O2 | 'mix' |
| Initial $pCO_2$ (ppmv) | init_pCO2 | 'mix' |
| Initial $\delta^{13}C$ (‰) | init_d13C | 'mix' |
| Initial $R^{14}C$ (pmc) | init_R14C | 'mix' |

199    2. Express initial gas chemistry as a mixing between two end-members (e.g.
200       soil gas and a second gas).

201  For input Method 1, enter numeric values for the relevant initial gas chemistry
202  inputs (e.g. 'Initial $\delta^{13}C$' and 'Initial $pCO_2$'). This will disregard the values
203  entered for the soil gas and second gas end-members. For input Method 2,
204  set these parameters to 'mix' (their default value), and use the 'Second Gas
205  Fraction' input to specify the volumetric fraction of the second gas end-member
206  present in the mixture — the remainder is defined by the soil gas end-member.
207  This method is provided to allow users to easily simulate the co-variation in
208  solution $pCO_2$, $\delta^{13}$C, radiocarbon and oxygen content expected due to mixing of
209  any two gases (e.g. a deep carbon-rich gas and a younger respired gas). CaveCalc
210  does not allow for diffusional exchange of soil gas with the atmosphere, though

Table 3: CaveCalc inputs for specifying non-bedrock metal sources. 'Parameter' gives the user-friendly name of the input, while 'Model Name' gives the name used internally by CaveCalc. kgw signifies 'kilogram water'. These inputs are discussed in Section 3.2.

| Parameter | Model Name | Default Value |
|---|---|---|
| Soil Ba (mmol/kgw) | soil_Ba | 0 |
| Soil Ca (mmol/kgw) | soil_Ca | 0 |
| Soil Mg (mmol/kgw) | soil_Mg | 0 |
| Soil Sr (mmol/kgw) | soil_Sr | 0 |
| Soil $\delta^{44/40}Ca$ (‰) | soil_d44Ca | 0 |

211 this could be added in future versions.

### 3.2. Soil & Aerosol Metals

213 While most metals present in cave dripwater likely originate from the host
214 bedrock, some may have arrived in the overlying soil via other means. Metals
215 may, for example, be transported to the cave site as aerosols, or be derived from
216 biological materials or dissolution of silicates. To account for non-carbonate
217 metal sources, CaveCalc allows users to define the initial soil water content of
218 Ba, Sr, Ca and Mg. (Table 3). Any metals specified in this way are treated as
219 chloride salts for charge balance purposes. If soil Ca is added, the user may also
220 specify its isotopic composition.

### 3.3. Bedrock Dissolution

222 Bedrock dissolution occurs when soil water (defined by the inputs described
223 in Sections 3.1 & 3.2) interacts with a carbonate bedrock. The inputs available
224 to describe the nature of this process are given in Table 4.

225 Carbonate bedrock may be specified as either calcite or dolomite ('Bedrock
226 lithology'). In addition, the user may define bedrock Mg/Ca, Sr/Ca and Ba/Ca
227 ratios, and the isotopic compositions of carbon, oxygen and calcium. It is
228 assumed that bedrock contains no radiocarbon. Furthermore, the 'Bedrock
229 Mg/Ca (mmol/mol)' input is ignored if 'Bedrock lithology' is set to 'Dolomite'.

Table 4: CaveCalc inputs for specifying bedrock chemistry and the conditions under which it dissolves. 'Parameter' gives the user-friendly name of the input, while 'Model Name' gives the name used internally by Cavecalc. These inputs are discussed in Section 3.3.

| Parameter | Model Name | Default Value |
|---|---|---|
| Bedrock lithology | bedrock_mineral | 'Calcite' |
| Bedrock Mg/Ca (mmol/mol) | bedrock_MgCa | 0 |
| Bedrock Sr/Ca (mmol/mol) | bedrock_SrCa | 0 |
| Bedrock Ba/Ca (mmol/mol) | bedrock_BaCa | 0 |
| Bedrock $\delta^{13}C$ (‰) | bedrock_d13C | 0 |
| Bedrock $\delta^{18}O$ (‰) | bedrock_d18O | 0 |
| Bedrock $\delta^{44}Ca$ (‰) | bedrock_d44Ca | 0 |
| Bedrock Pyrite (moles) | bedrock_pyrite | 0 |
| Gas Volume (L) | gas_volume | 10 |
| Allow Calcite Reprecipitation | reprecip | FALSE |

CaveCalc performs bedrock dissolution calculations by quantitatively dissolving the carbonate bedrock phase in soil water until the solution reaches saturation with respect to calcite. This process may be modified to mimic three additional processes:

**Bedrock Pyrite (moles)** This input specifies the moles of pyrite present during bedrock dissolution. Note that this does not necessarily mean the pyrite will dissolve — the extent of pyrite dissolution depends strongly on the oxygen concentration in soil water. The input specifies the total pyrite available for dissolution.

**Open or semi-open gas exchange** Soil-water equilibrates in CaveCalc with a large volume of soil-gas with a user-defined $pCO_2$. When replicating closed-system soils, this soil-water then reacts with carbonate rock without the continued presence of the gas phase. When replicating open-system soils, the soil-water and carbonate rock react in the presence of an additional user-defined volume of gas (of identical composition to the original soil-gas). In both cases, the reaction causes dissolution of carbon-

Table 5: CaveCalc inputs for defining cave air chemistry. 'Parameter' gives the user-friendly name of the input, while 'Model Name' gives the name used internally by Cavecalc. These inputs are discussed in Section 3.4.

| Parameter | Model Name | Default Value |
|---|---|---|
| Cave Air O2 (%) | cave_O2 | 0.21 |
| Cave Air pCO2 (ppmv) | cave_pCO2 | 1000 |
| Cave Air d13C (per mil) | cave_d13C | -10 |
| Cave Air R14C (pmc) | cave_R14C | 100 |
| Cave Air d18O (per mil) | cave_d18O | 0 |
| Cave Air Volume (L) | cave_air_volume | 0 |

ate rock to partially neutralise the acidity of the soil water and increase its carbonate ion. In the open-system case, the presence of additional gas causes greater dissolution (hence higher soil-water carbonate and $Ca^{2+}$) and, importantly, the dilution of rock-phase carbon isotopes to decrease the dead-carbon fraction in the soil-water. The degree of open-system behaviour is controlled by altering "Gas Volume (L)". Entering zero leads to closed system behaviour. Selection of non-zero values allows a range of openness to be investigated (relative to the 1kg of soil-water used in CaveCalc reactions).

**Allow Calcite Reprecipitation** This input, if set to TRUE, allows calcite to re-precipitate during bedrock dissolution in chemical and isotopic equilibrium with the solution. This may be used to simulate congruent dissolution in dolomite cave systems. However, finer control on this process may be achieved in other ways (see Example 4 from the model distribution).

*3.4. Cave Air*

Cave air chemistry is relevant to dripwater chemistry and speleothem growth for several reasons. Firstly, the difference in $pCO_2$ between dripwater emerging into a cave and the cave air itself determines the extent of $CO_2$ degassing, and

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Table 6: Other CaveCalc inputs. 'Parameter' gives the user-friendly name of the input, while 'Model Name' gives the name used internally by Cavecalc. These inputs are discussed in Section 3.5.

| Parameter | Model Name | Default Value |
|---|---|---|
| Temperature (Degrees C) | temperature | 25 |
| Rainfall $\delta^{18}O$ (‰) | atm_d18O | -10 |
| Run Mode | kinetics_mode | |
| $CO_2$(g) removal per step (fraction) | co2_decrement | 0.5 |
| Calcite supersaturation limit (SI) | calcite_sat_limit | 5 |

264  hence the extent of calcite precipitation. Secondly, cave air $CO_2$ may exchange

265  with dripwater DIC, typically driving dripwater $\delta^{13}$C to heavier values [34].

266  CaveCalc allows the user to specify cave air chemistry and isotopes using the

267  inputs in Table 5. 'Cave Air pCO2' is used to determine the end-point of models

268  in most Degassing/Precipitation modes (Section 3.6); dripwater evolution is

269  complete once it reaches equilibrium with cave air $pCO_2$. The full cave air

270  chemistry ($pCO_2$, $O_2$, $\delta^{13}$C, $\delta^{18}$O and a$^{14}$C) are used for any equilibration

271  reactions between dripwater and cave air. This functionality is used in the

272  'single_step_degassing' Degassing/Precipitation mode (Section 3.6), and may

273  also be accessed in any user-written models. 'Cave Air Volume' sets the initial

274  volume of cave air present during such reactions.

275  *3.5. General*

276  Model inputs unrelated to any specific process are given in Table 6. 'Tem-

277  perature (Degrees C)' specifies the temperature of the whole system, thereby

278  reflecting mean annual temperature. This affects equilibrium constants, parti-

279  tion coefficients and isotope fractionation factors as defined in the oxotope.dat

280  database file. Rainfall $\delta^{18}$O specifies the oxygen isotope ratio of soil water.

281  The remaining inputs given in Table 6 are not geochemical, but relate to

282  the scripting of model runs. The $CO_2$-decrement input specifies the fraction of

283  aqueous $CO_2$ that will degas when a kinetic degassing reaction step is performed,

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for example during a $CO_2$ degassing & PCP calculation. This is primarily used to control model resolution during these calculations; a large value (e.g. 0.5) will result in faster model computation and is suitable for most situations; smaller values will increase the resolution of $CO_2$ degassing and PCP calculations at the cost of increased model run time. 'Calcite supersaturation limit' is an input used only by the 'ss' Degassing/Precipitation mode (see Section 3.6) to define the saturation index at which calcite may precipitate. 'Cave Air $pCO_2$' defines the model end-point where $CO_2$ degassing reactions will no longer occur.

### 3.6. $CO_2$ degassing and carbonate precipitation settings

Degassing of $CO_2$, and the precipitation of carbonate that may result, can occur in a number of different ways in cave settings. CaveCalc has a number of Degassing/Precipitation modes to allow modelling of various degassing scenarios. There are six pre-defined Degassing/Precipitation modes, described below (although others could be written by the user). Use of a Degassing/Precipitation mode is convenient for scripting, and is required if using the Graphical User Interface (GUI).

All provided Degassing/Precipitation modes begin by calculating soil water chemistry. This is followed by bedrock dissolution. After this point, Degassing/-Precipitation modes diverge in the way they represent $CO_2$ degassing and calcite precipitation. These allow simulation of different kinetic environments, and also provide less computationally-intensive options where only certain processes are of interest. Available Degassing/Precipitation modes are described below.

**multi_step_degassing** The water repeatedly undergoes $CO_2$ degassing & calcite precipitation reactions until the solution reaches equilibrium with cave air — effectively a Rayleigh distillation process. Through this degassing loop calcite precipitates to maintain a saturation of 1.0, with

Figure 1: A schematic of a typical CaveCalc model run. The order of reactions is controlled by the Degassing/Precipitation mode (see Section 3.6), or may be written explicitly by the user. This example illustrates the 'multi_step_degassing' Degassing/-Precipitation mode. Additional details of the PHREEQC code generated by CaveCalc are available in the file log_0_annotated.pdf. For any simulation, the user can opt to view the PHREEQC input file by selecting 'Log PHREEQC input' option and defining an 'Output Directory' in the input GUI. Step by step PHREEQC calculation-output can additionally be produced and viewed by running 'phreeqc input_file output_file oxcal.dat'.

a composition set by given trace-element partition coefficients and isotope fractionation factors. This is shown schematically in Figure 1. This mode does not allow $CO_2$ isotope equilibration between dripwater and cave air $CO_2$ — degassing is assumed to be unidirectional. This mode represents $CO_2$ degassing and calcite precipitation during PCP and speleothem growth and is the default Degassing/Precipitation mode.

**single_step_degassing** In this mode $CO_2$ degassing and calcite precipitation are calculated in a single step. The water is allowed to equilibrate with cave air so it, and precipitated calcite, are influenced by the isotope composition of this air. The impact of the cave air is set by the 'Cave Air Volume' input (Table 5). This mode is representative of slow precipitation and degassing environments, where waters equilibrate with cave air (e.g. cave pools).

**allow_supersaturation** This mode is similar to 'multi_step_degassing' with the exception that calcite is only allowed to precipitate once repeated $CO_2$ degassing reactions have driven the dripwater to a defined calcite saturation index. When precipitation occurs, calcite saturation is restored ($\Omega = 1$) and $CO_2$ degassing continues. This process repeats until dripwater reaches equilibrium with cave air $pCO_2$. The calcite saturation index at which precipitation will occur is given by the input 'Calcite Supersaturation Limit' (Table 6). This mode is useful for simulating situations where $CO_2$ degassing is rapid, and calcite nucleation and/or growth rates are too slow to maintain calcite saturation.

**allow_supersaturation_max** This model is identical to 'allow_supersaturation' with the exception that 'Calcite Supersaturation Limit' is not used. Instead $CO_2$ degasses until equilibrium is reached with cave $pCO_2$, at which point calcite precipitates. This process repeats until no more degassing oc-

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curs. Like 'allow_supersaturation' mode, this may be useful for modelling environments where calcite precipitation is limited by kinetic factors.

**degas_only** Following bedrock dissolution, waters are only allowed to undergo $CO_2$ degassing — no calcite precipitation occurs. This simulates environments where calcite precipitation is impossible or extremely limited.

**diss_only** Using this mode, CaveCalc does not perform any further calculations after the bedrock dissolution reaction. This saves computation time when only the bedrock dissolution product is of interest (e.g. when modelling calcite growth at the speleothem apex in cases where it is known that PCP does not occur).

## 4. Model Output

After each reaction step, the chemistry and isotopic composition of the resulting solution (and, if present, any calcite precipitated) are recorded. This includes data concerning bulk solution chemistry, pH, DIC speciation, C & O isotope compositions and distributions between species. On model completion, these results are saved to the file 'results.pkl'. In addition, CaveCalc saves a complete record of the model settings used to the file 'settings.pkl' in the selected output directory.

CaveCalc includes tools to quickly visualise model output, as well as the facility to convert model outputs to formats readily useable with Python, MATLAB, or spreadsheet programmes (e.g. Excel). These tools are discussed in the user manual distributed with CaveCalc.

## 5. An Example

To demonstrate working with CaveCalc this section walks through a simple example, comparing dripwater chemistry modelled for two sites that differ only

18

Figure 2: A Python script to run the example models described in Section 5, and plot some model output. Note that only non-default settings need to be defined. By including both 'Calcite' and 'Dolomite' in the 'bedrock_mineral' input, CaveCalc will automatically run two models, one for each unique combination of input parameters.

```
from cavecalc.forward_models import ForwardModels
import cavecalc.analyse as cca

# define non-default settings to be used
s = {  'bedrock_mineral' :        ['Calcite', 'Dolomite'],
       'cave_pCO2' :              500,
       'temperature'    :         15,              # degrees C
       'soil_pCO2' :              15000,           # ppmv gas equivalent
       'soil_d13C' :              -20,             # per mil, VPDB
       'bedrock_MgCa' :           5,               # mmol/mol
       'kinetics_mode' :          'closed_system_rayleigh'
     }

# Run Models
p = ForwardModels(  settings = s )  # initialise the model
p.run_models()                      # run the model using the Run Mode
    given
p.save()                            # save model output to current
    directory

# Load Output Data and make plots
e = cca.Evaluate()        # initialise an 'Evaluate' object
e.load_data()             # load data from the current directory

e2 = e.filter_by_index(0, n=True)  # filter out the first model step
e2.plot_models(x_key='Ca(mol/kgw)', y_key='pH', label_with = '
    bedrock_mineral')
e2.plot_models(x_key='Ca(mol/kgw)', y_key='d13C', label_with = '
    bedrock_mineral')
cca.plt.show()
```

362 in bedrock mineralogy (one calcite, one dolomite). This could, for example,

363 represent two drip-sites in the same cave, one of which is overlain by a dolomite

364 member in the host bedrock, while the other is overlain by limestone. The

365 resulting difference in dripwater and speleothem Mg/Ca is obvious, however

366 little attention has been paid to the impact of such a bedrock mineralogy change

367 on other aspects of dripwater chemistry. This example shows how CaveCalc may

368 be applied to a problem of this nature. Note that the purpose of this example

369 is to briefly demonstrate CaveCalc usage and the form of output provided; it is

370 not intended to provide a realistic simulation of any particular cave system.

371 These models may be run either via the GUI or written into a simple Python

372 script, as shown in Figures 3 and 2, respectively. The models are defined

373 with some reasonable input parameters, varying only bedrock lithology between

Figure 3: GUI input to run the example models described in Section 5. When opened, the GUI is automatically populated with default values. For representative modelling of a specific cave environment, users are advised to check that all values are representative of the time period, soil and plant types applicable to their site. This window has been set with the same settings as the script shown in Figure 2 — both will produce the same output. As with the script example, including multiple values for a single input (in this case, 'Bedrock Lithology') causes CaveCalc to run a separate model for each unique combination of input parameters.

374 the two models: cave $pCO_2 = 500\,ppmv$, temperature $= 15\,°C$, soil $pCO_2 =$
375 $15\,000\,ppmv$, soil $\delta^{13}C = -20\,‰$ and bedrock $Mg/Ca = 5\,mmol\,mol^{-1}$ for calcite
376 bedrock. The Degassing/Precipitation mode is set to 'multi_step_degassing'.
377 Bedrock lithology is set to both calcite and dolomite; when multiple values are
378 specified, CaveCalc will run a model for each unique combination of parameters.
379 This feature is very useful when the user requires a suite of models that vary
380 one or more parameters across a wide range — they may all be set up at once
381 to run in sequence. All input parameters left unspecified are automatically set
382 to their default values.

383 The Python and GUI methods will give the same results. When run, Cave-
384 Calc will save two files in the specified output directory (the current directory,
385 in this case): settings.pkl and results.pkl. These files store the settings used for
386 the model runs and the results generated, respectively.

387 These results may be handled in a number of ways, including converted to
388 .mat and .csv files. For this example, some plots are shown to visualise the
389 modelled evolution of dripwater through $CO_2$ degassing and PCP, and how
390 those results vary between calcite and dolomite bedrock (Figure 4).

391 Figure 4 shows the co-evolution of solution Ca concentration, $\delta^{13}C$ and pH
392 between these two models. Many other aspects of dripwater chemistry could be
393 visualised — these were chosen simply for illustrative purposes. Notable features
394 include the initial, post-bedrock dissolution chemistry of each dripwater, the
395 progressive loss of Ca and movement to higher pH and $\delta^{13}C$ as $CO_2$ degassing
396 and calcite precipitation occur, and the end-point at which dripwater reaches
397 equilibrium with cave air $pCO_2$ ($500\,ppmv$ in this case). It is interesting that
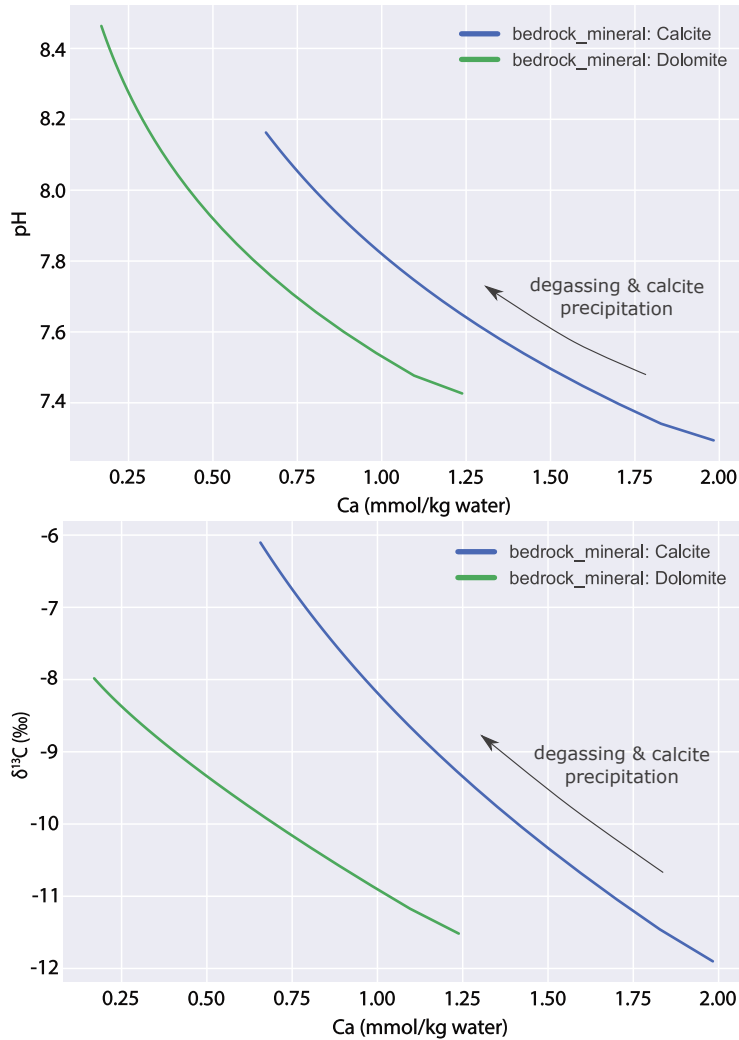398 simply changing bedrock mineralogy affects all of these features in the model
399 output.

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Figure 4: Example CaveCalc output (see Section 5). Top: pH evolution during $CO_2$ degassing and calcite precipitation. Bottom: Bulk solution $\delta^{13}C$ evolution during $CO_2$ degassing and calcite precipitation. In both cases, the highest Ca concentration represents the solution immediately following bedrock dissolution and the lowest Ca concentration represents the point at which the solution reaches equilibrium with cave air $pCO_2$ and degassing ceases. All dripwaters evolve to higher pH and more enriched $\delta^{13}C$ as Ca is removed by calcite precipitation. In blue are calculations using calcite bedrock, and in green using dolomite bedrock.

## 6. Conclusions

In this paper we have introduced CaveCalc, a new numerical model for cave dripwater and speleothem chemistry and isotopes. CaveCalc is able to simulate the effects of various soil, karst and cave processes on key geochemical proxies and may prove helpful in the interpretation of cave monitoring datasets, as well as speleothem time-series. Users may determine the order and type of reactions calculated to simulate a variety of karst environments.

CaveCalc improves upon many previous models by using PHREEQC to couple a DIC system model with bulk solution chemistry, allowing coupled modelling of DIC proxies (e.g. $\delta^{13}$C & $\delta^{18}$O) with bulk solution properties and metal chemistry (e.g. Mg/Ca & $\delta^{44/40}$Ca). Furthermore, CaveCalc is able to model bedrock dissolution under semi-open conditions, where the user has control over the volume and composition of any gas phase present. This makes CaveCalc an ideal tool for modelling bedrock dissolution under a wide range of conditions.

CaveCalc provides a framework for future model development — it may be readily expanded to include new reactions, isotope systems and environmental processes. The PHREEQC database used may be updated as new laboratory and in-situ calibration data become available. This paper is distributed with the model source code, installation and basic operation instructions.

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