```
#     IPhreeqc input log.

DATABASE /Users/chrisd/anaconda3/envs/py35/lib/python3.5/site-packages/cavecalc-
1.0-py3.5.egg/cavecalc/data/oxotope.dat

This example PHREEQC input file was generated by CaveCalc. It is included for
interested users, who want more detail on how CaveCalc performs model
simulations with PHREEQC. Repetitive steps have been removed and blue text
provides additional information.

All CaveCalc users can save the input for their simulations by selecting the
'Log PHREEQC input' option and setting an 'Output Directory' in the input GUI.
Detailed PHREEQC output is generated by running the command 'phreeqc input_file
output_file oxcal.dat', cf. PHREEQC documentation for running PHREEQC from the
command line.

#--------------------

Step 0: work out chemical equilibrium between 1L water and x ppmV soil pCO2
specified by the user. This step is conducted separately with phreeqc input in
log_0_init.phr

Step 1: calculate solution and gas isotopic compositions based on 1L of solution
from step 0 achieving isotopic equilibrium with 1000L of soil gas with d13C and
soil gas R14C specified by user (e.g. in GUI). This step is conducted separately
with Phreeqc input in log_0_d13C.phr

SELECTED_OUTPUT
-totals             Ca Mg Sr Ba C O
    -molalities          CO2 HCO3- CO3-2
    -isotopes            R(13C)_CO2(aq)  R(18O)_CO2(aq) R(14C)_CO2(aq) R(14C)
                         R(44Ca) R(18O) R(13C)

    -solid_solutions     Calcite

SOLUTION 1 Soilwater
    temp                 8
    units   mmol/kgw
    pH             4.71065    charge
    Ca                   0
    Mg                   0
    Sr                   0
    Ba                   0
    Cl                   0
    C              1.17375    # calculate using _get_init_co() Step 0
    O(0)                 0    # calculate using _get_init_co()Step 0
    [18O]              -10    # permil Step 1
    [13C]          -26.136    # permil Step 1
    [14C]          99.7671    # pmc Step 1
    [44Ca]               0    # permil
    -water  1    # kg

REACTION             # force isotopic equilibration
    H2O(g)   0
SAVE solution 1
END


#--------------------
```

```
Step 2: solution 1 from above is now 'equilibrated' with bedrock and either 0L
of extra soil gas (closed system) or xL of extra soil gas (simulating different
degrees of system openness)

USE solution 1

PHASES
Bedrock

Ca0.7530256571[44Ca]0.0162051121Mg0.2307692308C0.9889434148[13C]0.011056585202.9
939964383[18O]0.0060035617 = 0.7530256571Ca+2 + 0.0162051121[44Ca]+2 +
0.0110565852[13C]O3-2 + 0.0060035617CO2[18O]-2 + 0.9829398531CO3-2 +
0.2307692308Mg+2
      log_k -8.480
      delta_h     -2.297
      -analytic -171.9065 -0.077993 2839.319 71.595


EQUILIBRIUM_PHASES
    Pyrite  0    0.0  dissolve_only
    Calcite 0    Bedrock 10.0 dissolve_only Our solution dissolves bedrock until
Calcite reaches saturation in solution
        -force_equality




GAS_PHASE Mixed Initial Gas
    -fixed_pressure
    -pressure              1.001
    -volume                   10 In this case, an extra 10L of soil gas with
user-prescribed chemical and isotopic composition is equilibrated with the
solution/bedrock system
    -temperature               8
    CO2(g)             0.0197216
    CO[18O](g)       8.25575E-05
    C[18O]2(g)                 0
    [13C]O2(g)       0.000215879
    [13C]O[18O](g)             0
    [13C][18O]2(g)             0
    [14C]O2(g)       2.35413E-14
    [14C]O[18O](g)             0
    [14C][18O]2(g)             0
    O2(g)                      0
    O[18O](g)                  0
    Q2(g)                0.98098


SAVE solution 2
END


#--------------------

Step 3_1: this example is based on the 'multi_step_degassing'
Degassing/Precipitation mode, i.e. CO2(aq) simply degasses from the solution
with no input or exchange with cave air CO2(g).

USE solution 2
```

```
REACTION
    CO2              0.985083 Fraction of 12CO16O16(aq) leaving the solution
    [13C]O2         0.0107758 Fraction of 13CO16O16(aq) leaving the solution
    CO[18O]        0.00414127 Fraction of 12CO16O18(aq) leaving the solution
    -0.000408642 Total amount of CO2 removal from solution in the first of
multiple degassing steps.


SOLID_SOLUTION 1 Calcite Definition of the calcite solid-solution (secondary
calcite): i) d44/40Ca defined by solution d44/40Ca (in turn defined by soil and
bedrock d44/40Ca user input) and the d44/40Ca fractionation factor between solid
and solution; ii) Mg-content controlled by solution Mg composition (in turn
defined by soil and bedrock Mg/Ca) and D(Mg) partition coefficient between solid
and solution.
    Calcite
    -comp Calcite 0
    -comp CaCO2[18O](s) 0
    -comp CaCO[18O]2(s) 0
    -comp CaC[18O]3(s) 0
    -comp Ca[13C]O3(s) 0
    -comp Ca[13C]O2[18O](s) 0
    -comp Ca[13C]O[18O]2(s) 0
    -comp Ca[13C][18O]3(s) 0
    -comp [44Ca]CO3(s) 0
    -comp [44Ca]CO2[18O](s) 0
    -comp [44Ca]CO[18O]2(s) 0
    -comp [44Ca]C[18O]3(s) 0
    -comp [44Ca][13C]O3(s) 0
    -comp [44Ca][13C]O2[18O](s) 0
    -comp [44Ca][13C]O[18O]2(s) 0
    -comp [44Ca][13C][18O]3(s) 0
    # -comp Ca[14C]O3(s) 0   # radiocarbon may cause non-convergence
    # -comp Ca[14C]O2[18O](s) 0
    # -comp Ca[14C]O[18O]2(s) 0
    # -comp Ca[14C][18O]3(s) 0
    # -comp [44Ca][14C]O3(s) 0
    # -comp [44Ca][14C]O2[18O](s) 0
    # -comp [44Ca][14C]O[18O]2(s) 0
    # -comp [44Ca][14C][18O]3(s) 0
   # Mg components:          -
    -comp MgCO3(s) 0
    -comp MgCO2[18O](s) 0
    -comp MgCO[18O]2(s) 0
    -comp MgC[18O]3(s) 0
    -comp Mg[13C]O3(s) 0
    -comp Mg[13C]O2[18O](s) 0
    -comp Mg[13C]O[18O]2(s) 0
    -comp Mg[13C][18O]3(s) 0
    # -comp Mg[14C]O3(s) 0
    # -comp Mg[14C]O2[18O](s) 0
    # -comp Mg[14C]O[18O]2(s) 0
    # -comp Mg[14C][18O]3(s) 0


SAVE solution 3 This batch reaction between the calcite solid-solution and our
flow solution is performed and the solution composition saved
END


#--------------------
```

Step 3_2: a second aliquot of CO2(aq) is removed from solution

```
USE solution 3

REACTION
    CO2              0.985078
    [13C]O2         0.0107804
    CO[18O]        0.00414127
    -0.000325027


USE SOLID_SOLUTION 1

SAVE solution 4
END
```

../…

Step 3_22

```
USE solution 21

REACTION
    CO2                0.98504
    [13C]O2          0.0108191
    CO[18O]        0.00414127
    -2.89756E-05


USE SOLID_SOLUTION 1

SAVE solution 22
END
```

The degassing continues until the solution CO2(aq) is in chemical equilibrium with the cave air CO2(g).