**Formation of large karstic cave systems in carbonate rocks by cooling hydrothermal fluids**

Roi Roded,1,2\* Einat Aharonov,3,1\* Amos Frumkin,1 Nurit Weber,5 Boaz Lazar,1 and Piotr Szymczak6

1Institute of Earth Sciences, The Hebrew University, Jerusalem, Israel

2Civil and Environmental Engineering, Duke University, Durham, NC, USA

3The Njord Centre, Departments of Geosciences and Physics, University of Oslo, Oslo, Norway

5Department of Earth and Planetary Sciences, The Weizmann Institute of Science, Rehovot, Israel

6Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, Warsaw, Poland

**Corresponding authors:** R.R. ([roi.roded@mail.huji.ac.il](mailto:roi.roded@mail.huji.ac.il)), E.A. ([einatah@mail.huji.ac.il](mailto:einatah@mail.huji.ac.il))

**Example for PhreeqC script for groundwater from Tel shoket6 borehole, carbonate aquifer at temperature of 20⁰C**

DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.7.0-15749\database\llnl.dat

SOLUTION\_MASTER\_SPECIES

Al Al+3 0 Al 26.9815

Si SiO2 0 SiO2 28.0855

SOLUTION\_SPECIES

Al+3 = Al+3

-llnl\_gamma 9.0000

log\_k 0

-delta\_H 0 kJ/mol # Calculated enthalpy of reaction Al+3

SiO2 = SiO2

-llnl\_gamma 3.0000

log\_k 0

-delta\_H 0 kJ/mol # Calculated enthalpy of reaction SiO2

# Enthalpy of formation: -209.775 kcal/mol

4H2O + Al+3 = Al(OH)4- + 4 H+

-llnl\_gamma 4.0

log\_k -22.851

-analytic 6.761926e+02 2.074159e-01 -3.498514e+04 -2.620590e+02 9.728766e+05 -6.794820e-05

-Vm 8.4938 12.9576 0.6570 -3.3147 1.0403 #TS01

H2O + Al+3 = Al(OH)+2 + H+

-llnl\_gamma 4.5

log\_k -4.964

-analytic 4.876919e+02 1.174365e-01 -2.522243e+04 -1.831424e+02 1.126238e+06 -2.890362e-05

-Vm -0.4532 -8.8878 9.2434 -2.4116 1.5897 #TS01

3H2O + Al+3 = Al(OH)3 + 3 H+

-llnl\_gamma 3.0

log\_k -17.044

-analytic 1.698129e+03 4.425076e-01 -8.348751e+04 -6.455354e+02 3.670657e+06 -1.242598e-04

-Vm 5.4624 5.5560 3.5662 -3.0087 0 #TS01

2H2O + Al+3 = Al(OH)2+ + 2 H+

-llnl\_gamma 4.0

log\_k -10.921

-analytic 1.378643e+03 3.661170e-01 -6.661347e+04 -5.249904e+02 2.937298e+06 -1.044802e-04 # TS01

-Vm 2.4944 -1.6909 6.4146 -2.7091 0.5324 # TS01

Al+3 + SiO2 + 2 H2O = AlH3SiO4+2 + H+

-llnl\_gamma 4.5

log\_k -2.613

-analytic 2.028449e+03 5.556364e-01 -9.187336e+04 -7.763264e+02 4.216938e+06 -1.677843e-04

-Vm 0.16 -7.23 8.61 -2.4800 0.88000 # TS01

4H2O + Na+ + Al+3 = NaAl(OH)4 + 4 H+

-llnl\_gamma 3.0

log\_k -22.9

-analytic -1.711218e+02 -9.243056e-02 -3.384201e+03 7.554937e+01 -3.703544e+05 4.899537e-05

-Vm 9.1267 14.3411 0.1121 -3.3719 0 # TS01

SiO2 + H2O = HSiO3- + H+

-llnl\_gamma 4.0

log\_k -9.842

-analytic 5.434886e+03 1.537747e+00 -2.417723e+05 -2.094080e+03 1.190645e+07 -4.999253e-04

-Vm 2.9735 -0.5158 5.9467 -2.7575 1.5511

SiO2 + Na+ + H2O = NaHSiO3 + H+

-llnl\_gamma 3.0

log\_k -8.011

-analytic 6.170122e+03 1.686468e+00 -2.788451e+05 -2.367426e+03 1.412272e+07 -5.219411e-04

-Vm 3.4928 0.75 5.4483 -2.8100 -0.038

SiO2 + Mg+2 + H2O = Mg(HSiO3)+ + H+

-llnl\_gamma 4.0

log\_k -8.582

-analytic 6.991775e+03 1.925345e+00 -3.158859e+05 -2.683919e+03 1.595435e+07 -5.970318e-04

-Vm 0.6289 -6.2428 8.1967 -2.5209 0.9177

SiO2 + Ca+2 + H2O = Ca(HSiO3)+ + H+

-llnl\_gamma 4.0

log\_k -8.832

-analytic -8.283895E+02 -3.440430E-01 2.115267E+04 3.404640E+02 -2.962864E+05 1.357884E-04

-Vm 1.0647 -5.1787 7.7785 -2.5649 0.5831

PHASES

Illite

K.85Fe.25Al2.35Si3.4O10(OH)2 + 8.4000 H+ = 0.8500 K+ + 2.3500 Al+3 + 5.2000 H2O + 3.4000 SiO2 + 0.2500 Fe+2

log\_k 9.68

-analytic 5.1079e2 1.2823e-1 -8.3236e3 -2.0525e2 0.0000E+00 -3.9850e-5

-Vm 140.67

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Step 1: Get initial solution composition by Tel shoket6 borehole with carbonate aquifer and gas at 20C##########

SOLUTION 0

temp 20

pH 7.22

units mmol/l

Br 0.0025

C 4.062

Ca 1.2975

Cl 1.8052 charge

K 0.0588

Mg 1.0286

Na 1.9575

S 0.3227

-water 1 # kg

GAS\_PHASE 0

-fixed\_pressure ###Consider a gas phase of CH4, H2O and CO2 (fixed\_pressure) as main gas components in the subsurface###

-pressure 1

-temperature 20

CO2(g) 0

CH4(g) 0

H2O(g) 0

Reaction 1

CO2(g) 1

CH4(g) 0

H2O(g) 0

0.002 moles

EQUILIBRIUM\_PHASES 0

Calcite 0 80.58

Dolomite 0 5.64

Quartz 0 3.86

K-Feldspar 0 0.32

Illite 0 0.12

Kaolinite 0 0.18

Save Solution 1

SELECTED\_OUTPUT 1

-file Base\_Mk Tel Shoket 6\_0.002mol\_Carbonate aquifer\_200c.out

-temperature true

-pH true

-totals Ca Mg C Si Al Fe Na

-saturation\_indices CO2(g)

-equilibrium\_phases Quartz K-feldspar Albite Calcite Kaolinite Pyrite Dolomite Siderite Illite1

-gases CO2(g) CH4(g) H2O(g)

End

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Step 2: Recalculate the changes of gas phase and minerals at 20 C ##

Use Solution 1

GAS\_PHASE 1

-fixed\_pressure

-pressure 1

-temperature 20

CO2(g) 0

CH4(g) 0

H2O(g) 0

Reaction 1

CO2(g) 1

CH4(g) 0

H2O(g) 0

0.002 moles

REACTION\_TEMPERATURE 1

20

REACTION\_PRESSURE 1

1

EQUILIBRIUM\_PHASES 1

Calcite 0 80.58

Dolomite 0 5.64

Quartz 0 3.86

K-Feldspar 0 0.32

Illite 0 0.12

Kaolinite 0 0.18

Save Solution 2

Save GAS\_PHASE 2

Save EQUILIBRIUM\_PHASES 2

END

#############################################################################

Step 3: Increase Step-wisely the temperature and pressure of the system to mimic burial. ##########

Use Solution 2

Use GAS\_PHASE 2

Use EQUILIBRIUM\_PHASES 2

REACTION\_TEMPERATURE 1

30

REACTION\_PRESSURE 1

50.35

Save Solution 3

Save GAS\_PHASE 3

Save EQUILIBRIUM\_PHASES 3

END

Use Solution 3

Use GAS\_PHASE 3

USE EQUILIBRIUM\_PHASES 3

REACTION\_TEMPERATURE 2

40

REACTION\_PRESSURE 2

99.69

Save Solution 4

Save GAS\_PHASE 4

Save EQUILIBRIUM\_PHASES 4

END

Use Solution 4

Use GAS\_PHASE 4

USE EQUILIBRIUM\_PHASES 4

REACTION\_TEMPERATURE 3

50

REACTION\_PRESSURE 3

140.04

Save Solution 5

Save GAS\_PHASE 5

Save EQUILIBRIUM\_PHASES 5

END

Use Solution 5

Use GAS\_PHASE 5

USE EQUILIBRIUM\_PHASES 5

REACTION\_TEMPERATURE 4

60

REACTION\_PRESSURE 4

198.38

Save Solution 6

Save GAS\_PHASE 6

Save EQUILIBRIUM\_PHASES 6

END

Use Solution 6

Use GAS\_PHASE 6

USE EQUILIBRIUM\_PHASES 6

REACTION\_TEMPERATURE 5

70

REACTION\_PRESSURE 5

247.73

Save Solution 7

Save GAS\_PHASE 7

Save EQUILIBRIUM\_PHASES 7

END

Use Solution 7

Use GAS\_PHASE 7

USE EQUILIBRIUM\_PHASES 7

REACTION\_TEMPERATURE 6

80

REACTION\_PRESSURE 6

297.08

Save Solution 8

Save GAS\_PHASE 8

Save EQUILIBRIUM\_PHASES 8

END

Use Solution 8

Use GAS\_PHASE 8

USE EQUILIBRIUM\_PHASES 8

REACTION\_TEMPERATURE 7

90

REACTION\_PRESSURE 7

364.42

Save Solution 9

Save GAS\_PHASE 9

Save EQUILIBRIUM\_PHASES 9

END

Use Solution 9

Use GAS\_PHASE 9

USE EQUILIBRIUM\_PHASES 9

REACTION\_TEMPERATURE 8

100

REACTION\_PRESSURE 8

395.77

Save Solution 10

Save GAS\_PHASE 10

Save EQUILIBRIUM\_PHASES 10

END

Use Solution 10

Use GAS\_PHASE 10

USE EQUILIBRIUM\_PHASES 10

REACTION\_TEMPERATURE 9

110

REACTION\_PRESSURE 9

445.12

Save Solution 11

Save GAS\_PHASE 11

Save EQUILIBRIUM\_PHASES 11

END

Use Solution 11

Use GAS\_PHASE 11

USE EQUILIBRIUM\_PHASES 11

REACTION\_TEMPERATURE 10

120

REACTION\_PRESSURE 10

494.46

Save Solution 12

Save GAS\_PHASE 12

Save EQUILIBRIUM\_PHASES 12

END

Use Solution 12

Use GAS\_PHASE 12

USE EQUILIBRIUM\_PHASES 12

REACTION\_TEMPERATURE 11

130

REACTION\_PRESSURE 11

543.81

Save Solution 13

Save GAS\_PHASE 13

Save EQUILIBRIUM\_PHASES 13

END

Use Solution 13

Use GAS\_PHASE 13

USE EQUILIBRIUM\_PHASES 13

REACTION\_TEMPERATURE 12

140

REACTION\_PRESSURE 12

593.15

Save Solution 14

Save GAS\_PHASE 14

Save EQUILIBRIUM\_PHASES 14

END

Use Solution 14

Use GAS\_PHASE 14

USE EQUILIBRIUM\_PHASES 14

REACTION\_TEMPERATURE 13

150

REACTION\_PRESSURE 13

642.50

Save Solution 15

Save GAS\_PHASE 15

Save EQUILIBRIUM\_PHASES 15

END

Use Solution 15

Use GAS\_PHASE 15

USE EQUILIBRIUM\_PHASES 15

REACTION\_TEMPERATURE 14

160

REACTION\_PRESSURE 14

691.85

Save Solution 16

Save GAS\_PHASE 16

Save EQUILIBRIUM\_PHASES 16

END

Use Solution 16

Use GAS\_PHASE 16

USE EQUILIBRIUM\_PHASES 16

REACTION\_TEMPERATURE 15

170

REACTION\_PRESSURE 15

741.19

Save Solution 17

Save GAS\_PHASE 17

Save EQUILIBRIUM\_PHASES 17

END

Use Solution 17

Use GAS\_PHASE 17

USE EQUILIBRIUM\_PHASES 17

REACTION\_TEMPERATURE 16

180

REACTION\_PRESSURE 16

790.54

Save Solution 18

Save GAS\_PHASE 18

Save EQUILIBRIUM\_PHASES 18

END

Use Solution 18

Use GAS\_PHASE 18

USE EQUILIBRIUM\_PHASES 18

REACTION\_TEMPERATURE 17

190

REACTION\_PRESSURE 17

839.88

Save Solution 19

Save GAS\_PHASE 19

Save EQUILIBRIUM\_PHASES 19

END

Use Solution 19

Use GAS\_PHASE 19

USE EQUILIBRIUM\_PHASES 19

REACTION\_TEMPERATURE 18

200

REACTION\_PRESSURE 18

889.23

Save Solution 20

Save GAS\_PHASE 20

Save EQUILIBRIUM\_PHASES 20

END