

Geological Society Supplementary Publication No. SUP18745: The five modelling input files are provided to ensure retraceability of our modelling approach and its results.

Supplementary material 1: Phreeqc input file '1'

Supplementary material 2: Phreeqc input file '3'

Supplementary material 3: Phreeqc input file '6'

Supplementary material 4: Phreeqc input files '8' and '9'

Supplementary material 5: Phreeqc input file '11'

Supplementary material 1: Phreeqc input file '1' (ready to copy, paste, and run; use the U.S. Geological Survey's Phreeqc Interactive 3.1.4-8929 computer code and its phreeqc.dat database (Parkhurst & Appelo 2013))

TITLE 1

ACF Generation in Siliciclastic Source Rocks by KMP (Kerogen Maturation Products)

#----- definition of additional Acetate species from minteq.v4.dat

SOLUTION_MASTER_SPECIES

Acetate Acetate- 1.0 59.045 59.045

SOLUTION_SPECIES

Acetate- = Acetate-
log_k 0

H+ + Acetate- = H(Acetate)

log_k 4.757
delta_h 0.41 kJ
-gamma 0 0
Id: 3309921
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

Ca+2 + Acetate- = Ca(Acetate)+

log_k 1.18
delta_h 4 kJ
-gamma 0 0
Id: 1509920
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

Na+ + Acetate- = Na(Acetate)

log_k -0.18
delta_h 12 kJ
-gamma 0 0
Id: 5009920
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

K+ + Acetate- = K(Acetate)

log_k -0.1955
delta_h 4.184 kJ
-gamma 0 0
Id: 4109921
log K source: NIST46.4
Delta H source: NIST46.2
#T and ionic strength: 0.10 25.0

SOLUTION 1 # pore water composition prior to the addition of KMP; solution equilibrated with quartz, kaolinite,
calcite, anorthite, albite, and K-feldspar

-pH 7.772
-pe 5.991
-temp 85.0
-units mol/kgw

Al	1.178e-005
C	5.121e-005
Ca	1.044e-001
Cl	1.000e+000
K	9.545e-003
Na	7.818e-001
Si	5.065e-004

EQUILIBRIUM_PHASES 1

Quartz	0.0	0.48
Kaolinite	0.0	0.48
Calcite	0.0	0.01
Anorthite	0.0	0.01
Albite	0.0	0.01
K-feldspar	0.0	0.01

REACTION_PRESSURE 1

305

REACTION 1

KMP formation summarized by the overall reaction:

R-CH₂-CH₂-CH₃ + 4H₂O = R + 2CO₂ + CH₄ + 5H₂ (KMP); Seewald (2003) and van Berk et al., 2009

CO ₂	1.9
CH ₄	0.9
H ₂	5.0
H(Acetate)	0.1

10 moles in 20 steps

GAS_PHASE 1

-fixed_pressure	
-pressure	305.0
-temperature	85.0
CH ₄ (g)	0.0
CO ₂ (g)	0.0
H ₂ (g)	0.0

END

Supplementary material 2: Phreeqc input file '3' (ready to copy, paste, and run)

TITLE 3

ACF Generation in Siliciclastic Source Rocks by KMP (Kerogen Maturation Products) / 1.0 mol KMP

#----- definition of additional Acetate species from minteq.v4.dat

SOLUTION_MASTER_SPECIES

Acetate Acetate- 1.0 59.045 59.045

SOLUTION_SPECIES

Acetate- = Acetate-
log_k 0

H+ + Acetate- = H(Acetate)

log_k 4.757
delta_h 0.41 kJ
-gamma 0 0
Id: 3309921
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

Ca+2 + Acetate- = Ca(Acetate)+

log_k 1.18
delta_h 4 kJ
-gamma 0 0
Id: 1509920
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

Na+ + Acetate- = Na(Acetate)

log_k -0.18
delta_h 12 kJ
-gamma 0 0
Id: 5009920
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

K+ + Acetate- = K(Acetate)

log_k -0.1955
delta_h 4.184 kJ
-gamma 0 0
Id: 4109921
log K source: NIST46.4
Delta H source: NIST46.2
#T and ionic strength: 0.10 25.0

SOLUTION 1

-pH 7.0 charge
-temp 85.0
-units mol/kgw
Cl 1.0
Na 1.0

REACTION_PRESSURE 1

305

EQUILIBRIUM_PHASES 1

Quartz 0.0 10

Kaolinite	0.0	10
Calcite	0.0	10
Anorthite	0.0	10
Albite	0.0	10
K-feldspar	0.0	10

SAVE solution 2
END

USE solution 2

EQUILIBRIUM_PHASES 2

Quartz	0.0	0.48
Kaolinite	0.0	0.48
Calcite	0.0	0.01
Anorthite	0.0	0.01
Albite	0.0	0.01
K-feldspar	0.0	0.01

REACTION_PRESSURE 2
305

REACTION 2

KMP formation summarized by the overall reaction:

$R-CH_2-CH_2-CH_3 + 4H_2O = R + 2CO_2 + CH_4 + 5H_2$ (KMP); Seewald (2003) and van Berk et al., 2009

CO2	1.9
CH4	0.9
H2	5.0
H(Acetate)	0.1

1.0 moles

GAS_PHASE 2

-fixed_pressure
-pressure 305.0
-temperature 85.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0
END

Supplementary material 3: Phreeqc input file '6' (ready to copy, paste, and run)

TITLE 6
ACF establish calcite saturation by the reaction with sufficient amounts of calcite (saturation; SI = 0) at at 85°C/305 atm
before entering the carbonate reservoir rock
KMP = 1.0 mol

#----- definition of additional Acetate species from minteq.v4.dat
SOLUTION_MASTER_SPECIES
Acetate Acetate- 1.0 59.045 59.045

SOLUTION_SPECIES
Acetate- = Acetate-
log_k 0

H+ + Acetate- = H(Acetate)
log_k 4.757
delta_h 0.41 kJ
-gamma 0 0
Id: 3309921
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

Ca+2 + Acetate- = Ca(Acetate)+
log_k 1.18
delta_h 4 kJ
-gamma 0 0
Id: 1509920
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

Na+ + Acetate- = Na(Acetate)
log_k -0.18
delta_h 12 kJ
-gamma 0 0
Id: 5009920
log K source: NIST46.4
Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0

K+ + Acetate- = K(Acetate)
log_k -0.1955
delta_h 4.184 kJ
-gamma 0 0
Id: 4109921
log K source: NIST46.4
Delta H source: NIST46.2
#T and ionic strength: 0.10 25.0

SOLUTION 1 # ACF 1.0 mol KMP
-pH 4.278
-pe -2.122
-temp 85.0
-units mol/kgw
Acetate 9.572e-002
Al 8.553e-007
C 3.161e-001
Ca 1.191e-001
Cl 9.572e-001

K 1.871e-002
Na 7.578e-001
Si 4.561e-004

REACTION_PRESSURE 1
305

EQUILIBRIUM_PHASES 1
Calcite 0.0 100
Quartz 0.0 0.0 # potential secondary phase
Kaolinite 0.0 0.0 # potential secondary phase

GAS_PHASE 1
-fixed_pressure
-pressure 305.0
-temperature 85.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0
END

Supplementary material 4: Phreeqc input files '8' and '9' (ready to copy, paste, and run)

```
TITLE 8
#----- 1.0 molal NaCl solution
SOLUTION 1
-pH      6.194
-temp    85.0
-units   mol/kgw
Cl       1.000e+000
Na       1.000e+000
```

```
EQUILIBRIUM_PHASES 1
Calcite  0.0      100
CO2(g)   1.0 # pCO2(g) = 10 atm
```

```
REACTION_PRESSURE 1
305
END
```

```
TITLE 9
#----- 1.0 molal NaCl solution
SOLUTION 1
-pH      6.518
-temp    55.0
-units   mol/kgw
Cl       1.000e+000
Na       1.000e+000
```

```
EQUILIBRIUM_PHASES 1
Calcite  0.0      100
CO2(g)   1.0 # pCO2(g) = 10 atm
```

```
REACTION_PRESSURE 1
205
END
```


Supplementary material 5: Phreeqc input file '11' (ready to copy, paste, and run)

```
TITLE 11
# ACF (SI calcite = 0 at 305 atm/85°C) enter the carbonate reservoir
# 1D advective transport through the reservoir at decreasing pressure/temperature

#----- definition of additional Acetate species from minteq.v4.dat
SOLUTION_MASTER_SPECIES
Acetate      Acetate- 1.0      59.045  59.045

SOLUTION_SPECIES
Acetate- = Acetate-
      log_k 0

H+ + Acetate- = H(Acetate)
      log_k 4.757
      delta_h 0.41      kJ
      -gamma 0      0
      #      Id: 3309921
      #      log K source: NIST46.4
      #      Delta H source: NIST46.4
      #T and ionic strength: 0.00 25.0

Ca+2 + Acetate- = Ca(Acetate)+
      log_k 1.18
      delta_h 4      kJ
      -gamma 0      0
      #      Id: 1509920
      #      log K source: NIST46.4
      #      Delta H source: NIST46.4
      #T and ionic strength: 0.00 25.0

Na+ + Acetate- = Na(Acetate)
      log_k -0.18
      delta_h 12      kJ
      -gamma 0      0
      #      Id: 5009920
      #      log K source: NIST46.4
      #      Delta H source: NIST46.4
      #T and ionic strength: 0.00 25.0

K+ + Acetate- = K(Acetate)
      log_k -0.1955
      delta_h 4.184      kJ
      -gamma 0      0
      #      Id: 4109921
      #      log K source: NIST46.4
      #      Delta H source: NIST46.2
      #T and ionic strength: 0.10 25.0

#to print the calculated amounts of calcite in different cells in an excel-file
Selected_Output
-file Scenario11.xls
-equilibrium_phases Calcite

#----- Pore water prior to ACF influx (in equilibrium with calcite)
SOLUTION 1
-pH 8.630
-pe -3.052
-temp 82
-units mol/kgw
C 1.331e-003
```

Ca 1.331e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 2

-pH 8.680
-pe -3.077
-temp 79
-units mol/kgw
C 1.306e-003
Ca 1.306e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 3

-pH 8.731
-pe 5.566
-temp 76
-units mol/kgw
C 1.278e-003
Ca 1.278e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 4

-pH 8.784
-pe -3.171
-temp 73
-units mol/kgw
C 1.249e-003
Ca 1.249e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 5

-pH 8.838
-pe -3.230
-temp 70
-units mol/kgw
C 1.218e-003
Ca 1.218e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 6

-pH 8.893
-pe 5.963
-temp 67
-units mol/kgw
C 1.186e-003
Ca 1.186e-000
Cl 1.000e+000
Na 1.000e+000

SOLUTION 7

-pH 8.950
-pe -3.320
-temp 64
-units mol/kgw
C 1.153e-003
Ca 1.153e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 8

-pH 9.009
-pe -3.371
-temp 61
-units mol/kgw
C 1.118e-003
Ca 1.118e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 9

-pH 9.068
-pe 6.375
-temp 58
-units mol/kgw
C 1.083e-003
Ca 1.083e-003
Cl 1.000e+000
Na 1.000e+000

SOLUTION 10

-pH 9.130
-pe 6.518
-temp 55
-units mol/kgw
C 1.046e-003
Ca 1.046e-003
Cl 1.000e+000
Na 1.000e+000

EQUILIBRIUM_PHASES 1-10

Calcite	0.0	100
Quartz	0.0	0
Kaolinite	0.0	0

REACTION_PRESSURE 1

295
REACTION_Temperature 1
82

GAS_PHASE 1

-fixed_pressure
-pressure 295.0
-temperature 82.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 2

285
REACTION_Temperature 2
79

GAS_PHASE 2

-fixed_pressure
-pressure 285.0
-temperature 79.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 3

275
REACTION_Temperature 3

76

GAS_PHASE 3

-fixed_pressure
-pressure 275.0
-temperature 76.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 4

265
REACTION_Temperature 4
73

GAS_PHASE 4

-fixed_pressure
-pressure 265.0
-temperature 73.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 5

255
REACTION_Temperature 5
70

GAS_PHASE 5

-fixed_pressure
-pressure 255.0
-temperature 70.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 6

245
REACTION_Temperature 6
67

GAS_PHASE 6

-fixed_pressure
-pressure 245.0
-temperature 67.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 7

235
REACTION_Temperature 7
64

GAS_PHASE 7

-fixed_pressure
-pressure 235.0
-temperature 64.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 8

225

REACTION_Temperature 8
61

GAS_PHASE 8
-fixed_pressure
-pressure 225.0
-temperature 61.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 9
215
REACTION_Temperature 9
58

GAS_PHASE 9
-fixed_pressure
-pressure 215.0
-temperature 58.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

REACTION_PRESSURE 10
205
REACTION_Temperature 10
55

GAS_PHASE 10
-fixed_pressure
-pressure 205.0
-temperature 55.0
CH4(g) 0.0
CO2(g) 0.0
H2(g) 0.0

SOLUTION 0 #Influx of ACF (SICalcite= 0) generated at 85°C/305 bar from 1.0 mole KMP
-pH 4.897
-pe -2.751
-temp 85.0
-units mol/kgw
Acetate 9.571e-02
Al 1.421e-07
C 3.034e-01
Ca 1.422e-01
Cl 9.571e-01
K 1.871e-02
Na 7.577e-01
Si 4.538e-04

ADVECTION
-cells 10
-shifts 10000
END