Supplementary Material 2

# PHREEQC code of model 1-3

Model 1 is identical to model 3 (which is published below), except for that Al(OH)3(a) is entered instead of Gibbsite in the equilibrium phase functionality and the augite block under the ‘RATES’ function is entered as below.

Augite

-start

10 REM Rate law froml Palandri and Kharaka (2004)

20 REM Affinity ON

30 moles = 0

40 IF(M <= 0 OR SI("Augite") > 0) THEN GOTO 270

50 rssa = PARM(1)

60 r\_conc = PARM(2)

70 wporosity = PARM(3)

80 afrac = PARM(4)

90 a0 = rssa\*r\_conc\*afrac/wporosity

100 v = PARM(5)

110 dif\_temp = 1/TK-1/298.15

120 k\_acid = 10^-6.82

130 eapp\_acid = 78

140 n\_acid = 0.7

150 k\_neut = 10^-11.97

160 eapp\_neut = 78.0

170 k\_base = 0

180 eapp\_base = 0

190 n\_base = 0

200 hplus = MOL("H+")

210 r\_acid = k\_acid\*EXP((-eapp\_acid/8.314e-3)\*dif\_temp)\*(hplus^n\_acid)

220 r\_neut = k\_neut\*EXP((-eapp\_neut/8.314e-3)\*dif\_temp)

230 r\_base = k\_base\*EXP((-eapp\_base/8.314e-3)\*dif\_temp)\*(hplus^n\_base)

240 r\_all = r\_acid+r\_neut+r\_base

250 rate = (a0/v)\*(M/M0)^0.67\*r\_all\*(1-SR("Augite"))

260 moles = rate\*TIME

270 SAVE moles

-end

## Model 2

Model 2 is identical to model 3 (which is published below), except for that Al(OH)3(a) is entered instead of Gibbsite in the equilibrium phase functionality.

## Model 3

TITLE Potato experiment

SOLUTION\_MASTER\_SPECIES

Ti Ti(OH)4 0.0 Ti 47.88

SOLUTION\_SPECIES

Ti(OH)4 = Ti(OH)4

log\_k 0

-delta\_H 0

#(Blanc et al,, 2012);

PHASES

Augite

Ca0.9Mg0.9Na0.1Al0.4Fe0.2Si1.9Ti0.1O6 + 4H+ + 2H2O = 0.9Ca+2 + 0.9Mg+2 + 0.1Na+ + 0.4Al+3 + 0.2Fe+2 + 0.1Ti(OH)4 + 1.9H4SiO4 + 1.3 e-

log\_k 19.894

delta\_h -32.348 kcal

#source: supporting information tayler et al. 2016, log K & delta H of Diopside (CaMgSi2O6) as a proxy #(Ball & Nordstrom, 1991);

plagioclase # as labradorite

Ca0.5Na0.5Al1.5Si2.5O8 + 6.4H+ + 1.6H2O + 0.4OH- = 1.5Al+3 + 0.5Ca+2 + 2.5H4SiO4 + 0.5Na+

log\_k 16.34

delta\_h -213.1 kcal

olivine # as Forsterite

Mg1.04Fe0.96SiO4 + 4H+ = 0.96Fe+2 + H4SiO4 + 1.04Mg+2

log\_k 28.306

delta\_h -48.578 kcal

#(Ball & Nordstrom, 1991);

Illite

K0.6Mg0.25Al2.3Si3.5O10(OH)2 + 11.2H2O = 0.6K+ + 0.25Mg+2 + 2.3Al(OH)4- + 3.5H4SiO4 + 1.2H+

-log\_k -40.267

-delta\_h 54.684 kcal

-Vm 141.48

Chlorite(14A) #as clinochlore chlorite

Mg5Al2Si3O10(OH)8 + 16H+ = 5Mg+2 + 2Al+3 + 3H4SiO4 + 6H2O

-log\_k 68.38

-delta\_h -151.494 kcal

Magnesite #from core10.dat

MgCO3 + H+ = HCO3- + Mg+2

log\_k 2.2936

-delta\_H -44.4968 kJ/mol

# deltafH -265.63 kcal/mol

-analytic -1.6665e2 -4.9469e-2 6.4344e3 6.5506e1 1.0045e2

# Range 0-350

-Vm 28.018

# Extrapol supcrt92

# Ref HDN+78

Siderite

FeCO3 = Fe+2 + CO3-2

-log\_k -10.89

-delta\_h -2.480 kcal

-Vm 29.2

Nesquehonite #wateq4f.dat

MgCO3:3H2O = Mg+2 + CO3-2 + 3H2O

log\_k -5.621

delta\_h -5.789 kcal

Hydromagnesite #wateq4f.dat

Mg5(CO3)4(OH)2:4H2O + 2H+ = 5Mg+2 + 4CO3-2 + 6H2O

log\_k -8.762

delta\_h -52.244 kcal

Gibbsite

Al(OH)3 +3.0000 H+ = + 1.0000 Al+3 + 3.0000 H2O

log\_k 7.7560

-delta\_H -102.788 kJ/mol # Calculated enthalpy of reaction Gibbsite

# Enthalpy of formation: -309.065 kcal/mol

-analytic -1.1403e+002 -3.6453e-002 7.7236e+003 4.3134e+001 1.2055e+002

# -Range: 0-300

SELECTED\_OUTPUT 1

-file potatoexperiment\_basalt\_model3.tsv

-totals N Na Ca Mg K Al Si Fe Mn Sr Ba

P C(4) Alkalinity Hfo\_s Hfo\_w

-molalities CaX2 KX MgX2 NaX FeX2 MnX2 SrX2 AlX3 BaX2

Hfo\_wH2PO4 Hfo\_wHPO4-

-equilibrium\_phases Calcite SiO2(a) Gibbsite CO2(g) O2(g)

Goethite Kaolinite Fe(OH)3(a) Pyrolusite Plagioclase olivine Augite Magnesite Siderite Dolomite Nesquehonite Hydromagnesite

-saturation\_indices Calcite SiO2(a) Gibbsite CO2(g) O2(g)

Fe(OH)3(a) Pyrolusite Plagioclase Olivine Augite Illite Chlorite(14A) Nesquehonite Hydromagnesite

-kinetic\_reactants Pyrolusite Plagioclase olivine Augite Illite Chlorite(14A) Nesquehonite Hydromagnesite

USER\_PUNCH 1

-headings SurfH\_Ca SurfH\_Mg SurfH\_H Hfo\_PO4

-start

10 PUNCH SURF("Ca","H") SURF("Mg","H") SURF("H","H") SURF("P","Hfo")

-end

#solutions

SOLUTION 0 Leachate for no-basalt planted control - simulates weathering of soil minerals and plant in no-basalt columns

temp 12

pH 7.64

pe 4

redox pe

units mg/l

density 1

Al 0.032

Ca 226.61

Fe 0.109

K 16.366

Mg 18.83

Cu 0.023

Mn 1.306

Na 48.61

Si 8.31

Zn 0.0309

N(3) 0.211

S(6) 441.321 #measured = 147.106 (mgS/L) \*96g SO4/32 g S = 441.32

N(5) 1.705

P 0.138

Alkalinity 129 gfw 100 #as CaCO3 (mg/L) = 129 mgCaCO3/L (=2.57 meq/L(TA)\*50 gCaCO3/eq)

-water 1 # kg

SOLUTION 1-20 Leachate for no-basalt planted control

temp 12

pH 7.64

pe 4

redox pe

units mg/l

density 1

Al 0.032

Ca 226.61

Fe 0.109

K 16.366

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P 0.138

Alkalinity 129 gfw 100 #as CaCO3 (mg/L) = 130 mgCaCO3/L (=2.57 meq/L(TA)\*50 g/eq)

-water 1 # kg

#Our column lenght is 1 meter. Dividing this into cells of 5 cm, we get 20 cells, solutions and equilluibrium phases.

#CO2 increases with depth to 0.5m according to PCO2 based on respiration fluxes and fick's law and then remains constant up to 1m depth as in Nan et al;

#fix pe at 4

EQUILIBRIUM\_PHASES 1 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -2.80 10 ;Dolomite 0 0;Magnesite 0 0;Siderite 0 0 ; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 2 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -2.28 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 3 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -2.05 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 4 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0;Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.90 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 5 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.79 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 6 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.70 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 7 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.63 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 8 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.57 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 9 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.51 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 10 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 11 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 12 O2(g) -2; Calcite 0 0; SiO2(a) 0 0;Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 13 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 14 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 15 O2(g) -2 ; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 16 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 17 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 18 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 19 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

EQUILIBRIUM\_PHASES 20 O2(g) -2; Calcite 0 0; SiO2(a) 0 0; Gibbsite 0 0; Pyrolusite 0 0; Fe(OH)3(a) 0 0; CO2(g) -1.46 10;Dolomite 0 0;Magnesite 0 0;Siderite 0 0; Nesquehonite 0 0; Hydromagnesite 0 0

END

EXCHANGE 1-20

X 0.5216

# CEC in mol equivalents/ L\_porewater 521.6 meq/Lpw

# CEC = 5.19 meq/100g soil \* (10\*100gsoil/kg soil)\* 1.407 kg soil/L soil (=Bulkdensity) / (0.14L porewater/L soil) = 521.595 meq/L porewater

-equilibrate with solution 1

-pitzer\_exchange\_gammas true

END

SURFACE\_MASTER\_SPECIES

# Monodentate 60%

H\_a H\_aH; H\_b H\_bH; H\_c H\_cH; H\_d H\_dH

H\_e H\_eH; H\_f H\_fH; H\_g H\_gH; H\_h H\_hH

# Diprotic 40%

H\_ab H\_abH2; H\_ad H\_adH2; H\_af H\_afH2; H\_ah H\_ahH2

H\_bc H\_bcH2; H\_be H\_beH2; H\_bg H\_bgH2; H\_cd H\_cdH2

H\_cf H\_cfH2; H\_ch H\_chH2; H\_de H\_deH2; H\_dg H\_dgH2

SURFACE\_SPECIES

H\_aH = H\_aH; log\_k 0; H\_bH = H\_bH; log\_k 0; H\_cH = H\_cH; log\_k 0; H\_dH = H\_dH; log\_k 0;

H\_eH = H\_eH; log\_k 0; H\_fH = H\_fH; log\_k 0; H\_gH = H\_gH; log\_k 0; H\_hH = H\_hH; log\_k 0;

H\_abH2 = H\_abH2; log\_k 0; H\_adH2 = H\_adH2; log\_k 0; H\_afH2 = H\_afH2; log\_k 0;

H\_ahH2 = H\_ahH2; log\_k 0; H\_bcH2 = H\_bcH2; log\_k 0; H\_beH2 = H\_beH2; log\_k 0;

H\_bgH2 = H\_bgH2; log\_k 0; H\_cdH2 = H\_cdH2; log\_k 0; H\_cfH2 = H\_cfH2; log\_k 0;

H\_chH2 = H\_chH2; log\_k 0; H\_deH2 = H\_deH2; log\_k 0; H\_dgH2 = H\_dgH2; log\_k 0;

# Protons

H\_aH = H\_a- + H+; log\_k -1.59

H\_bH = H\_b- + H+; log\_k -2.70

H\_cH = H\_c- + H+; log\_k -3.82

H\_dH = H\_d- + H+; log\_k -4.93

H\_eH = H\_e- + H+; log\_k -6.88

H\_fH = H\_f- + H+; log\_k -8.72

H\_gH = H\_g- + H+; log\_k -10.56

H\_hH = H\_h- + H+; log\_k -12.40

H\_abH2 = H\_abH- + H+; log\_k -1.59; H\_abH- = H\_ab-2 + H+; log\_k -2.70

H\_adH2 = H\_adH- + H+; log\_k -1.59; H\_adH- = H\_ad-2 + H+; log\_k -4.93

H\_afH2 = H\_afH- + H+; log\_k -1.59; H\_afH- = H\_af-2 + H+; log\_k -8.72

H\_ahH2 = H\_ahH- + H+; log\_k -1.59; H\_ahH- = H\_ah-2 + H+; log\_k -12.40

H\_bcH2 = H\_bcH- + H+; log\_k -2.70; H\_bcH- = H\_bc-2 + H+; log\_k -3.82

H\_beH2 = H\_beH- + H+; log\_k -2.70; H\_beH- = H\_be-2 + H+; log\_k -6.88

H\_bgH2 = H\_bgH- + H+; log\_k -2.70; H\_bgH- = H\_bg-2 + H+; log\_k -10.56

H\_cdH2 = H\_cdH- + H+; log\_k -3.82; H\_cdH- = H\_cd-2 + H+; log\_k -4.93

H\_cfH2 = H\_cfH- + H+; log\_k -3.82; H\_cfH- = H\_cf-2 + H+; log\_k -8.72

H\_chH2 = H\_chH- + H+; log\_k -3.82; H\_chH- = H\_ch-2 + H+; log\_k -12.40

H\_deH2 = H\_deH- + H+; log\_k -4.93; H\_deH- = H\_de-2 + H+; log\_k -6.88

H\_dgH2 = H\_dgH- + H+; log\_k -4.93; H\_dgH- = H\_dg-2 + H+; log\_k -10.56

# Mg From Lofts and Tipping, 2000

H\_aH + Mg+2 = H\_aMg+ + H+; log\_k -3.30

H\_bH + Mg+2 = H\_bMg+ + H+; log\_k -3.30

H\_cH + Mg+2 = H\_cMg+ + H+; log\_k -3.30

H\_dH + Mg+2 = H\_dMg+ + H+; log\_k -3.30

H\_eH + Mg+2 = H\_eMg+ + H+; log\_k -7.12

H\_fH + Mg+2 = H\_fMg+ + H+; log\_k -7.12

H\_gH + Mg+2 = H\_gMg+ + H+; log\_k -7.12

H\_hH + Mg+2 = H\_hMg+ + H+; log\_k -7.12

H\_abH2 + Mg+2 = H\_abMg + 2H+; log\_k -6.60

H\_adH2 + Mg+2 = H\_adMg + 2H+; log\_k -6.60

H\_afH2 + Mg+2 = H\_afMg + 2H+; log\_k -10.42

H\_ahH2 + Mg+2 = H\_ahMg + 2H+; log\_k -10.42

H\_bcH2 + Mg+2 = H\_bcMg + 2H+; log\_k -6.60

H\_beH2 + Mg+2 = H\_beMg + 2H+; log\_k -10.42

H\_bgH2 + Mg+2 = H\_bgMg + 2H+; log\_k -10.42

H\_cdH2 + Mg+2 = H\_cdMg + 2H+; log\_k -6.60

H\_cfH2 + Mg+2 = H\_cfMg + 2H+; log\_k -10.42

H\_chH2 + Mg+2 = H\_chMg + 2H+; log\_k -10.42

H\_deH2 + Mg+2 = H\_deMg + 2H+; log\_k -10.42

H\_dgH2 + Mg+2 = H\_dgMg + 2H+; log\_k -10.42

# Calcium, Lofts and Tipping, 2000

H\_aH + Ca+2 = H\_aCa+ + H+; log\_k -3.20

H\_bH + Ca+2 = H\_bCa+ + H+; log\_k -3.20

H\_cH + Ca+2 = H\_cCa+ + H+; log\_k -3.20

H\_dH + Ca+2 = H\_dCa+ + H+; log\_k -3.20

H\_eH + Ca+2 = H\_eCa+ + H+; log\_k -6.99

H\_fH + Ca+2 = H\_fCa+ + H+; log\_k -6.99

H\_gH + Ca+2 = H\_gCa+ + H+; log\_k -6.99

H\_hH + Ca+2 = H\_hCa+ + H+; log\_k -6.99

H\_abH2 + Ca+2 = H\_abCa + 2H+; log\_k -6.40

H\_adH2 + Ca+2 = H\_adCa + 2H+; log\_k -6.40

H\_afH2 + Ca+2 = H\_afCa + 2H+; log\_k -7.45

H\_ahH2 + Ca+2 = H\_ahCa + 2H+; log\_k -10.2

H\_bcH2 + Ca+2 = H\_bcCa + 2H+; log\_k -6.40

H\_beH2 + Ca+2 = H\_beCa + 2H+; log\_k -10.2

H\_bgH2 + Ca+2 = H\_bgCa + 2H+; log\_k -10.2

H\_cdH2 + Ca+2 = H\_cdCa + 2H+; log\_k -6.40

H\_cfH2 + Ca+2 = H\_cfCa + 2H+; log\_k -10.2

H\_chH2 + Ca+2 = H\_chCa + 2H+; log\_k -10.2

H\_deH2 + Ca+2 = H\_deCa + 2H+; log\_k -10.2

H\_dgH2 + Ca+2 = H\_dgCa + 2H+; log\_k -10.2

# Copper

H\_aH + Cu+2 = H\_aCu+ + H+; log\_k -0.63

H\_bH + Cu+2 = H\_bCu+ + H+; log\_k -0.63

H\_cH + Cu+2 = H\_cCu+ + H+; log\_k -0.63

H\_dH + Cu+2 = H\_dCu+ + H+; log\_k -0.63

H\_eH + Cu+2 = H\_eCu+ + H+; log\_k -3.75

H\_fH + Cu+2 = H\_fCu+ + H+; log\_k -3.75

H\_gH + Cu+2 = H\_gCu+ + H+; log\_k -3.75

H\_hH + Cu+2 = H\_hCu+ + H+; log\_k -3.75

H\_abH2 + Cu+2 = H\_abCu + 2H+; log\_k -1.26

H\_adH2 + Cu+2 = H\_adCu + 2H+; log\_k -1.26

H\_afH2 + Cu+2 = H\_afCu + 2H+; log\_k -4.38

H\_ahH2 + Cu+2 = H\_ahCu + 2H+; log\_k -4.38

H\_bcH2 + Cu+2 = H\_bcCu + 2H+; log\_k -1.26

H\_beH2 + Cu+2 = H\_beCu + 2H+; log\_k -4.38

H\_bgH2 + Cu+2 = H\_bgCu + 2H+; log\_k -4.38

H\_cdH2 + Cu+2 = H\_cdCu + 2H+; log\_k -1.26

H\_cfH2 + Cu+2 = H\_cfCu + 2H+; log\_k -4.38

H\_chH2 + Cu+2 = H\_chCu + 2H+; log\_k -4.38

H\_deH2 + Cu+2 = H\_deCu + 2H+; log\_k -4.38

H\_dgH2 + Cu+2 = H\_dgCu + 2H+; log\_k -4.38

# Zinc

H\_aH + Zn+2 = H\_aZn+ + H+; log\_k -1.7

H\_bH + Zn+2 = H\_bZn+ + H+; log\_k -1.7

H\_cH + Zn+2 = H\_cZn+ + H+; log\_k -1.7

H\_dH + Zn+2 = H\_dZn+ + H+; log\_k -1.7

H\_eH + Zn+2 = H\_eZn+ + H+; log\_k -4.9

H\_fH + Zn+2 = H\_fZn+ + H+; log\_k -4.9

H\_gH + Zn+2 = H\_gZn+ + H+; log\_k -4.9

H\_hH + Zn+2 = H\_hZn+ + H+; log\_k -4.9

H\_abH2 + Zn+2 = H\_abZn + 2H+; log\_k -2.4

H\_adH2 + Zn+2 = H\_adZn + 2H+; log\_k -2.4

H\_afH2 + Zn+2 = H\_afZn + 2H+; log\_k -6.6

H\_ahH2 + Zn+2 = H\_ahZn + 2H+; log\_k -6.6

H\_bcH2 + Zn+2 = H\_bcZn + 2H+; log\_k -2.4

H\_beH2 + Zn+2 = H\_beZn + 2H+; log\_k -6.6

H\_bgH2 + Zn+2 = H\_bgZn + 2H+; log\_k -6.6

H\_cdH2 + Zn+2 = H\_cdZn + 2H+; log\_k -2.4

H\_cfH2 + Zn+2 = H\_cfZn + 2H+; log\_k -6.6

H\_chH2 + Zn+2 = H\_chZn + 2H+; log\_k -6.6

H\_deH2 + Zn+2 = H\_deZn + 2H+; log\_k -6.6

H\_dgH2 + Zn+2 = H\_dgZn + 2H+; log\_k -6.6

# Cadmium

H\_aH + Cd+2 = H\_aCd+ + H+; log\_k -1.52

H\_bH + Cd+2 = H\_bCd+ + H+; log\_k -1.52

H\_cH + Cd+2 = H\_cCd+ + H+; log\_k -1.52

H\_dH + Cd+2 = H\_dCd+ + H+; log\_k -1.52

H\_eH + Cd+2 = H\_eCd+ + H+; log\_k -5.57

H\_fH + Cd+2 = H\_fCd+ + H+; log\_k -5.57

H\_gH + Cd+2 = H\_gCd+ + H+; log\_k -5.57

H\_hH + Cd+2 = H\_hCd+ + H+; log\_k -5.57

H\_abH2 + Cd+2 = H\_abCd + 2H+; log\_k -3.04

H\_adH2 + Cd+2 = H\_adCd + 2H+; log\_k -3.04

H\_afH2 + Cd+2 = H\_afCd + 2H+; log\_k -7.09

H\_ahH2 + Cd+2 = H\_ahCd + 2H+; log\_k -7.09

H\_bcH2 + Cd+2 = H\_bcCd + 2H+; log\_k -3.04

H\_beH2 + Cd+2 = H\_beCd + 2H+; log\_k -7.09

H\_bgH2 + Cd+2 = H\_bgCd + 2H+; log\_k -7.09

H\_cdH2 + Cd+2 = H\_cdCd + 2H+; log\_k -3.04

H\_cfH2 + Cd+2 = H\_cfCd + 2H+; log\_k -7.09

H\_chH2 + Cd+2 = H\_chCd + 2H+; log\_k -7.09

H\_deH2 + Cd+2 = H\_deCd + 2H+; log\_k -7.09

H\_dgH2 + Cd+2 = H\_dgCd + 2H+; log\_k -7.09

# Plumbum (Lead)

H\_aH + Pb+2 = H\_aPb+ + H+; log\_k -0.81

H\_bH + Pb+2 = H\_bPb+ + H+; log\_k -0.81

H\_cH + Pb+2 = H\_cPb+ + H+; log\_k -0.81

H\_dH + Pb+2 = H\_dPb+ + H+; log\_k -0.81

H\_eH + Pb+2 = H\_ePb+ + H+; log\_k -3.04

H\_fH + Pb+2 = H\_fPb+ + H+; log\_k -3.04

H\_gH + Pb+2 = H\_gPb+ + H+; log\_k -3.04

H\_hH + Pb+2 = H\_hPb+ + H+; log\_k -3.04

H\_abH2 + Pb+2 = H\_abPb + 2H+; log\_k -1.62

H\_adH2 + Pb+2 = H\_adPb + 2H+; log\_k -1.62

H\_afH2 + Pb+2 = H\_afPb + 2H+; log\_k -3.85

H\_ahH2 + Pb+2 = H\_ahPb + 2H+; log\_k -3.85

H\_bcH2 + Pb+2 = H\_bcPb + 2H+; log\_k -1.62

H\_beH2 + Pb+2 = H\_bePb + 2H+; log\_k -3.85

H\_bgH2 + Pb+2 = H\_bgPb + 2H+; log\_k -3.85

H\_cdH2 + Pb+2 = H\_cdPb + 2H+; log\_k -1.62

H\_cfH2 + Pb+2 = H\_cfPb + 2H+; log\_k -3.85

H\_chH2 + Pb+2 = H\_chPb + 2H+; log\_k -3.85

H\_deH2 + Pb+2 = H\_dePb + 2H+; log\_k -3.85

H\_dgH2 + Pb+2 = H\_dgPb + 2H+; log\_k -3.85

END

# Surface constants are taken from Appelo and Postma (2005)

SURFACE 1-20 # H is the ensemble of exchangeable sites on the particulate organic carbon in the soil (Soil\_C\_Org (0.831%)).

H\_a 0.05930 4.65E+04 83.516 # Total concentration of sites (moles/L\_porewater), OC specific surface area (m2/g), Total mass concentration OC (g/L\_porewater)

# g/L pw = g orgC/g soil \* g soil/ mL soil \* ml soil/ ml Pw \* 1000 mL pw /L pw = 0.00831 \*1.407/0.14\* 1000=83.516

#H\_a ==> H\_d: carboxylic sites

#H\_e ==> H\_h: fenolic sites of humic acids

H\_b 0.05930; H\_c 0.05930, H\_d 0.05930

H\_e 0.02964; H\_f 0.02964, H\_g 0.02964, H\_h 0.02964

H\_ab 0.00985; H\_ad 0.00985, H\_af 0.00985, H\_ah 0.00985

H\_bc 0.00985; H\_be 0.00985, H\_bg 0.00985, H\_cd 0.00985

H\_cf 0.00985; H\_ch 0.00985, H\_de 0.00985, H\_dg 0.00985

-Donnan

# source HFO Kelland et al (2020): HFO is from the National Soil Inventory - 4.05% - Measured by ICP of an aqua regia digest

#600 m2/g ==> pg 341 Apello and postma 2005

# g/L pw = 0.0405 g HFO/g soil \* 1.407 g soil/ mL soil \* 1000 ml soil/ L soil / 0.14 Lpw/Lsoil = 0.0405 \*1.407/0.14\* 1000= 407.025 gHFO/L pw

#number of sites (mol) ==> 407.025 g FeOOH/89 g/mol \*0.2 mol Hfo\_w/mol HFO = 0.914 mol HFO\_w

Hfo\_w 0.914 600 407.025 # Total number of sites (moles/L\_porewater), HFO specific surface area (m2/g), Total mass HFO (g/L pw)

Hfo\_s 0.0228 #2.5% of HFO\_weak sites are strong sites

-equilibrate 1

END

RATES

Augite

-start

10 REM Rate law from Palandri and Kharaka (2004)

20 REM Affinity ON

30 moles = 0

40 IF(M <= 0 OR SI("Augite") > 0) THEN GOTO 270

50 rssa = PARM(1)

60 r\_conc = PARM(2)

70 wporosity = PARM(3)

80 afrac = PARM(4)

90 a0 = rssa\*r\_conc\*afrac/wporosity

100 v = PARM(5)

110 dif\_temp = 1/TK-1/298.15

120 k\_acid = 2.88\*10^(-10)

200 hplus = MOL("H+")

210 r\_acid = k\_acid\*(hplus^0.18)\*EXP((-78/8.314e-3)\*dif\_temp)

240 r\_all = r\_acid

250 rate = (a0/v)\*(M/M0)^0.67\*r\_all\*(1-SR("Augite"))

260 moles = rate\*TIME

270 SAVE moles

-end

Plagioclase # labradorite

-start

10 REM Rate law from Palandri and Kharaka (2004)

20 REM Affinity ON

30 moles = 0

40 IF(M <= 0 OR SI("Plagioclase") > 0) THEN GOTO 270

50 rssa = PARM(1)

60 r\_conc = PARM(2)

70 wporosity = PARM(3)

80 afrac = PARM(4)

90 a0 = rssa\*r\_conc\*afrac/wporosity

100 v = PARM(5)

110 dif\_temp = 1/TK-1/298.15

120 k\_acid = 10^-7.87

130 eapp\_acid = 42.1

140 n\_acid = 0.626

150 k\_neut = 10^-10.91

160 eapp\_neut = 45.2

170 k\_base = 4\*10^-15.6

180 eapp\_base = 71

190 n\_base = -0.572

200 hplus = MOL("H+")

210 r\_acid = k\_acid\*EXP((-eapp\_acid/8.314e-3)\*dif\_temp)\*(hplus^n\_acid)

220 r\_neut = k\_neut\*EXP((-eapp\_neut/8.314e-3)\*dif\_temp)

230 r\_base = k\_base\*EXP((-eapp\_base/8.314e-3)\*dif\_temp)

240 r\_all = r\_acid+r\_neut+r\_base

250 rate = (a0/v)\*(M/M0)^0.67\*r\_all\*(1-SR("Plagioclase"))

260 moles = rate\*TIME

270 SAVE moles

-end

Olivine # Forsterite

-start

10 REM Rate law from Palandri and Kharaka (2004)

20 REM Affinity ON

30 moles = 0

40 IF(M <= 0 OR SI("Olivine") > 0) THEN GOTO 270

50 rssa = PARM(1)

60 r\_conc = PARM(2)

70 wporosity = PARM(3)

80 afrac = PARM(4)

90 a0 = rssa\*r\_conc\*afrac/wporosity

100 v = PARM(5)

110 dif\_temp = 1/TK-1/298.15

120 k\_acid = 10^-6.85

130 eapp\_acid = 67.2

140 n\_acid = 0.47

150 k\_neut = 10^-10.64

160 eapp\_neut = 79

170 k\_base = 0

180 eapp\_base = 0

190 n\_base = 0

200 hplus = MOL("H+")

210 r\_acid = k\_acid\*EXP((-eapp\_acid/8.314e-3)\*dif\_temp)\*(hplus^n\_acid)

220 r\_neut = k\_neut\*EXP((-eapp\_neut/8.314e-3)\*dif\_temp)

230 r\_base = k\_base\*EXP((-eapp\_base/8.314e-3)\*dif\_temp)\*(hplus^n\_base)

240 r\_all = r\_acid+r\_neut+r\_base

250 rate = (a0/v)\*(M/M0)^0.67\*r\_all\*(1-SR("Olivine"))

260 moles = rate\*TIME

270 SAVE moles

-end

# Illite -> Neglected as kinetics lack and clay mineral illite will have a small influence on overall weathering and could not be found

# -start

# 10 REM Rate law from Palandri and Kharaka (2004)

# 20 REM Affinity ON

# 30 moles = 0

# 40 IF(M <= 0 OR SI("Illite") > 0) THEN GOTO 270

# 50 rssa = PARM(1)

# 60 r\_conc = PARM(2)

# 70 wporosity = PARM(3)

# 80 afrac = PARM(4)

# 90 a0 = rssa\*r\_conc\*afrac/wporosity

# 100 v = PARM(5)

# 110 dif\_temp = 1/TK-1/298.15

# # 120 k\_acid = 10^-12.71

# # 130 eapp\_acid = 48

# # 140 n\_acid = 0.22

# # 150 k\_neut = 10^-14.41

# # 160 eapp\_neut = 48

# # 170 k\_base = 10^-14.41

# # 180 eapp\_base = 48

# # 190 n\_base = -0.13

# 200 hplus = MOL("H+")

# 210 r\_acid = k\_acid\*EXP((-eapp\_acid/8.314e-3)\*dif\_temp)\*(hplus^n\_acid)

# 220 r\_neut = k\_neut\*EXP((-eapp\_neut/8.314e-3)\*dif\_temp)

# 230 r\_base = k\_base\*EXP((-eapp\_base/8.314e-3)\*dif\_temp)\*(hplus^n\_base)

# 240 r\_all = r\_acid+r\_neut+r\_base

# 250 rate = (a0/v)\*(M/M0)^0.67\*r\_all\*(1-SR("Illite"))

# 260 moles = rate\*TIME

# 270 SAVE moles

# -end

Chlorite(14A) # Chlorite

-start

10 REM Rate law from Palandri and Kharaka (2004)

20 REM Affinity ON

30 moles = 0

40 IF(M <= 0 OR SI("Chlorite(14A)") > 0) THEN GOTO 270A

50 rssa = PARM(1)

60 r\_conc = PARM(2)

70 wporosity = PARM(3)

80 afrac = PARM(4)

90 a0 = rssa\*r\_conc\*afrac/wporosity

100 v = PARM(5)

110 dif\_temp = 1/TK-1/298.15

120 k\_acid = 10^-11.11

130 eapp\_acid = 88.0

140 n\_acid = 0.5

150 k\_neut = 10^-12.52

160 eapp\_neut = 88

170 k\_base = 10^-21.2

180 eapp\_base = 0

190 n\_base = 0

200 hplus = MOL("H+")

210 r\_acid = k\_acid\*EXP((-eapp\_acid/8.314e-3)\*dif\_temp)\*(hplus^n\_acid)

220 r\_neut = k\_neut\*EXP((-eapp\_neut/8.314e-3)\*dif\_temp)

230 r\_base = k\_base\*EXP((-eapp\_base/8.314e-3)\*dif\_temp)\*(hplus^n\_base)

240 r\_all = r\_acid+r\_neut+r\_base

250 rate = (a0/v)\*(M/M0)^0.67\*r\_all\*(1-SR("Chlorite(14A)"))

260 moles = rate\*TIME

270 SAVE moles

-end

INCREMENTAL\_REACTIONS true

KINETICS 1-4

# Parameters for the minerals

Augite

-formula Ca0.9Mg0.9Na0.1Al0.4Fe0.2Si1.9Ti0.1O6 1

-m 0.26443 # moles per litre pores

-m0 0.26443

-parms 9.226 25 0.14 0.38173 1.0 # Rock specific surface area (m2\_rock/g\_rock); rock conc in soil (g\_rock/L\_soil) # water-filled porosity; mineral area fraction in rock (m2\_minrl/m2\_rock); volume pore water (L)

-tol 1e-008

Plagioclase # labradorite

-formula Ca0.5Na0.5Al1.5Si2.5O8 1

-m 0.16190 # moles per litre pores

-m0 0.16190

-parms 9.226 25 0.14 0.34837 1.0 # Rock specific surface area (m2\_rock/g\_rock); rock conc in soil (g\_rock/L\_soil)

# water-filled porosity; mineral area fraction in rock (m2\_minrl/m2\_rock); volume pore water (L)

-tol 1e-008

Olivine # Forsterite

-formula Mg1.04Fe0.96SiO4 1

-m 0.03656 # moles per litre pores

-m0 0.03656

-parms 9.226 25 0.14 0.08475 1.0 # Rock specific surface area (m2\_rock/g\_rock); rock conc in soil (g\_rock/L\_soil)

# water-filled porosity; mineral area fraction in rock (m2\_minrl/m2\_rock); volume pore water (L)

-tol 1e-008

#illite is excluded as no good thermodynamical data was found and contribution to weathering is expected to be limited

Chlorite(14A) # Chlorite

-formula Mg5Al2Si3O10(OH)8 1

-m 0.01125 # moles per litre pores

-m0 0.01125

-parms 9.226 25 0.14 0.09041 1.0 # Rock specific surface area (m2\_rock/g\_rock); rock conc in soil (g\_rock/L\_soil)

# water-filled porosity; mineral area fraction in rock (m2\_minrl/m2\_rock); volume pore water (L)

-cvode true

-cvode\_order 5

-cvode\_steps 100

TRANSPORT

-cells 20

-shifts 102 # shifts for 5 years

-time\_step 1544667.984 # seconds/cell

-lengths 20\*0.05

-dispersivities 20\*0

-print\_cells 4 # Last basalt-containing cell

-punch\_cells 1-20