

Geochemical modeling of water-rock interactions in granitic rocks, eastern Taiwan

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Abstract

Crystalline rocks such as granite have been considered as potential host rocks of radioactive waste repository. As groundwater flows through fractured-rock aquifers, the water-rock interactions could induce dissolution and precipitation of minerals and change the geochemical, structural, and mineral characteristics of the host rocks. Therefore, study of possible water-rock reaction processes and mechanisms is crucial for suitability evaluation of potential host rocks. The granitic rocks in eastern Taiwan are mainly surrounded by marble, which could be predicted that the groundwater quality (especially pH value) will mainly controlled by carbonate system. In this study, the groundwater and rock compositions in eastern Taiwan were used for reaction-path modeling by 3 scenario cases (shallow open fracture, deep open fracture and deep closed fracture), which can be used to understand the conditions of rock composition and the surrounding water quality, and their chemical changes over time, e.g., the variation of pH and Eh and the formation of secondary minerals. The simulation results show that the calcite and sericite are the major secondary minerals under the final equilibrium state. Besides calcite and sericite, the rest of the main secondary minerals will change gradually from andradite, saponite-Ca to dolomite, nontronite-Na, and dawsonite when the fugacity of carbon dioxide increases. For the fractured-rock aquifers in eastern Taiwan granitic rocks, the simulated pH and Eh ranges (pH = 7.12 to 8.93 and Eh = -0.37 volts to -0.15 volts) should be considered in the sensitivity analysis of the nuclide solubility and/or adsorption characteristics. Compared to the similar simulation results in Taiwan's granitic offshore island (pH = 6.99 to 9.75 and Eh = -0.45 volts to -0.17 volts), it shows that the groundwater characteristics (especially pH value) of granitic rocks in eastern Taiwan are obviously affected by carbonate system and with less pH fluctuations.

1. Introduction

Crystalline rocks such as granite have been considered as suitable host rocks of radioactive waste repository. As groundwater flows through fractured-rock aquifers, the water-rock interactions could induce dissolution and precipitation of minerals and change the geochemical, structural, and mineral characteristics of the host rocks. Therefore, study of possible water-rock reaction processes and mechanisms is crucial for suitability evaluation of potential disposal host rocks.

In Taiwan, granitic rocks are mainly distributed in eastern Taiwan and western offshore islands. The granitic rocks in eastern Taiwan are mainly surrounded by marble. Outcrop and core observations also found fractures in the granitic rocks would be easily filled and sealed by carbonate precipitation (see Fig. 1).

Petrographic analysis of core samples [1] indicated the granitic rock in eastern Taiwan is mainly composed of quartz, plagioclase, biotite, potassium feldspar, and muscovite. Second and accessory minerals include epidote, calcite, chlorite, sphene,

apatite, zircon, garnet, allanite, and opaque minerals (e.g., pyrite and magnetite) [2].

As mentioned previously, the granitic rocks in eastern Taiwan are mainly surrounded by marble, therefore, the groundwater quality (especially, pH value) is expected to be mainly controlled by carbonate system. In other words, pH fluctuations are expected to be small for both surface water and groundwater in this area. Table 1 showed the average water quality of 11 shallow groundwater samples in eastern Taiwan [3], which called SGW_{CGS} in this study. The average temperature and pH of SGW_{CGS} are approximately 23.5°C and 8.1 respectively, and belongs to Ca-HCO₃ type groundwater.

The purpose of this study is to estimate the possible variations of pH and Eh of groundwater in granitic rocks, and the possible secondary minerals formed by water-rock interaction, which should be considered in the sensitivity analysis of the nuclide solubility and/or adsorption characteristics in the safety assessment. Reaction path modeling is used to estimate above possible variations in this study.

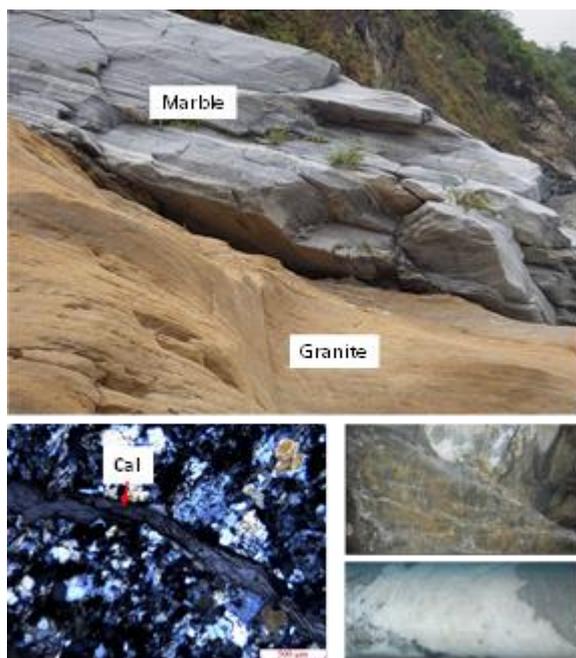


Fig. 1. The geological background of the study area.

Table 1: The average shallow groundwater quality in the study area

Item	unit	SGW _{CGS}
Depth	m	20~100
Temp.	°C	23.5
EC	mS/cm	0.320
pH	*	8.1
Eh	V	0.281
Cl _{tot}	mole/L	1.24E-04
C _{tot}	mole/L	2.82E-03
S _{tot}	mole/L	2.64E-04
N _{tot}	mole/L	1.60E-05
Na _{tot}	mole/L	5.45E-04
K _{tot}	mole/L	3.38E-05
Ca _{tot}	mole/L	9.72E-04
Mg _{tot}	mole/L	3.78E-04
Fe _{tot}	mole/L	7.16E-07
Mn _{tot}	mole/L	9.02E-07
As _{tot}	mole/L	1.84E-07

2. Methods

The GWB (Geochemist's Workbench®, Version 9) [4], a commercial software package, and its thermodynamic database - thermo.com.V8.R6+.dat was used in this study to perform reaction path modeling of 3 different cases (see Fig. 2). The purpose and assumptions of each case were listed in the Table 2. Some common assumptions for the simplicity reason were as follows:

- The initial rock compositions were assumed to be the same for all locations before weathering. The minerals of a fresh core sample (sampling depth = 499 m to 500 m) was used as the initial rock composition. According to petrographic analysis, it is mainly composed of quartz (30 vol.%), K-

feldspar (20 vol.%), plagioclase (20 vol.%), biotite (10 vol.%), muscovite (10 vol.%), calcite (4 vol.%), epidote (5 vol.%) and opaque minerals (1 vol.%). Due to the different ways of naming or the lack of thermodynamic information, the mineral name must be properly classified or assumed based on the thermodynamics database of the software before modeling. In this study, K-feldspar is represented by microcline. Plagioclase is assumed to be composed of 85% albite and 21% anorthite [5]. Biotite is assumed to be composed of 60% annite and 40% phlogopite [5].

- The initial deep groundwater compositions were assumed to be the same for all locations. The groundwater property of DGW_b (= DGW_a @ t = 0, DGW_a = SGW_{CGS} equilibrate with calcite @ T = 32.6 °C) was used as the initial deep groundwater composition, and the 32.6 °C is a hypothetical temperature based on geophysical well logging at 500 m depth [6].
- The initial shallow groundwater compositions were assumed to be the same for all locations. The groundwater property of SGW_b (= SGW_a @ t = 0, SGW_a = SGW_{CGS} equilibrate with calcite @ T = 23.5 °C) was used as the initial shallow groundwater composition.
- The theoretical fugacity values of carbon dioxide and oxygen of the initial deep and shallow groundwater were assumed equal to their partial pressure (P_{CO₂} and P_{O₂}), and estimated by GWB in this study.

Theoretically, there could be many different paths (processes) between any two different thermodynamic (equilibrium) states. One of these (reaction) paths, the reasonable one, must involve the formation of those secondary minerals found in the weathering rock samples. This provide a chance to constrain a reasonable reaction path.

In reaction path modeling, especially for natural reaction systems, it is impossible to calculate the reaction rates of all possible reactions by kinetic approaches because of the kinetic information is very limited in reality, and the numerical calculation will be a big challenge if there are huge difference in numerical values of reaction rates for reactions occurred at same time. By coupling kinetic and equilibrium approaches, the GWB can simulate the reaction path and express results as a function of reaction time. In this study, our interested timescale is up to million years in order to understand the long-term chemical evolution for the concerns of deep geological disposal of radioactive waste, therefore, only the precipitation and dissolution reactions of the initial rock composition (except calcite) were treated by kinetic approach, and the mathematical functions and their associated parameters compiled by Palandri and Kharaka [7] were used to describe their reaction

rates. The rest of all possible chemical reactions, including the precipitation and dissolution of the rest minerals, ion association reactions in aqueous phase, etc., were treated by equilibrium approach.

3. Results

The variations of pH and Eh as function of reaction progress during the reaction path modeling of our study cases were shown in Fig. 3 to Fig. 5. Among them, the higher pH value (10.31) in the deep closed fracture scenario (case1) is due to the gradual depletion of CO₂ in the reaction system. On the other hands, the lower pH value (7.12) in the open fracture scenario (case4) is caused by the higher CO₂ value (equal to the CO₂ partial pressure in the soil layer).

In addition, the case2 and case4 were designed to understand the chemical evolutions of groundwater in deep and shallow open fractures, the simulated pH and Eh ranges of these two cases (pH = 7.12 to 8.93 and Eh = -0.37 volts to -0.15 volts) could be used to constraint the possible pH and Eh ranges in the water conductive features in our study area. Compared to the similar simulation results in Taiwan's granitic offshore island (pH = 6.99 to 9.75 and Eh = -0.45 volts to -0.17 volts) [8], it shows that the groundwater characteristics (especially pH value) of granitic rocks in eastern Taiwan is obviously affected by carbonate system and with less pH fluctuations. As for Eh variation, there is no obvious difference between them.

Fig. 6 to Fig. 8 showed the variations of mineral phases as function of time during the reaction path modeling of our study cases. In these figures, the gray lines represent the initial reactants (minerals), such as quartz, microcline, anorthite, albite, annite, phlogopite, muscovite, epidote and calcite. The other colors represent secondary minerals that occur or disappear with the time during the reaction path modeling:

- Case1 (deep closed fracture): In the absence of continuous supply of CO₂, the minerals such as calcite, muscovite group (i.e., sericite), andradite and saponite-Ca are the major secondary minerals in the final equilibrium state.
- Case2 (deep open fracture): When the supply of CO₂ is continuous, the minerals such as calcite, dolomite, nontronite-Na and muscovite group (i.e., sericite) are the major secondary minerals in the final equilibrium state.
- Case4 (shallow open fracture): When CO₂ content is higher and the supply of CO₂ is continuous, the minerals such as quartz, dawsonite, calcite, dolomite, nontronite-Na and muscovite group (i.e., sericite) are the major secondary minerals in the final equilibrium state.

Overall, the simulation results of 3 cases show that calcite and muscovite group (i.e., sericite) are the major secondary minerals in the final equilibrium state. Besides calcite and muscovite group (i.e., sericite), the

rest of the main secondary minerals will change gradually from andradite, saponite-Ca to dolomite, nontronite-Na, dawsonite when the amount of CO₂ increase, which could be related to the increase in the amount of albite dissolved.

4. Conclusions

The following important conclusions were drawn:

- The calcite and sericite are the major secondary minerals in the final equilibrium state in this study.
- For the fractured-rock aquifers in eastern Taiwan granitic rocks, the simulated pH and Eh ranges (pH = 7.12 to 8.93 and Eh = -0.37 volts to -0.15 volts) should be considered in the sensitivity analysis of the nuclide solubility and/or adsorption characteristics.
- Compared to the similar simulation results in Taiwan's granitic offshore island (pH = 6.99 to 9.75 and Eh = -0.45 volts to -0.17 volts), it shows that the groundwater characteristics (especially pH value) of granitic rocks in eastern Taiwan are obviously affected by carbonate system and with less pH fluctuations.

ACKNOWLEDGEMENTS

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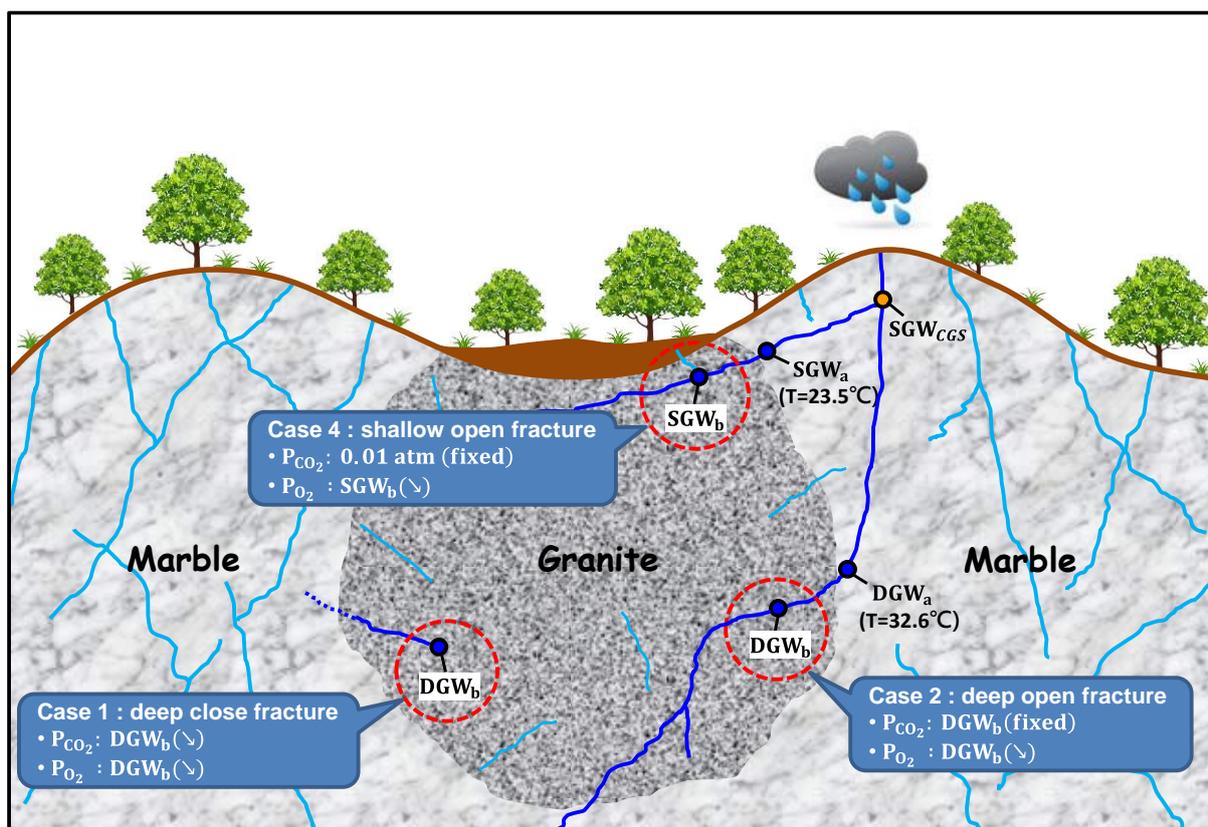


Fig. 2. Illustration of simulation cases used in this study

Table 2: Purpose and assumptions of simulation cases used in this study

Case ID & name	Purpose	Major Assumptions	
		Initial condition	Boundary condition
Deep close fracture (case 1)	To estimate the final equilibrium state (chemical condition) in a deep and well isolated environment.	<ul style="list-style-type: none"> The initial rock composition = H-20 The initial groundwater composition = DGW_b ($=DGW_a$ @ $t = 0$) The initial value of P_{CO_2} = eq. with DGW_b The initial value of P_{O_2} = eq. with DGW_b 	No mass transfer and no energy transfer across the system boundary
Deep open fracture (case 2)	To estimate the possible chemical condition in the water conductive fracture at the expected disposal depth.	<ul style="list-style-type: none"> The initial rock composition = H-20 The initial groundwater composition = DGW_b ($=DGW_a$ @ $t = 0$) The initial value of P_{O_2} = eq. with DGW_b 	The value of P_{CO_2} = constant = eq. with DGW_b
Shallow open fracture (case 4)	To estimate the possible chemical condition in the water conductive fracture at the shallow depth.	<ul style="list-style-type: none"> The initial rock composition = H-20 The initial groundwater composition = SGW_b ($=SGW_a$ @ $t = 0$) The initial value of P_{O_2} = eq. with SGW_b 	The value of P_{CO_2} = constant = 0.01 atm (eq. with soil)

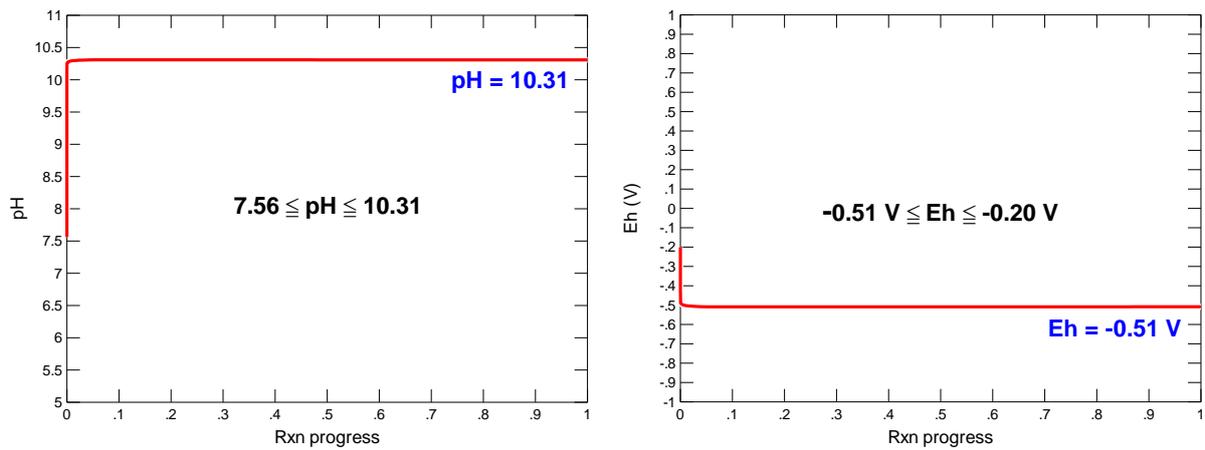


Fig. 3: The simulated pH and Eh as function of reaction progress (case 1)

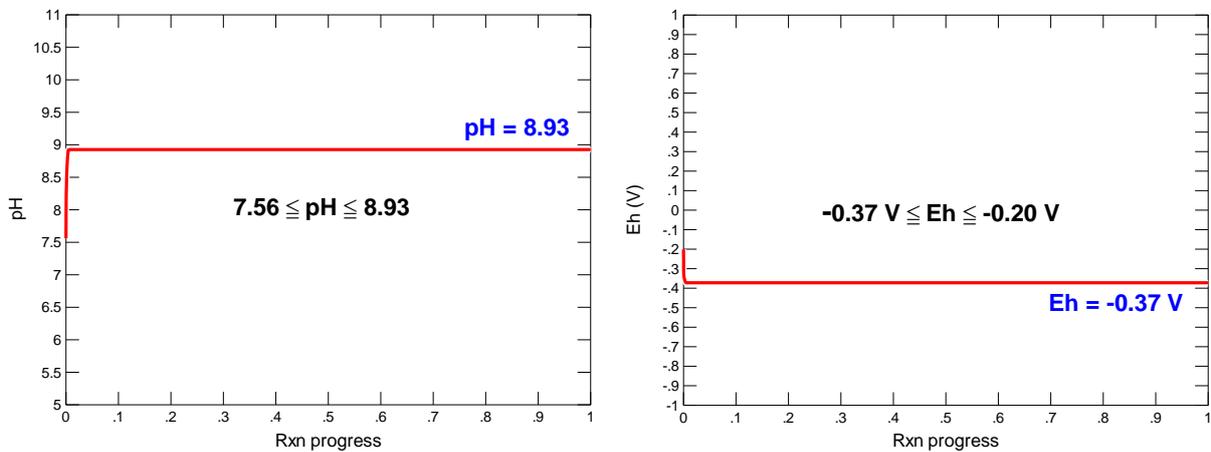


Fig. 4: The simulated pH and Eh as function of reaction progress (case 2)

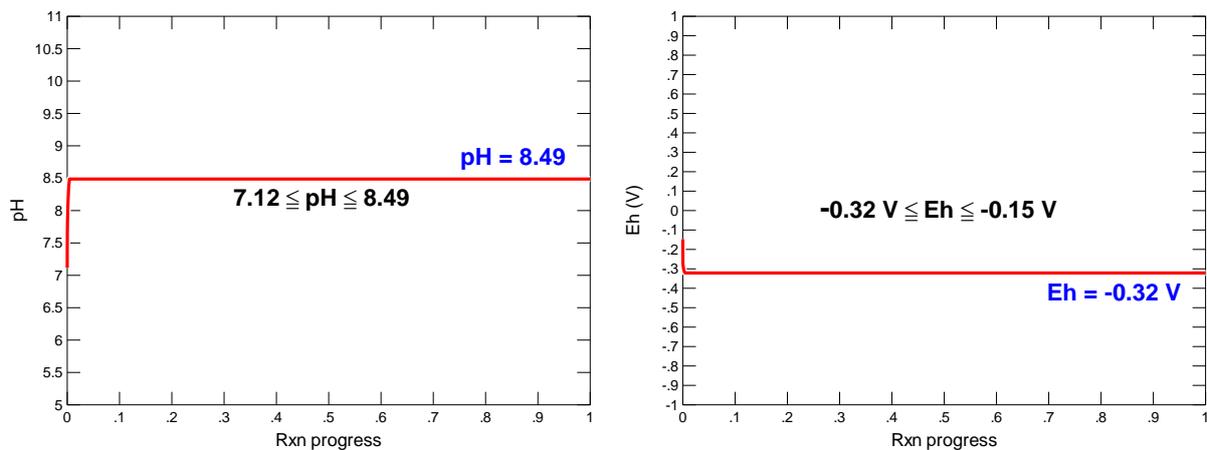


Fig. 5: The simulated pH and Eh as function of reaction progress (case 4)

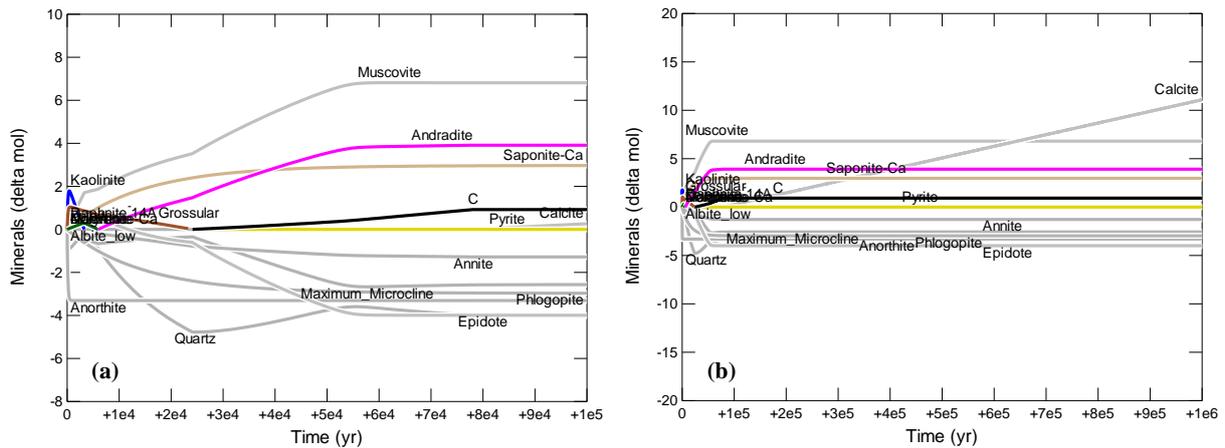


Fig. 6: The simulated mineral phase assemblage as function of reaction time (case 1)

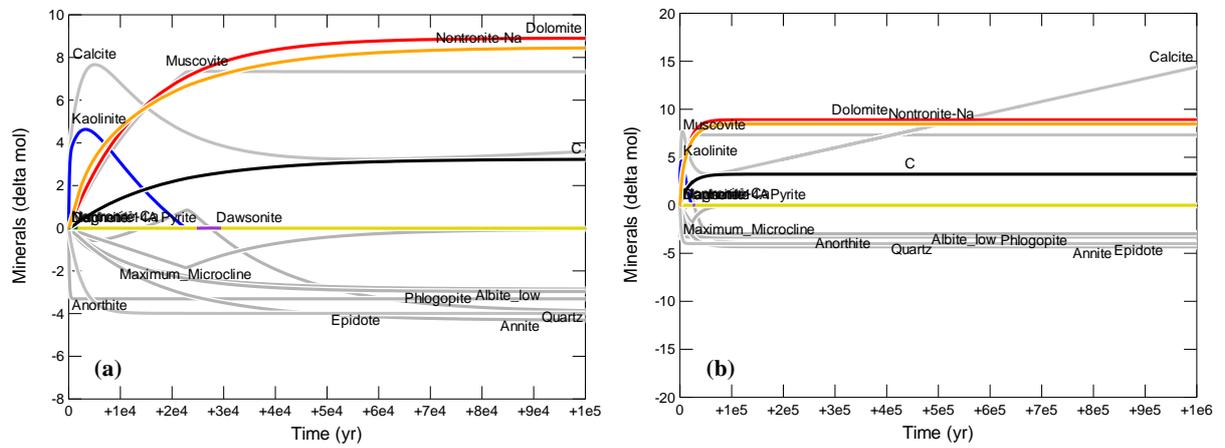


Fig. 7: The simulated mineral phase assemblage as function of reaction time (case 2)

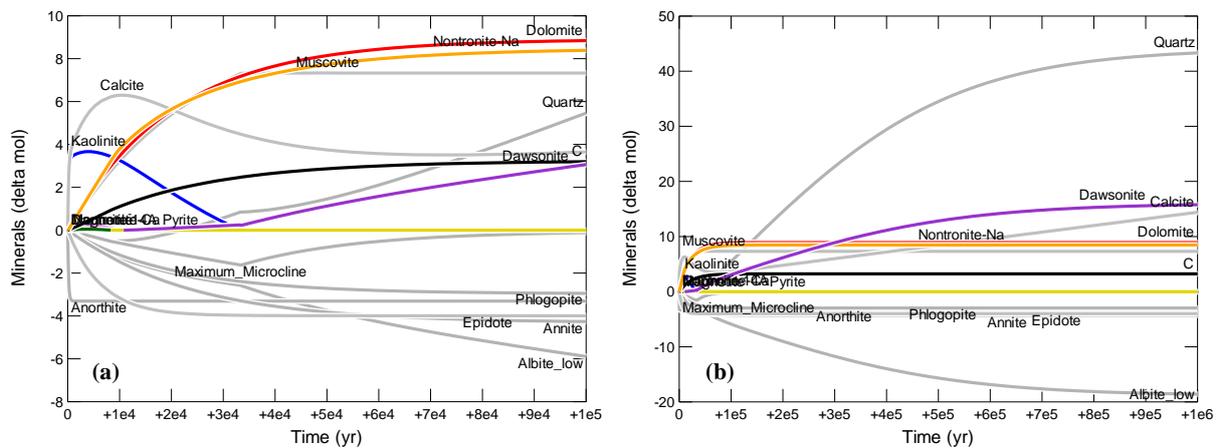


Fig. 8: The simulated mineral phase assemblage as function of reaction time (case 4)