# CO$_2$ mineralization by olivine at hydrothermal conditions

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## ABSTRACT

The interaction of CO$_2$-rich water with olivine was studied using geochemical reaction modelling in order to gain insight into the effects of temperature, acid supply (CO$_2$) and extent of reaction on the secondary mineralogy, water chemistry and mass transfer. Olivine (Fo93) was dissolved at 150 and 250ºC and $p$CO$_2$ of 2 and 20 bar in a closed system and an open system with secondary minerals allowed to precipitate. The progressive water–rock interaction resulted in increased solution pH, with gradual carbonate formation starting at pH 5 and various Mg-OH and Mg-Si minerals becoming dominant at pH>8. The major factor determining olivine alteration is the pH of the water. In turn, the pH value is determined by acid supply, reaction progress and temperature.

## Introduction

Carbonate mineral scaling is commonly associated with geothermal fluid utilization, both in the reservoir as well as in production and re-injection wells and surface pipelines (Gunnlaugsson 2012; Gunnlaugsson *et al.*, 2014). Understanding the CO$_2$−water−rock interaction at geothermal conditions is therefore important in terms of geothermal utilization. Olivine is a major constituent of mafic rocks and commonly associated with geothermal systems. Moreover, it contains a limited number of main elements (Mg, Fe$^{2+}$, Si and O) and may serve as a suitable system to demonstrate and test geochemical reaction modelling with observations from experiments.

A number of studies have focused on CO$_2$−water−rock interaction by geochemical modelling and laboratory experiments. Under geothermal conditions these include, for example, forsterite dissolution and magnesite formation (Giammar *et al.*, 2005) and CO$_2$–water–basalt interaction (Gysi and Stefánsson, 2011, 2012*a,b,c*; Galeczka *et al.*, 2014). Most of these studies have implemented relatively simple models though some recent work has tried to include a fully kinetic approach (Hellevang *et al.*, 2013).

The aim of the present study was to examine the interaction of CO$_2$-rich water with olivine under hydrothermal conditions using geochemical reaction modelling, in particular, to investigate the effects of acid supply, reaction progress ($\xi$) on the overall reaction path and the rate of mass transfer.

## Model calculations

Reaction-path simulations were carried out at 150−250ºC in order to study the effects of temperature, CO$_2$ supply, extent of reaction, and time on the CO$_2$−water−olivine alteration process (geochemical system with CO$_2$-H$_2$O-MgO-FeO-SiO$_2$ chemical components). The calculations were carried out using the *PHREEQC* geochemical program, version 2.18,

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(Parkhurst and Appelo, 1999) and the Wateq database with updates listed below. The reaction-path calculations were carried out on the interaction between forsterite (Fo93) and solutions of variable $CO_2$ concentration. The initial solution contained 10 to 200 mmol kg$^{-1}$ of dissolved $CO_2$ ($pCO_2 = \sim 2$ and $\sim 20$ bar), the solutions were titrated stepwise with 1.378 mol of olivine (200 mg olivine) and the reaction progress was followed. Two types of calculations were used: closed (limited $CO_2$) and open (unlimited $CO_2$) systems. In the present study, the moles of progressively dissolved olivine per kilogram of solution were taken to represent the reaction progress ($\xi$) of the system. In the calculation, secondary mineral precipitation reactions were assumed to be controlled by instantaneous equilibration upon saturation in solution. The secondary minerals considered include goethite (FeOOH), talc ($Mg_3Si_4O_{10}(OH)_2$), chrysotile ($Mg_3Si_2O_5(OH)_4$), antigorite ($Mg_{48}Si_{34}O_{85}(OH)_{62}$), chlorite-Al free ($Mg_6Si_4O_{10}(OH)_8$), anthophyllite ($Mg_7Si_8O_{22}(OH)_2$), brucite ($Mg(OH)_2$), magnesite ($MgCO_3$), siderite ($FeCO_3$) and Fe-Mg carbonates ($Mg_{0.25}Fe_{0.75}CO_3$, $Mg_{0.5}Fe_{0.5}CO_3$,

$Mg_{0.75}Fe_{0.25}CO_3$). These mineral solubilities and the appropriate $CO_2$-aqueous speciation dataset were updated in the present work using recent literature data (Palmer and Wesolowski, 1997; Holland and Powell, 2011; Gysi and Stefánsson, 2011; Stefánsson *et al.*, 2013; 2014). The mass exchanges in the system were assumed to be controlled by the rate of olivine dissolution, the rate expression taken from Rimstidt *et al.* (2012).

### $CO_2$−olivine interaction

Initially the solution pH was between 3.8 and 4.2 at 150ºC, depending on $pCO_2$. Upon progressive $CO_2$−water−rock interaction, the pH increased due to consumption of H$^+$ upon olivine dissolution. At first, the pH was buffered at ~6 by the ionization of carbonic acid and formation of talc, carbonates and either chlorite or chrysotile. Such mildly acid to neutral conditions are characterized either by high initial acid supply and low to moderate extent of the reaction or a low acid supply and low extent of reaction. When most of the $CO_2$ has been mineralized, the pH rises rapidly to >8 and is buffered by the coexistence of brucite, carbonates and either chlorite or
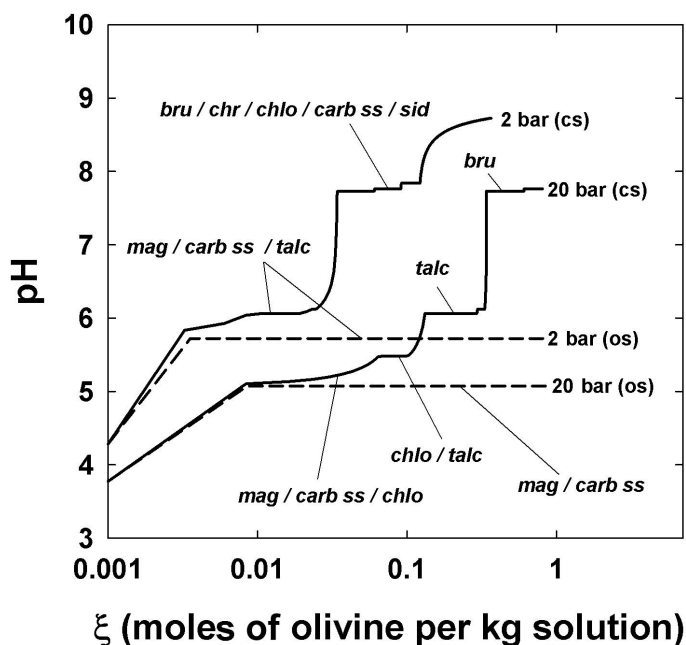


FIG. 1. Changes in pH upon reaction progress ($\xi$) at $pCO_2 = 2-20$ bar for open (os) and closed systems (cs) at 150ºC. Indication of the minerals when pH is buffered is included on the diagram also. Mineral abbreviations: bru − brucite, carb − carbonates, chlo − chlorite, chr − chrysotile, mag − magnesite, sid − siderite.
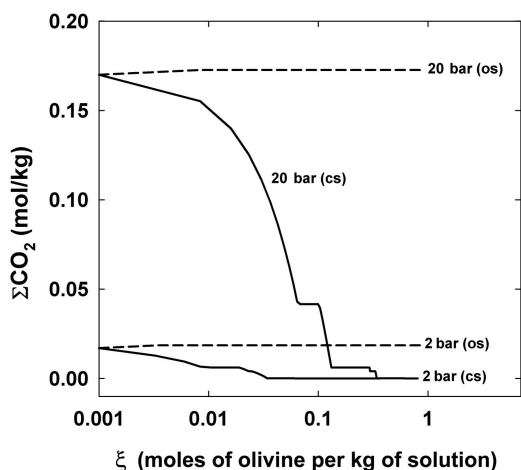
FIG. 2. The concentration of $\Sigma CO_2$ (sum of $CO_2$ aqueous speciation) in solution as a function of reaction progress ($\xi$) at 150ºC for open (os) and closed (cs) systems.

chrysotile (Figs 1, 2 and 3). This results in decreased mobility and concentrations of Mg and Si in solution. Consequently, the carbonates were found to become increasingly more Fe rich upon reaction progress and increased pH (Fig. 3). Insignificant amounts of olivine are needed at low initial $CO_2$ concentration to increase the pH to alkaline conditions. With increasing initial $CO_2$ concentration, more olivine dissolution is needed to increase the pH of the water.

For open systems with unlimited $CO_2$ supply the pH is buffered at 5−5.7, depending on $pCO_2$ (Fig. 1), upon dissolution of a limited amount of olivine and consequent precipitation of talc and a solid solution of Mg-Fe carbonates (Figs 1, 3). With increasing reaction progress, pH remains fixed at such comparatively low values by mineral-solution equilibria due to the continuous supply of $CO_2$ which triggers further dissolution of olivine accompanied by precipitation of talc
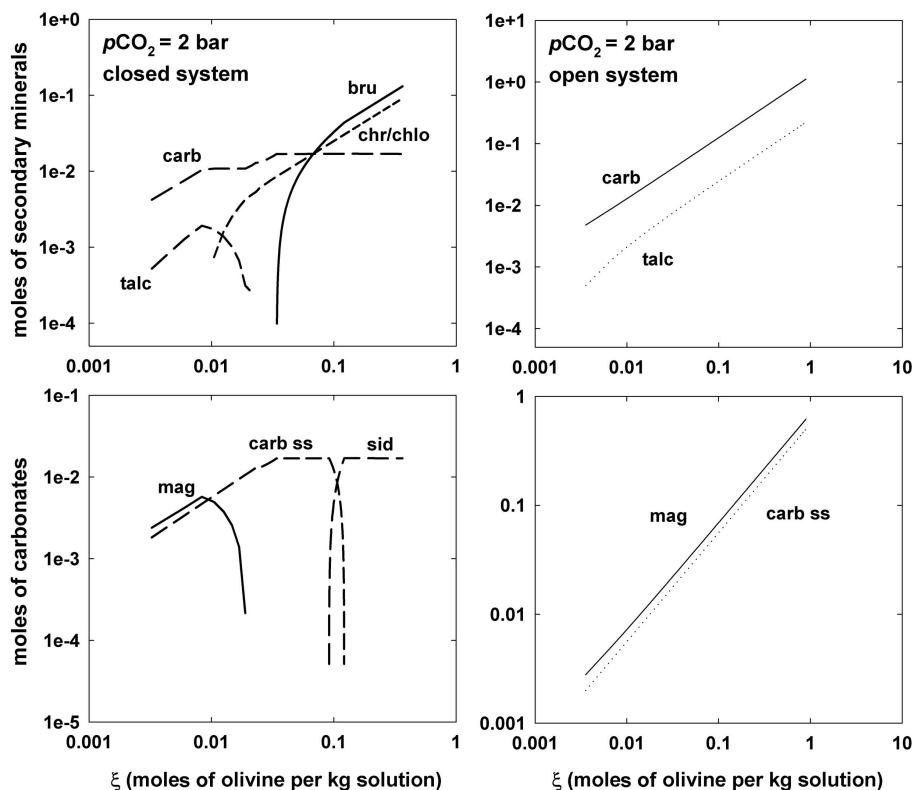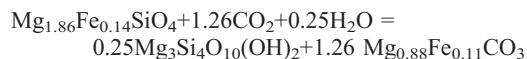


FIG. 3. The moles of secondary minerals formed as a function of reaction progress at $pCO_2$ = 2 bar and for open (os) and closed (cs) systems at 150ºC. Mineral abbreviations: bru − brucite, carb − carbonates, carb ss − carbonate solid solutions, mag − magnesite, sid − siderite.

1475

and carbonates as indicated schematically by the reaction:

$$Mg_{1.86}Fe_{0.14}SiO_4 + 1.26CO_2 + 0.25H_2O =$$
$$0.25Mg_3Si_4O_{10}(OH)_2 + 1.26\ Mg_{0.88}Fe_{0.11}CO_3$$

In other words, a steady state is attained, with constant composition of both the aqueous solution and the carbonate solid solution as well as a constant ratio between the masses of precipitating secondary minerals.

Based on this, one can conclude that the very fine variations in pH at a particular temperature constitute the dominant parameter in determining secondary-mineral composition. In turn, pH is controlled by acid supply, partial pressure and extent of reaction.

The rate of olivine dissolution and overall mass transfer is also related to the pH of the solution as well as the temperature (Figs 1, 4). The dissolution rate of olivine decreases with increasing pH. It follows that progressive $CO_2$–water–olivine interaction result in decreased olivine dissolution rate and the overall mass transfer within the system. On the other hand, increased temperature increases the dissolution rate and the overall mass movement of the system. However, temperature does not have a

significant influence on the overall reaction path with carbonates predominant at pH<7 and Mg-Si and Mg-OH minerals at pH>8.

The variety of conditions presented and their effect on olivine alteration represent theoretical scenarios, reaction paths, for natural fluid−rock interactions at geothermal conditions.

## Conclusions

The interaction of $CO_2$-rich water with olivine under hydrothermal conditions (150 and 250ºC) was studied using geochemical modelling. In particular, the effects of acid supply and reaction progress on the overall reaction path as well as rate of mass exchanges within the system under consideration were investigated. The progressive water−rock interaction resulted in increased solution pH, with carbonate formation starting at pH 5 and various Mg-OH and Mg-Si minerals becoming predominant under alkaline conditions. As a result, the carbonates were Mg-rich at mildly acid conditions but became increasingly Fe-rich with increasing pH. The major factor determining olivine alteration is the pH of the water. In turn, the pH value is determined by acid supply, reaction progress and temperature.
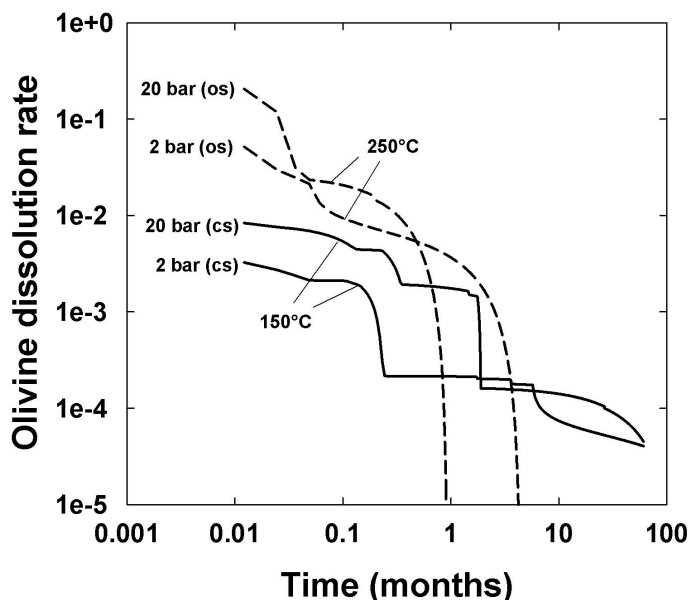


FIG. 4. The dissolution rate of olivine (Rimstidt et al., 2012) as a function of reaction progress in time at 150ºC and 250ºC and $pCO_2$ = 2 and 20 bar for open (os) and closed systems (cs). As observed, mass movement is influenced by pH as well as temperature. In turn, the pH is affected by the reaction progress and initial $CO_2$ concentration.

## Acknowledgements

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