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Dissolution kinetics of fosteritic olivine at 90–150 °C including effects of the presence of CO_2

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Abstract

The steady state dissolution rate of San Carlos olivine [$Mg_{1.82}Fe_{0.18}SiO_4$] in dilute aqueous solutions was measured at 90, 120, and 150 °C and pH ranging from 2 to 12.5. Dissolution experiments were performed in a stirred flow-through reactor, under either a nitrogen or carbon dioxide atmosphere at pressures between 15 and 180 bar. Low pH values were achieved either by adding HCl to the solution or by pressurising the reactor with CO_2, whereas high pH values were achieved by adding LiOH. Dissolution was stoichiometric for almost all experiments except for a brief start-up period. At all three temperatures, the dissolution rate decreases with increasing pH at acidic to neutral conditions with a slope of close to 0.5; by regressing all data for $2 \leqslant \text{pH} \leqslant 8.5$ and $90\,°\text{C} \leqslant T \leqslant 150\,°\text{C}$ together, the following correlation for the dissolution rate in CO_2-free solutions is obtained:

$$r = Aa_{\text{H}^+}^{n} \exp\left(\frac{-E_\text{a}}{RT}\right)$$

with $A = 0.0854$ (+0.67 to −0.076), the activation energy $E_\text{a} = 52.9 \pm 6.9\ \text{kJ mol}^{-1}\,\text{K}^{-1}$, $n = 0.46 \pm 0.03$ ($R^2 = 0.98$) and r in [$\text{mol cm}^{-2}\,\text{s}^{-1}$], based on a 95% confidence interval. Data were fitted to a shrinking particle model, being based on the assumption of surface controlled dissolution throughout the whole experiment, with dissolution extent varying from less than 1% up to complete dissolution, depending on the experimental conditions. In the presence of CO_2 and at low pH, dissolution rates exhibited the same behaviour as a function of pH, however at pH > 5 the rate decreased much more rapidly with pH than in the presence of N_2. The presence of citric acid, an organic ligand, increased dissolution rates in respect to the baseline HCl solution significantly.

1. Introduction

The dissolution and reactivity of silicate minerals on the Earth's surface have proceeded throughout geological time in response to and in concert with changes in atmospheric chemistry and geophysical phenomena as manifested by global tectonics. The interaction of natural waters with silicate minerals plays an important role in the global carbon cycle and, in particular, the release of magnesium and calcium during silicate mineral dissolution comprises an important aspect of the global sequestration of atmospheric CO_2. In addition, magnesium silicate dissolution and hydrolysis equilibria play a fundamental role in defining important aspects of the chemistry of seafloor hydrothermal systems and the alteration of oceanic crust. However, the kinetics of all the relevant heterogeneous mineral equilibria are essentially unknown under hydrothermal conditions.

The aim of this study is to provide kinetic data for the dissolution of olivine at elevated temperature and under high CO_2 pressure and to study effects of solution composition. The dissolution of olivine, and that of other silicates like serpentine, is one of the main rate-limiting steps of mineral carbonation, a novel technology which strives to store anthropogenically generated CO_2 in solid Mg- and

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Ca-carbonates. It involves the dissolution of Mg- and Ca-rich silicates in aqueous solutions, at high temperatures and under high CO_2 pressure, followed by the precipitation of carbonates. The idea of mineral carbonation was first developed by Lackner et al. (1995) and is part of a portfolio of different carbon dioxide capture and storage (CCS) technologies, intended to reduce human-induced carbon dioxide emissions into the atmosphere (IPCC, 2005).

Dissolution kinetics for olivine and serpentine, the two main source minerals for mineral carbonation, have been studied for several decades; especially, olivine has attracted noticeable interest, mainly due to its structural simplicity and high reactivity (Wogelius and Walther, 1991; Chen and Brantley, 2000; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Oelkers, 2001). However, almost all studies were conducted at temperatures between 25 and 65 °C and at ambient pressure (see overview by Rosso and Rimstidt, 2000), whereas the optimal reaction temperatures for the process of mineral carbonation have been found to be between 150 and 200 °C and at CO_2 pressures of up to 250 bar (O'Connor et al., 2004). In addition, the presence of CO_2, a major factor in the carbonation results reported so far, has only been looked at in a few cases (Pokrovsky and Schott, 2000). Other factors, like the effect of ligands have only been studied at ambient temperature (Grandstaff, 1986; Wogelius and Walther, 1991).

It has been recognised in the literature that dissolution rates of silicates are typically reproducible to within ± 0.25 log units within one laboratory and to within two orders of magnitude among different laboratories, which illustrates the difficulties one faces in comparing reported dissolution rates (Kump et al., 2000). These differences stem both from the varying properties of natural minerals and from experimental difficulties, e.g., very low aqueous concentrations.

In the following, we report dissolution rates of olivine at 90, 120, and 150 °C, the effect of CO_2 and citric acid, and discuss these results in comparison with previous studies.

2. Dissolution of olivine

2.1. General dissolution kinetics

The dissolution rate of olivine exhibits a marked dependence on the solution pH, as it has been noted with other silicate minerals. This dependence represents a trend that is independent of the absolute value of the dissolution rate, and is based upon a quite large dataset. At acid to neutral conditions and ambient temperature, the exponent, n, in the relationship $r \propto a_{\mathrm{H}^+}^n$ has been found in many dissolution studies to be close to 0.5 over the range of pH 2–6, with r being the dissolution rate and a_{H^+} the hydrogen ion activity. At basic conditions, the trend is less clear and only few results have been published; however, they indicate that the dissolution rate is no longer a function of pH above pH 7–8. An overview of previous studies of olivine dissolution is given in Table 1, listing the conditions under which experiments were carried out and the reported values for the dissolution rate, pH dependence, and activation energy.

Two different reaction mechanisms have been proposed by Pokrovsky and Schott (2000), a first one governing the dissolution at pH lower than 7, being pH dependent, and a second one becoming dominant at pH higher than 8 and exhibiting no pH dependence. The first mechanism involves the adsorption of one H^+ ion onto two elemental cells of olivine, resulting in the cited pH dependence. This is accompanied by the extraction of Mg^{2+} ions and the formation of a very thin Mg-depleted layer on the surface. The second mechanism is based upon the formation of $\mathrm{MgOH_2}^+$ surface groups, which form after the extraction of SiO_2, whose concentration determines the dissolution rate, and whose formation and detachment is independent of pH, thus explaining the independence of the dissolution rate of pH. A thin Si-depleted surface layer is formed under these conditions (Pokrovsky and Schott, 2000). There is no clear agreement about whether the pH dependence changes with increasing temperatures, with two studies reporting no change with temperature, and two others finding values for n between 0.33 and 0.7 at higher temperatures (see Table 1).

Another quantity, the activation energy, is less well estimated, with reported values varying between 25 and 125 kJ/mol. This range can be narrowed, however, as a more detailed discussion will show later.

Under the assumption that the pH dependence is independent of temperature, the following correlation can be used to describe dissolution rates:

$$r = A a_{\mathrm{H}^+}^n \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{1}$$

with r being the dissolution rate [mol cm^{-2} s^{-1}], A a pre-exponential factor [mol cm^{-2} s^{-1}], E_a the activation energy [kJ mol^{-1}], T the temperature [K], $R = 8.3145$ kJ mol^{-1} K^{-1} the gas constant, a_{H^+} the hydrogen ion activity [$-$], and n the reaction order with respect to H^+.

If one wants to account for a change in pH dependence with temperature—for which non-consistent results have been reported—it is either necessary to find a correlation for n with temperature, or to calculate a pH-dependent activation energy, leading to the following expression:

$$r = B \exp\left(\frac{-E_\mathrm{a}^*}{RT}\right) \tag{2}$$

where B is a pH-dependent pre-exponential factor [mol cm^{-2} s^{-1}], and E_a^* the pH-dependent activation energy. E_a^* for pH 0 is equal to the standard pH-independent activation energy. This approach has only been implemented by Chen and Brantley (2000), combining their own results with those of other groups.

Dissolution rates are usually expressed in moles per unit area per unit time, with the effective surface area being