

Oxalate-Promoted Dissolution of Chrysotile

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INTRODUCTION

The use of asbestos is currently banned or restricted because of its carcinogenic potential. However, their intensive use in the past due to their properties as insulator and its mechanical resistance has created many abandoned industrial and mining sites, which represent an environmental risk. About 95% of the asbestos used worldwide is the chrysotile variety of serpentine. Despite the growing interest of geochemical data in the fields of medical geology or environmental remediation, few studies have assessed the dissolution kinetics and the effect of weathering of these minerals in the laboratory and field.

On the other hand, the role of organic acids presents in soils in enhancing chemical weathering rates have been recognized for decades. Many studies show that polyfunctional acids such as oxalic and citric enhance silicate dissolution to a greater degree than monofunctional acids such as acetate (Huang and Kiang, 1972; Franklin et al., 1994). The study of chrysotile dissolution in presence of oxalic acid started early (e.g. Thomassin et al. 1977) and more recently Gualteri et al. (2008) and Turci et al. (2010) pointed out that oxalic acid can be used to transform chrysotile into a non-hazardous crystalline phase. The objective of this study is to investigate and quantify the catalytic effect of oxalate in the chrysotile alteration process.

METHODOLOGY

A pure chrysotile phase obtained from Mina Laurel (Málaga, Spain) was used as starting material. Short-term dissolution experiments (30 days) were carried out in batch reactors at 25°C with a solid/solution ratio of 2 g·L⁻¹. Two sets of experiments were performed using inorganic buffered solutions from pH 1-8 (series CrLx) and same solutions

plus 15 mM sodium oxalate (series CrOx). Aliquots were withdrawn from the suspension along time, filtered and analyzed for dissolved Si (by colorimetry) and Mg (by ion chromatography) in order to compare and quantify the alteration process with and without oxalate at different pHs. Moreover oxalate concentration was measured (ion chromatography) in some withdrawals to check for biodegradation. Once the experiments were finished the remaining solids were rinsed, dried and stored for further mineralogical analyses using DRX, FTIR and SEM.

Kinetic Calculations

Dissolution rates (mol/g·s) in batch reactors are usually obtained from the equation:

$$Rate_j = -\frac{1}{V_j} \frac{dC_j}{M dt} \quad (1)$$

where dC_j/dt is fitted by linear regression of the variation of component j concentration (Si or Mg) in the reactive solutions as time progresses, V is the volume of solution, M is the initial mineral mass and v_j stoichiometric coefficient of component j in the mineral formula.

The strong dissolution that chrysotile undergoes in solutions containing oxalate produces an intense drift of the solution pH. The instability of any of the rate controlling parameter (pH) does not allow us to derive dissolution rates at steady-state conditions. In order to compare results with and without oxalate other authors have used the initial rate method (Olsen and Rimstidt, 2008). The initial rate method determines the rate for the beginning of the experiment before any of the rate controlling parameters has changed from the original values. Initial rates have been calculated in both sets of experiments using the slopes from the first 6 days of reaction. The uncertainty

associated is better than 10%. A correction for sample withdrawal was applied in every case.

Saturation Calculations

The saturation state of the solution with respect to solid phases was calculated in terms of free energy of reaction, ΔG_r , from the ion activity product (IAP) using EQ3NR geochemical code (Wolery, 1992). The program was also used to model the capacity of oxalate to form aqueous complexes with Mg.

RESULTS AND DISCUSSION

The results obtained in this study show that chrysotile dissolves in both inorganic and oxalate solutions. As a general trend an initial lineal release of Mg and Si to the solution is observed. As reaction time progresses concentrations tend to stabilize as the solution becomes saturated. Fig. 1 shows the release of Si and Mg in two experiments at pH 4, with and without oxalate. The catalytic effect of oxalate is clear from the beginning of the experiments. The amount of Si and Mg dissolved is until 6-7 times higher in presence of oxalate. Moreover the Mg/Si ratio increases from 1.6 to 3.

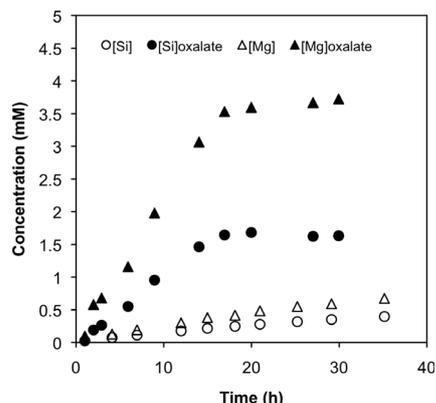


fig. 1 Evolution of Si and Mg released concentration vs time in two representative experiments at pH 4 without oxalate (open symbols) and with oxalate (solid symbols).

palabras clave: Crisotilo, Oxalato, Meteorización, Velocidad de disolución.

key words: Chrysotile, Oxalate, Weathering, Dissolution rate.

Calculated initial rates from Si concentrations are shown in Fig. 2a. In oxalate free solutions dissolution rates decrease with increasing pH, following a linear dependence from pH 1 to 8. EQ3NR calculations show values of $\Delta G_r < 5RT$ in all experiments with and without oxalate. The results also confirm undersaturation respect to chrysotile as well as other mineral phases like brucite or amorphous silica. Consequently, experiments take place under far from equilibrium conditions.

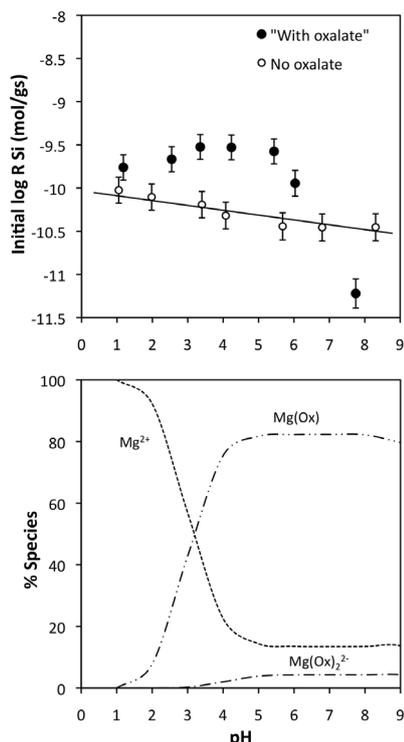


Fig. 2. a) Upper. Experimental initial dissolution rates calculated from [Si] in batch series with and without oxalate versus pH. b) Lower Speciation of Mg-oxalate soluble complexes calculated with EQ3NR.

The dependence of the initial dissolution rate vs pH becomes more complicated in presence of oxalate. At pH 1 the release of Si to the solution is similar with and without oxalate. However the release of Mg is significantly higher in presence of this ligand. XRD and FTIR results show an amorphous siliceous byproduct with a fibrous form observed by SEM. This suggests the complete removal of the brucite sheet from the chrysotile structure, which also was observed by other authors (e.g. Wypych et al., 2005).

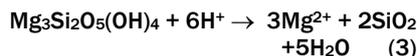
At pH 2 the presence of oxalate during the alteration causes:

- An intense drift on pH from 2 to 6.
- A preferential release of Mg vs Si together with the increase of Mg/Si

ratio 3 times.

- Finally, a decrease in the concentration of oxalate (from 15 to 7mM) is observed.

These three facts suggest that oxalate is able to complex magnesium forming a precipitate and shifting to the right the dissolution reaction:



XRD and FTIR confirm the formation of a new mineral phase of magnesium oxalate (glushinskite).

Between pH 3.6 and 5.4 dissolution rates in presence of oxalate reach a maximum increasing up to 0.8 logarithmic units respect to the oxalate free dissolution rate at the same pH. This could be due to the formation of an aqueous Mg(Ox) complex, which is favored in this pH range as it can be observed in the speciation (Fig. 2b).

Finally, at pH 7.8 dissolution rate decreases from -10.5 to -11.2 in presence of oxalate. Although the formation of the complex Mg(Ox) at this pH is still favored, the decrease of Mg solubility as well as the increase in saturation around neutral pHs causes this drop.

Alteration Mechanism

Based on these results two mechanisms can contribute to the enhancement of chrysotile dissolution rates in oxalate solutions:

The first one is the formation of aqueous Mg-oxalate complexes. This will cause a decrease of the activity of Mg^{2+} . However the design of batch experiments does not allow us to observe significant changes in ΔG_r , and confirm this hypothesis experimentally.

The second hypothesis is a ligand exchange reaction. A nucleophilic attack of an Ox^{2-} anion on the $>\text{MgOH}_2^+$ surface sites to produce the surface complex $>\text{Mg-Ox}$ and H_2O , followed by a fast detachment from the surface. Ox^{2-} anion is the reactive specie, whose catalytic effect is favored at $\text{pH} > 4.2$ (pK_{a2} for oxalic acid). This would explain that at lower pH, where dominant species are hydrogen oxalate and oxalic acid, other mechanisms are present, like the precipitation of glushinskite at pH 2 or the complete dissolution of the brucite sheet at pH 1. These processes need to

be studied in detail as they may have a potential utility in remediation of contaminated sites.

CONCLUSIONS

This study shows that oxalate strongly enhances chrysotile dissolution. This effect depends on pH. Dissolution is non stoichiometric, favoring the release of Mg to the solution. Our results do not allow to confirm the mechanism but suggest that both the formation of aqueous and/or surface Mg(Ox) complexes need to be studied to understand weathering processes and propose remediation plans for contaminated sites.

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