The mechanism of dissolution of forsterite, olivine and minerals of the orthosilicate group

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ABSTRACT

The dissolution of forsterite and other minerals of the olivine and phenakite silicate groups are described by a novel mechanism of dissolution. For many of these minerals, the order of reaction with respect to H^+ is close to 0.5 in the acidic region. The mechanism of dissolution proposed here correctly predicts these orders of reaction without any adjustable parameters. Recent work has shown that the order of reaction of forsterite with respect to H^+ changes from 0.5 in the acidic region to 0.25 in the region above a value of pH of approximately 6. Previously proposed models of dissolution cannot predict this change in order of reaction, whereas the mechanism proposed here does predict this change in reaction order, again without any adjustable parameters. The mechanism proposes that the reason for the change in order of reaction is that the H^+ needs to be positioned at the inner Helmholtz plane to be effective at higher values of pH. The acceleration of the rate of dissolution by organic acids and the retardation of the rate by dissolved silica and carbon dioxide are also correctly predicted. The mechanism predicts a change in the interfacial potential difference at the same value of pH that the order of reaction changes. This prediction is verified by measurements of the zeta potential, which reflects the predicted change in surface potential at a pH of approximately 6. The proposed mechanism provides a framework for the interpretation of the correlation between the rate of dissolution of the orthosilicates and the exchanges rates of water in the inner sphere of the corresponding metal aqua-ion.

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1. Introduction

The olivine group of minerals, which includes the minerals forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), and tephroite (Mn_2SiO_4), has received a lot of recent attention due to their utility for carbon dioxide sequestration and their potential significance for the origin of life (Kump et al., 2000; Kuszuba et al., 2013; Schuiling and Krijgsman, 2006). There is extra-terrestrial interest in the dissolution of olivine, driven by an interest in determining the extent to which the surface of Mars has been weathered by aqueous solutions (Olsen and Rimdstidt, 2007).

The dissolution of the olivine minerals also has industrial significance. Olivine weathering results in the formation of the nickel laterites used as the feed material to a number of hydrometallurgical plants around the world (Crundwell et al., 2011). The dissolution of rock-forming minerals is also important in whole-ore leaching operations, and the consumption of acid by gravel and rock layers of the leaching pad of a heap. Willemite (Zn_2SiO_4), a member of the phenakite group, and zinc-containing tephroite are sources of zinc (Terry and

Monhemius, 1983). The use of olivine to neutralize industrial acid waste has also been proposed (Jonckbloedt, 1998).

The dissolution of minerals is important in a number of scientific fields, such as mineral weathering, geochemistry, materials science, environmental science and hydrometallurgy. Knowledge of the mechanisms of dissolution is a primary goal of these fields. Such knowledge can aid in the design of operations where dissolution or etching is required. It can be used to understand the behaviour of minerals in rocks to weathering patterns, which are important in understanding climate and climate change.

Knowledge of how forsterite and other minerals of the orthosilicate group dissolve might help to develop a generalized mechanism of dissolution of silicates and understand the interactions between rocks, minerals and aqueous solutions on a more fundamental basis. The broad purpose of this study is to provide the framework for a novel mechanism of dissolution that can describe the kinetics of dissolution of orthosilicate minerals. The general aim of this work is to describe the dissolution of forsterite, which has been studied experimentally in significant detail. The results of more than 768 dissolution experiments are analysed in this paper, and it is shown that all of this data can be described by the dissolution theory presented by Crundwell (Accepted for publication, 2014a, 2014b). These experimental results are reviewed next, after which the specific aims of this work are presented.

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1.1. Review of the experimental results for the kinetics of dissolution of orthosilicate minerals

Forsterite and other orthosilicates dissolve in both acidic and alkaline solutions. The overall reaction stoichiometry is given as follows:

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+}(aq) + Si(OH)_4(aq) \qquad (1)$$

The rate of an irreversible dissolution reaction, such as that given in Eq. (1), is usually expressed mathematically in the following form (Crundwell, 2013; Holmes and Crundwell, 2000):

$$rate = k[c]^n \exp(-E_A/RT) \qquad (2)$$

where $[c]$ represents the concentration of a reactant, k the rate constant, n the order of reaction, E_A the activation energy, R the gas constant, and T the temperature.

The order of reaction, n, indicates how the rate of reaction depends on the concentration of the reactant. If the value of n is one and the reactant is H^+, the reaction is said to be first order in H^+. The order of reaction is the key parameter, and it is the goal of chemical kinetics to provide a derivation of the order of reaction based on a proposed mechanism of reaction in which all the individual steps are elementary reactions (Atkins and de Paulo, 2006; Murphy and Helgeson, 1987). In the next section the results for the orders of reaction with respect to H^+ for a wide variety of minerals in the acid region are presented. Following that presentation, more detailed results for forsterite are presented for a wider range of pH, and for the inhibition of the reaction by its products.

1.1.1. Orders of reaction of orthosilicate minerals in the acid region

The orders of reaction with respect to H^+ in the acidic region are given in Table 1. The values given in this table indicate that the order of reaction with respect to H^+ is close to 0.5.

The results given in Table 1 show a remarkable pattern. The activation energies are similar, many of which are between 49 and 62 kJ/mol. This suggests that a similar rate-determining step may control the dissolution for all of these minerals. This is in line with is the observation that the orders of reaction have similar values, that is, close to a value of one half. The two biggest outliers are fayalite and phenakite, with values of 0.69 and 0.3, respectively. However, only a limited number of experiments have been reported orders of reactions with respect to H^+ for fayalite and phenakite, as shown in Fig. 1. If, for example, the only study of forsterite was that of Grandstaff (1986), the order of reaction with respect to H^+ would be reported as 1.0; however, six subsequent studies in which 520 data points were recorded indicates that the order of reaction is between 0.46 and 0.54 in acidic solutions. The point is that the orders of reaction for phenakite and fayalite are probably also close to 0.5.
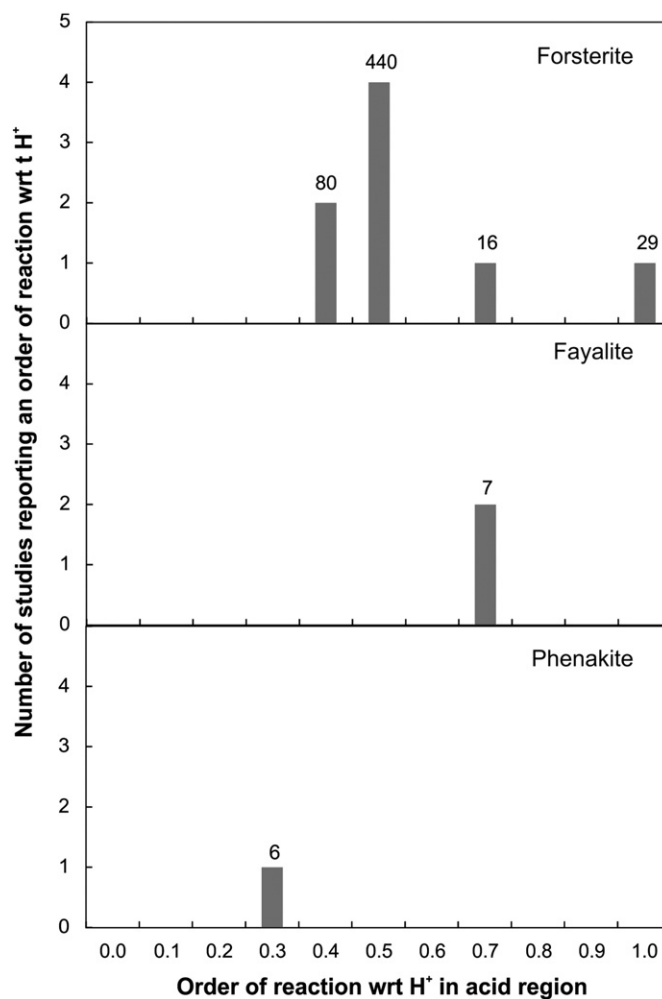

Fig. 1. The frequency of studies as a function of the values of the order of reaction with respect to H^+ in the acidic region reported for each study. Early studies of forsterite contributed significantly to the wide distribution of the reported orders. Few studies have been reported for fayalite and phenakite, which probably explains why the orders of reaction of these two minerals are significantly different from the average for the other orthosilicates.

1.1.2. Orders of reaction for forsterite in acid solutions

The orders of reaction in the acid region at values of the pH less than 4 are shown in Fig. 2 for various temperatures. These results, from Olsen and Rimstidt (2008), show that the order of reaction is independent of temperature and has a value of 0.5.

Table 1
Orders of reaction for the dissolution for the orthosilicate minerals in solutions with a pH value of less than 6.

Mineral	Mineral formula	Structure	Reaction order wrt H^+, n		Activation energy, E_A, kJ/mol	Reference
Forsterite	Mg_2SiO_4	Olivine	0.45 to 0.54	HCl	70.5	Brantley (2008), Westrich et al. (1993), Rimstidt et al. (2012)
Fayalite	Fe_2SiO_4	Olivine	0.69	HCl		Wogelius and Walther (1992), Brantley (2008)
Monticellite	$CaMgSiO_4$	Olivine	0.56	HCl	62	Westrich et al. (1993)
Co-olivine	Co_2SiO_4	Olivine	0.36	HCl	59	Westrich et al. (1993)
Tephroite	Mn_2SiO_4	Olivine	0.47	HCl	56	Westrich et al. (1993); Casey et al. (1993)
Ca-olivine	Ca_2SiO_4	Olivine	0.42	HCl		Westrich et al. (1993)
Co–Mn olivine	$CoMnSiO_4$	Olivine	0.42	HCl	50	Westrich et al. (1993)
Phenakite	Be_2SiO_4	Phenakite	0.3	HCl	59	Casey and Westrich (1992); Westrich et al. (1993)
Willemite	Zn_2SiO_4	Phenakite	0.45	HCl		Terry and Monhemius (1983)
			0.49	H_3PO_4		Terry and Monhemius (1983)
			0.53	H_2SO_4	49	Terry and Monhemius (1983)
			0.38	HNO_3	44.5	Terry and Monhemius (1983)
			0.40	$HClO_4$		Terry and Monhemius (1983)