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Experimental study of the effect of organic ligands on diopside dissolution kinetics

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Abstract

Diopside ($CaMgSi_2O_6$) dissolution rates were measured at 25 °C in a mixed-flow reactor as a function of concentration of nine organic ligands in circumneutral (pH = 5.3–7.0) and basic (pH = 10.4–10.9) solutions. At neutral pH, EDTA, citrate, oxalate, acetate, gluconate and 2,4-DHBA lead to an increase of the diopside dissolution rate. Alginic acids and glucosamine have no detectable effect on the dissolution rate, while the glucuronic acid weakly decreases the diopside dissolution rates. At basic pH, citrate and acetate do not affect the dissolution while the EDTA leads to an increase of the rates in a much smaller degree than at neutral pH. This is consistent with overall negative surface charge of diopside in basic solutions. Ligand-affected rates were rationalized using a phenomenological equation which postulates the Langmurian adsorption of a negatively-charged or neutral ligand on rate-controlling surface sites, presumably $>Mg(Ca)OH_2^+$. This model was qualitatively confirmed by electrophoretic measurements in the presence of organic ligands: a decrease of pH_{IEP} and zeta-potential occurs upon adsorption of ligands on diopside surface.

Results of this study demonstrate that very high concentrations (0.01–0.1 M) of organic ligands, whether they are originated from enzymatic degradation of organic matter, or bacterial metabolic activity are necessary to appreciably affect diopside dissolution. Thus, the effect of natural organic ligands on the weathering of diopside in soil environment is likely to be weak.

Keywords: Diopside; Kinetics; Dissolution; Organic ligands

1. Introduction

The weathering of basic silicates is one of the major processes controlling long-term biogeochemical cycles of carbon and silicon and thus the climate of the earth at the long-term scale (Berner, 1992; Dupré et al., 2003). Knowledge of silicate dissolution mechanisms and kinetics is therefore crucial to rigorously constrain the CO_2 budget at the surface of our planet. Numerous studies have been devoted to the effect of silicates weathering on global temperatures and CO_2 concentration in the atmosphere (e.g. Walker et al., 1981; Berner et al., 1983; Lasaga et al., 985; Volk, 1987; Brady, 1991; Berner, 1995; Brady

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and Gíslason, 1997). These models require reliable information on the dissolution kinetics of Mg and Ca-bearing silicates. Although the effect of pH and pCO_2 on basic silicates dissolution is rather well studied and quantified (Schott et al., 1981; Schott and Berner, 1985; Rimstidt and Dove, 1986; Eggleston et al., 1989; Knauss et al., 1993; Brantley and Chen, 1995; Hoch et al., 1996; Chen and Brantley, 1998; Pokrovsky and Schott, 2000; Oelkers and Gislason, 2001; Oelkers and Schott, 2001; Gíslason and Oelkers, 2003; Golubev et al., 2005) the effect of organic ligands is still poorly understood (Grandstaff, 1977, 1986; Wogelius and Walther, 1991). It has been widely argued (Antweiler and Drever, 1983; Drever, 1994) that the organic ligands should exert much higher effect on dissolution of basic silicates compared to alumosilicates. This somehow contradicts the recent observations of weak adsorption on the surface Mg centers and reactivity effect of organic ligands towards brucite (i.e., Pokrovsky et al., 2005) and Mg-montmorillonite (Golubev et al., 2006) but their strong interaction with aluminum, both at the mineral surface (Stumm, 1997; Kummert and Stumm, 1980) and in aqueous solution (Martell et al., 1997) leading to the strong acceleration of alumosilicates dissolution by dissolved organic ligands (Welch and Ullman, 1993, 1996; Stillings et al., 1996; Oelkers and Schott, 1998). The main obstacle in quantifying the effect of organics on mineral dissolution consists in distinguishing between the influence of pH and that of the dissolved organics. To improve our knowledge on silicate reactivities with respect to naturally-relevant organic ligands, we performed in the present study the measurements of ligands-affected diopside ($CaMgSi_2O_6$) dissolution in which we were able to separate the effect of pH and that of organic ligands using a mixed-flow reactor system.

In addition to carbonic acid and simple carboxylic and aromatic compounds routinely identified in soil solutions (Kaurichev et al., 1963; Whitehead, 1964; Manley and Evans, 1986; Leyval and Berthelin, 1991), microbes can produce extracellular acid and neutral polysaccharides, uronic acids (galacturonic, guloronic), peptides and aminoacids (Ullman et al., 1996; Welch et al., 1999). Mycobionts such as lichens are known to extract various low molecular weight organic carboxylic acids (oxalic, citric, tartaric, gluconic, lactic) and polyphenolic compounds called "lichen acids" (Adamo and Violante, 2000). While the effects of such organic molecules and polymers on alumosilicates dissolution (Huang and Keller, 1970; Huang and Kiang, 1972; Manley and Evans, 1986; Lundström and Ohman, 1990; Ochs et al., 1993; Welch et al., 1999; Welch and Ullman, 1999; Van Hees et al., 2002), or iron mobilization from silicates (Schalscha et al., 1967; White and Yee, 1985; Watteau and Berthelin, 1994; Liermann et al., 2000; Santelli et al., 2001) have been widely described, their interaction with Ca or Mg-bearing silicates is not well characterized.

This work is a part of concerted efforts aimed on the quantitative characterization of physico-chemical factors controlling the reactivity of major Ca and Mg-bearing rock-forming minerals in aqueous solutions at ambient temperatures. In previous works, we assessed the kinetics and mechanisms of olivine Mg_2SiO_4, brucite $Mg(OH)_2$, smectite $(Ca_{0.06}Na_{0.56})[Al_{3.08}Fe(III)_{0.38}Mg_{0.54}]\times[Si_{7.93}Al_{0.07}]O_{20}(OH)_4)$ and wollastonite $CaSiO_3$ dissolution as a function of pH and concentration of various organic and inorganic ligands, notably dissolved carbonate (Pokrovsky and Schott, 2001; Golubev et al., 2004; Pokrovsky et al., 2004, 2005; Golubev et al., 2006). In these studies the influence of various organic ligands on Mg- and Ca-bearing minerals dissolution has been modeled using a surface adsorption concept and mineral dissolution promoting via hydrolysis of Me–O bonds influenced by the adsorbed ligand. It has been demonstrated that for all studied minerals, very high concentrations of naturally-relevant organic substances (0.01–0.1 M) are necessary to appreciably affect the mineral dissolution rate. Because such concentrations are unlikely to be encountered in natural settings (Hue et al., 1986; Hongve et al., 2000), it has been suggested that the effect of extracellular organic products on the weathering rate of Ca-, Mg-bearing minerals is expected to be weak. The question remains how far this conclusion can be extended to other alkali-earth bearing minerals composing the crystalline basic silicate rocks, most susceptible to chemical weathering. The main goal of the present study, therefore, is to use diopside as a model to study the effect of naturally-occurring organic ligands and chemical analogues of bacterial metabolites and cell envelopes on all Ca,Mg-bearing silicates in aqueous solutions.

2. Materials and methods

2.1. Mineral samples

Natural crystals of diopside (Transbaikal region) described in previous study (Golubev et al., 2005) were used in the present work. The mineral chemical formula was found to be: $Ca_{0.99}Mg_{0.98}Fe_{0.02}Cr_{0.01}Si_2O_6$. X-ray diffraction analyses of the mineral