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Effects of surface orientation, fluid chemistry and mechanical polishing on the variability of dolomite dissolution rates

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Abstract

Recent studies of carbonate surface reactivity have underscored the fundamental variability of dissolution rates and the heterogeneous distribution of the reaction over the mineral surface due to the inhomogeneous distribution of surface energy. Dolomite dissolution rates relative to different cleavage planes (*r*-planes) and surfaces cut approximately perpendicular to the *c*-axis (*c*-planes) were studied at 50 °C as a function of pH ($3.4 \leq \text{pH} \leq 9.0$) and solution composition by vertical scanning interferometry (VSI) and atomic force microscopy (AFM), with the aim of providing an estimate of the intrinsic rate variation of dolomite single crystals and describing the surface reaction distribution and the rate controlling mechanisms. Surface normal retreat rates measured under acidic conditions increased linearly with time and were not visibly affected by the parallel increase of surface roughness. Mean total dissolution rates of *r*-planes decreased by over 200 times from pH 3.4 to pH 9.0 and CO_3^{2-}-rich solutions, whereas corresponding rate variations spanned over 3 orders of magnitude when also *c*-plane rate distributions were included in the analysis. At acid to near neutral pH, *c*-planes dissolved ~ three times faster than the adjoining *r*-planes but slower at basic pH and high total carbon concentration, displaying a distinctive morphologic evolution in these two regimes. The comparison of polished and unpolished crystals showed that polished cleavage planes dissolved about three times faster than the unpolished counterpart at near neutral to basic conditions, whereas no significant difference in reactivity was observed at pH < 5.

Although experimental data and observations indicate a tendency of dolomite faces to reach a low-energy topography over the course of the reaction, the evolution of the entire crystal morphology depends also on the reactivity of edge and corner regions, whose contribution to measured rates is not generally taken into account by laboratory experiments. The study of time-dependent mineral morphology and reactivity requires an integrated approach of kinetic modeling and experimentation, where measured rate variance and observed reaction mechanisms represent fundamental parameters for the improvement of geochemical models in predicting long-term reaction rates in a wide range of environmental conditions.

Keywords: Dolomite dissolution; Vertical scanning interferometry; Atomic force microscopy; Rate spectra; Reactive surface area; Surface topography; Rate variability; Mechanical polishing

1. INTRODUCTION

The extent to which mineral dissolution rates involved in various industrial processes and long-term weathering reactions can be accurately predicted depends on the knowledge of the fundamental mechanisms that take place at the

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mineral-fluid interface and on the understanding of the effects that the complex interplay of different physicochemical parameters, such as temperature, pH, $p\mathrm{CO}_2$, chemical composition of the fluid, presence of organic ligands, and the crystallographic and microstructural features of reactive surfaces, exerts on these reactions (cf. White and Brantley, 2003; Maher et al., 2009; Voltolini et al., 2012; Lüttge et al., 2013). Although large discrepancies generally exist between field-derived rates and laboratory measurements, the comparison of various experimental data also reveal the existence of significant variations in measured laboratory rates (cf. Arvidson et al., 2003; Beig and Lüttge, 2006; Lüttge et al., 2013). The origin of such differences mostly resides in the intrinsic variability of surface reactivity, which reflects the heterogeneous distribution of surface defects and active sites, and possibly the variation of grain size and grain-boundary density of the investigated solids (cf. Arvidson et al., 2003; Fischer et al., 2012, 2014). Clear evidence of the intrinsic variability of measured dissolution rates is provided by recent high-resolution studies conducted on single crystal surfaces by atomic force microscopy (AFM), optical profilometry [confocal profilometry (CP), phase-shift interferometry (PSI) and vertical scanning interferometry (VSI)] and other complementary techniques (e.g., Fischer et al., 2012; Godinho et al., 2012; Daval et al., 2013; King et al., 2014; Pollet-Villard et al., 2016), which illustrate the dependence of measured surface retreat rates on the crystallographic orientation, the physico-chemical microstructure of the investigated planes as well as the exposure time to the reactive fluid.

Knowledge of such inherent variability is particularly relevant within the carbonate system given the fundamental implication of major carbonate minerals (calcite and dolomite) in a wide variety of geological processes. The dissolution of calcite and dolomite plays an essential role in the regulation of the long-term C cycle (Berner et al., 1983; Mackenzie and Andersson, 2013) and significantly affects pH and alkalinity of natural waters; it controls the levels of trace metals released into groundwater (see Apps et al., 2010; Wunsch et al., 2013) and allows the development of carbonate reservoirs influencing their productivity (Worthington and Ford, 2009).

Many AFM and VSI studies were carried out over the last two decades to describe the elementary processes that control the dissolution of carbonate minerals, specifically investigating the formation of etch pits and the kinematics of monolayer steps under a wide variety of experimental conditions (e.g., Liang and Baer, 1997; Jordan and Rammensee, 1998; Shiraki et al., 2000; Lea et al., 2001; Higgins et al., 2002; Lüttge et al., 2003; Teng, 2004; Bisschop et al., 2006; Urosevic et al., 2012; Smith et al., 2013; Emmanuel, 2014). However, most of these works reported observations made on limited areas of the $\{10\bar{1}4\}$ cleavage surfaces and for relatively short experimental durations (typically ranging from a few minutes to several hours), so that the long-term evolution of representative portions of the mineral surface and the corresponding rates and distribution of the dissolution reaction were not adequately examined.

A limited number of publications looked at the influence of the crystallographic orientation and the effects of polishing and applied stress on the dissolution mechanisms of calcite. It was shown that the dissolution rates of calcite surfaces increase with the angle of miscut with respect to the $\{10\bar{1}4\}$ cleavage planes (Compton et al., 1986; Bisschop et al., 2006) but such difference decreases with increasing aqueous solution saturation (Smith et al., 2013). Schott et al. (1989) and MacInnis and Brantley (1992) reported an increase of dissolution rates by a factor of 2–3 for the cleavage planes of strained calcite samples whereas the rate dependence on dislocation density was generally found to be weak.

There have been few studies conducted on dolomite surface reactivity with atomic to nano-scale resolution compared to calcite (Lüttge et al., 2003; Higgins and Hu, 2005; Hu et al., 2005; Fenter et al., 2007; Kaczmarek and Sibley, 2007; Ruiz-Agudo et al., 2011; Urosevic et al., 2012; Xu et al., 2013; Putnis et al., 2014) and, although a notable progress in the understanding of the mechanisms and rates that control dolomite dissolution has been achieved, the complex nature of this mineral still requires detailed investigations to get to a more comprehensive picture of the processes that control its reactivity and formation in natural environments (cf. Kaczmarek and Sibley, 2014).

In this study we examine the effects of crystallographic orientation, pH and presence of defects generated by polishing on the mean rates of dolomite dissolution and the corresponding distribution of dissolution fluxes over the mineral surface with the two main objectives of: (i) providing experimental data that contribute to a more representative characterization of dolomite dissolution mechanisms and rates as a function of time and aqueous solution composition; (ii) improving our general understanding of mineral surface reactivity to help the advancement of modern computational tools in predicting long-term weathering reactions at the field-scale. The evolution of surface micro-topography and the surface normal retreats of mm-sized dolomite crystals were analyzed on both the $\{10\bar{1}4\}$ cleavage planes and miscut surfaces approximately parallel to the $\{0001\}$ crystallographic form. Because of the different morphologic characteristics and the different surface energies associated with these two planes, the analysis and comparison of their reactivity allow the description of the amplitude of dolomite rate variations and provide data that serve to model the evolution of the surface area of crystal grains as a function of time.

To express the observed variance of dissolution rates, recent AFM and VSI studies on calcite and dolomite (Fischer et al., 2012; Emmanuel, 2014; Emmanuel and Levenson, 2014) proposed the use of rate spectra providing information on range and distribution of surface dissolution fluxes and the frequency of corresponding energetic sites, as opposed to the use of single mean rate values obtained by traditional surface area normalization operations, which do not allow the description of the effects of these parameters on the intrinsic reaction rate variation. The use of this analytical tool is therefore of great relevance