Linking nm-scale measurements of the anisotropy of silicate surface reactivity to macroscopic dissolution rate laws: New insights based on diopside

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Abstract

The interfacial zone between a bulk fluid and a mineral surface is where all exchange of matter and energy occurs during chemical weathering. However, our knowledge is still limited with respect to understanding where and how the rate-determining dissolution reactions take place. A complicating factor is the commonplace formation of amorphous Si-rich surface layers (ASSLs), which may hinder contact between the fluid and the mineral surface. To address the role of ASSL, we investigated the dissolution of a common silicate (diopside), and related the bulk dissolution rate with the nanoscale dissolution rate and surface chemistry of its individual prevalent faces. While ASSL were evidenced on all of the investigated faces, only those formed on (110) and (1$\bar{1}$0) were passivating, thereby controlling the reactivity of the underlying faces. The (110) and (1$\bar{1}$0) faces intersect the highest density of Mg–O–Si and Fe–O–Si bonds, and this specificity may explain the passivating behavior of the corresponding ASSL. Moreover, we evidenced an inverse relation between aqueous silica concentration and the bulk dissolution rate of crushed diopside grains, which suggest that the (110) and (1$\bar{1}$0) faces are predominant in a powder. By considering ASSL as a separate phase that can control silicate dissolution rates, extrapolated laboratory-based rates at conditions relevant to the field can be lowered by up to several orders of magnitude, thereby decreasing the large gap between laboratory and natural rates. This has important implications for more accurately modeling chemical weathering reactions, so important today for the C cycle and CO_2 sequestration.
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1. INTRODUCTION

The chemical weathering of silicate materials plays a central role in many major engineering, environmental, and Earth science processes. Whether it determines the rates of denudation and soil formation (Godderis et al., 2010), CO_2 uptake and its impact on climate change (Le Hir et al., 2008; Beaulieu et al., 2012), hydrothermal circulation (Fritz et al., 2010), durability of radioactive waste confinement glasses (Cailleteau et al., 2008: Frugier et al., 2008) or geological sequestration of CO_2 (Knauss et al., 2005), the same strategy is commonly applied for determining the long term evolution of fluid–rock interactions. This strategy relies on the experimental determination of the

influence of a few parameters (mainly pH, temperature (T), ionic strength, and concentration of organic ligands) on the dissolution rate of single mineral powders in chemostats, almost always at far-from-equilibrium conditions. The derived kinetic rate laws are subsequently implemented into reactive transport codes (e.g. Knauss et al., 2005; Godderis et al., 2010). However, the utility of such laws to predict the rates of the abovementioned processes has been questioned for more than 20 years: it is well known that laboratory-based rates can be up to 5 orders of magnitude greater than those measured in the field, casting doubt both on the usefulness of laboratory rates and on the accuracy of reactive transport simulations (White et al., 1996; White and Brantley, 2003; Maher et al., 2004). Despite the emergence of some promising propositions to bridge the gap between laboratory and field measurements (e.g. Nugent et al., 1998; Lasaga and Luttge, 2001; Arvidson and Luttge, 2010; Maher, 2010; see detailed discussions in e.g. White and Brantley, 2003; Zhu, 2005), and aside from a limited number of studies which managed to reconcile experimental and field data at specific sites (e.g. Maher et al., 2009), upscaling laboratory results to the field essentially remains an elusive goal.

Addressing this challenge requires an in-depth understanding of silicate reactivity and the underlying nm-scale processes. A key parameter arises from the detailed investigation of weathered silicate surfaces. Hellmann et al. (2012) have recently extended more than 40 years of direct and indirect observations (e.g. Luce et al., 1972; Petit et al., 1987) by demonstrating that regardless of the reaction conditions (fluid composition, T, reaction duration and location (i.e. field or laboratory), mineral chemistry and structure, presence of biota), nm-thick amorphous surface altered layers enriched in silica were generally found to have formed on weathered silicate mineral surfaces (note however that the question as to whether or not the formation of such layers is ubiquitous remains open – see e.g. the work by Lee et al., 2008, which failed to find amorphous layers on weathered feldspars in spite of the use of state-of-the-art microscopic techniques). Therefore, as previously pointed out by e.g. Jordan et al. (1999) or Zhu et al. (2006), the basic question that needs to be addressed is: which part of the interfacial zone, defined as the chemically and structurally modified entity between the pristine mineral surface and the bulk fluid, ultimately controls the dissolution rate? The two candidates for answering this question are (a) the inner interface, defined as the boundary between the pristine mineral and the amorphous silica-rich surface layer (hereafter referred to as: ASSL), (b) the outer interface, where the bulk fluid contacts the ASSL. If the ASSL are not passivating, the inner interface will control the kinetics, and conversely, if they are passivating (i.e. totally non-permeable), the outer interface hinders access of the bulk fluid to the unaltered mineral surface, and thereby will control the dissolution process. Both cases have been reported for silicate glasses and minerals (e.g. Jordan et al., 1999; Daval et al., 2009a,b; Geisler et al., 2010; Hellmann et al., 2012 vs. Daux et al., 1997; Berger et al., 2002; Daval et al., 2011). In addition, the presence of passivating ASSL has not yet been integrated in current reactive trans-

port codes. This has important consequences because it can lead to a dramatic overestimation of dissolution rates, even in simple batch experiments (Daval et al., 2011). The quantitative recognition of the effects of passivation shows promise as a means for reconciling field and laboratory chemical weathering rates.

In the present study, we provide a detailed investigation of the face-specific dissolution of a common silicate mineral (diopside) and combine these results with macroscopic measurements of bulk diopside dissolution rates to shed light on key parameters that render certain ASSL passivating. Quite surprisingly, the results described below show that the passivating properties of ASSL are face-specific. This finding has important consequences on our ability to accurately model the kinetics of fluid–rock interactions, as well as the interpretation of experimental mineral dissolution results determined in the laboratory.

2. MATERIALS AND METHODS

The present study consists of two independent series of experiments aiming at investigating the effect of $SiO_2(aq)$ concentrations on diopside dissolution rates (R_{Di}), both on crushed grains at the macro-scale, and on selected faces at the nano-scale. The starting materials are cm-sized gems coming from Mererani (Tanzania), and were previously described in Daval et al. (2010). Based on electron microprobe analyses, the chemical composition of the diopside used in this study has the following composition: $Ca_{1.01}Mg_{0.96}$-$Fe_{0.05}Si_{1.98}O_6$, in close agreement with that reported in Daval et al. (2010).

2.1. Bulk dissolution experiments on diopside powders in mixed-flow reactors (MFR)

Samples were initially crushed, sieved to recover the 300–500 μm-sized fraction, and ultrasonically washed in absolute ethanol following the procedure described in Daval et al. (2010). The measured Kr BET specific surface area was $0.028 \, m^2 \, g^{-1}$. The experiments were conducted in a MFR system, using the exact same set-up as in Daval et al. (2010). In this previous study, a rate plateau was evidenced as long as the Gibbs free energy with respect to diopside dissolution ($\Delta G_r(Di)$) was below $-76 \, kJ \, mol^{-1}$. Consequently, to single out the intrinsic effect of $[SiO_2(aq)]$ only, all experiments of the present study were conducted at conditions where R_{Di} is $\Delta G_r(Di)$-independent (for all experiments, $\Delta G_r(Di) \leqslant -89 \, kJ \, mol^{-1}$). Consistent with Daval et al. (2010), the experiments were carried out at 90 °C and at 2 MPa fluid pressure, at $pH_{(90 \, °C)}$ close to 5 (4.97 ± 0.04). The input solutions contained an acetate pH buffer (6.4 mM sodium acetate and 5 mM acetic acid; see Daval et al., 2010 for details).

If the Si-rich layers which form on diopside are passivating, R_{Di} should exhibit a strong dependence on $[SiO_2(aq)]$. Assessing this point was performed by varying the inlet concentration of $SiO_2(aq)$ (by adding variable amounts of sodium metasilicate), with all of the other experimental parameters (sample mass and grain size, flow rate, reaction time, pH) remaining roughly constant from one run to the