



Dynamics of altered surface layer formation on dissolving silicates

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Abstract

The extrapolation of mineral dissolution kinetics experiments to geological timescales has frequently been challenged by the observation that mineral dissolution rates decrease with time. In the present study, we report a detailed investigation of the early stages of wollastonite dissolution kinetics, linking time-resolved measurements of wollastonite dissolution rate as a function of crystallographic orientation to the evolution of physicochemical properties (i.e., diffusivity, density, and thickness) of amorphous silica-rich layers (ASSLs) that developed on each surface. Batch dissolution experiments conducted at room temperature and at far-from-equilibrium conditions revealed that the initial (i.e., ASSL-free) dissolution rate of wollastonite ($R_{(hkl)}$) based on Ca release observe the following trend: $R_{(010)} \approx R_{(100)} > R_{(101)} > R_{(001)}$. A gradual decrease of the dissolution rate of some faces by up to one order of magnitude resulted in a modification of this trend after two days: $R_{(010)} \gg R_{(100)} \geq R_{(101)} \approx R_{(001)}$. In parallel, the diffusivity of ASSLs developed on each face was estimated based on the measurement of the concentration profile of a conservative tracer (methylene blue) across the ASSL using nanoSIMS. The apparent diffusion coefficients of methylene blue as a function of the crystallographic orientation ($D_{app}^{(hkl)}$) observe the following trend: $D_{app}^{(010)} \geq D_{app}^{(100)} > D_{app}^{(101)} \gg D_{app}^{(001)}$, and decreases as a function of time for the (100) and (101) faces. Finally, the density of ASSL was estimated based on the modeling of X-ray reflectivity patterns acquired as a function of time. The density of ASSLs developed on the (010) faces remains low and constant, whereas it increases for the ASSLs developed on the (001) faces. On the whole, our results suggest that the impact of the formation of ASSLs on the wollastonite dissolution rate is anisotropic: while some crystal faces are weakly affected by the formation of non-passivating ASSLs (e.g., the (010) face), the dissolution of other faces is hampered by passivating ASSLs within a few hours. The observed passivation is suggested to originate from the progressive densification of the ASSL, which limits the transport of reactive species from and to the dissolving wollastonite surface, as evidenced by the estimated diffusivity of the ASSLs. Because the apparent face-specific diffusivity of the ASSLs is correlated with the face-specific initial (i.e., ASSL-free) dissolution rate of wollastonite, we propose that the extent of ASSL densification (and the resulting impact on ion transport) is (at least partly) controlled by the absolute mineral dissolution rate. Overall, this study argues that the formation and microstructural evolution of ASSLs are likely

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candidates for mineral ageing, highlighting the need for determining the parameters controlling the spontaneous changes of ASSL diffusivity as a function of the reaction progress.

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1. INTRODUCTION

A fundamental understanding of the aqueous reactivity of silicate minerals is required to model a wide variety of (bio)geochemical processes occurring on the Earth's surface. Numerous experimental studies were therefore dedicated to investigate the effects of extrinsic parameters, such as temperature or fluid composition, on mineral dissolution (see Schott et al., 2009 and/or Brantley and Olsen, 2014 for extensive reviews). The resulting “kinetic rate laws” fueled reactive transport codes for decades, with varying success rates: upscaling laboratory results has often proven to be unsuccessful without the adjustment of several modeling parameters (Montes-H et al., 2005; Godderis et al., 2006). Modeled and measured mineral reactivities might differ by several orders of magnitude, and substantial deviation can be evidenced, even in experimental setups as simple as batch or column reactors, for durations as short as a couple of months (White and Brantley, 2003; Daval et al., 2011; Galeczka et al., 2014). More generally, the progressive decrease of mineral dissolution rates as a function of time, which has been extensively documented in the literature (Taylor and Blum, 1995; White et al., 1996; Maher et al., 2004; Fantle and DePaolo, 2006; Porder et al., 2007), challenges the definition of a unique rate constant for a given mineral and encourages studies aimed at unraveling the limitations of the conventional use of “kinetic rate laws”.

The apparent decrease of mineral reactivity with time might be related to the gradual evolution of the physico-chemical properties of the mineral's surface. Although long suggested by Luce et al. (1972), the impact of the physico-chemical modifications of the surface microstructure of the dissolving minerals on their dissolution rates as a function of the reaction progress has not received as much attention as the impact of extrinsic parameters. An interesting illustration of this assertion is based on the lack of agreement regarding the putative impact of the formation of amorphous silica-rich surface layers (ASSLs) on the dissolution rate of silicate minerals, which gives rise to various parametrizations of silicate dissolution kinetics. For instance, the early theoretical considerations of Aagaard and Helgeson (1982) suggested that the driving force of any dissolution reaction is the chemical affinity with respect to the primary mineral, thereby dismissing the effect of surface layers, if not their existence. Later on, the theoretical development by Oelkers (2001) emphasized that the dissolution process might be driven by thermodynamic properties of the so-called “leached layer”, such that the chemical affinity that should be considered for the dissolution reaction has to be defined with respect to the surface layer. Yet, several studies directly or indirectly demonstrated that water could freely reach the pristine surface of the dissolving silicates

(Jordan et al., 1999; Hellmann et al., 2003), restoring the pristine silicate surface as the interface where the rate-limiting reactions occur. The influence of ASSLs on the overall dissolution rate of silicates has been addressed in several studies since then (e.g., Bearat et al., 2006; Daval et al., 2009a, 2009b; Daval et al., 2011, 2013b; Ruiz-Agudo et al., 2012; Saldi et al., 2013, 2015; Wang and Giammar, 2013; Johnson et al., 2014; Maher et al., 2016; Wild et al., 2016). A general conclusion of these studies is that the passivating ability of ASSLs is not universal but rather directly originates from a combination of intrinsic properties of the dissolving silicates (e.g., chemical composition and crystal bonding structure) and extrinsic parameters (e.g., redox and chemical composition of the solution). Note that similar concerns have been raised by the scientific community working on glass corrosion, where the formation mechanisms of ASSLs and their passivating ability have been debated (e.g., Bourcier et al., 1989; Daux et al., 1997; Grambow and Muller, 2001; Cailleateau et al., 2008; Verney-Carron et al., 2011; Geisler et al., 2015; Gin et al., 2015; Hellmann et al., 2015; Icenhower and Steefel, 2015; Rébiscoul et al., 2015).

While the determination of the parameters leading to impermeable ASSL textures is still in its infancy, virtually nothing is known about the dynamics of the process. For instance, tentative equations, such as those developed by Daval et al. (2013b) or Maher et al. (2016) to account for the effect of passivating ASSLs on the silicate dissolution rate, consider that the passivation is instantaneous and invariant with time, which is a strong assumption regarding the kinetics of the process. In contrast, the few studies that were intended to probe the dynamics of ASSL formation on glass suggested that ASSLs might undergo progressive densification with time, leading to an ultimate modification of their transport properties (Rébiscoul et al., 2003, 2004; Cailleateau et al., 2008). Similarly, Casey et al. (1993) and Schott et al. (2012b) showed that the ASSLs that formed on wollastonite underwent a gradual restructuring, as evidenced from the temporal modification of their polymerization state.

The precise characterization of the dynamics of ASSL formation on the surface of altered silicates and the quantification of their effects on the reactivity of the underlying silicate mineral seem essential. To achieve these goals, wollastonite has often been used as a model mineral due to (i) its rapid dissolution kinetics and (ii) the relatively thick layers that form on its surface during dissolution, thereby enabling the application of a broad range of characterization tools (e.g., Rimstidt and Dove, 1986; Casey et al., 1993; Xie and Walther, 1994; Weissbart and Rimstidt, 2000; Green and Lutge, 2006; Huijgen et al., 2006; Daval et al., 2009a, 2009b; Hellmann et al., 2012; Ruiz-Agudo et al., 2012, 2016; Schott et al., 2012b).

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