



Time-dependent feldspar dissolution rates resulting from surface passivation: Experimental evidence and geochemical implications

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ARTICLE INFO

Article history:

Received 15 January 2018

Received in revised form 23 May 2018

Accepted 27 June 2018

Available online xxxx

Editor: M. Bickle

Keywords:

dissolution kinetics
chemical weathering
nanoscale characterizations
fluid/silicate interface

ABSTRACT

To which extent does the apparent negative correlation reported between silicate weathering rates and time result from the spontaneous physicochemical evolution of the fluid–mineral interface? To address this question, labradorite powders inserted in nylon bags and buried into two different topsoil horizons for four years were subjected to nanoscale characterization of their near-surface regions using transmission electron microscopy. These characterizations revealed the occurrence of a 30 to 70 nm-thick discontinuous amorphous silica-rich surface layer (ASSL) with a sharp crystalline-amorphous interfacial boundary between labradorite and the layer. Dissolution experiments conducted in mixed-flow reactors at ambient temperature and acidic pH demonstrated that the reactivity of fresh and naturally weathered labradorite powders decreased with time, with the dissolution rate of fresh powders remaining systematically greater than that of naturally weathered powders, all over the duration of the experiments (3 weeks). In addition, the dissolution rate of all labradorite batches was noticeably lower in solutions containing elevated concentrations of $\text{SiO}_2(\text{aq})$, which we attributed to the passivating effect of the ASSLS. This suggestion was confirmed with a simple passivation model, which enabled to capture (i) the greater reactivity of fresh powders; (ii) the dependence of the dissolution rate on $[\text{SiO}_2(\text{aq})]$; (iii) the gradual decline of powder dissolution rate with time and (iv) the discontinuous occurrence of ASSLS. The model further supports that surface passivation could be one of the (non-exclusive) mechanisms that could account for the so-called kinetic “field-lab discrepancy”. The geochemical implications of the recognition of the passivation mechanism are broad, ranging from the need to revisit the kinetic rate laws implemented in geochemical codes to the questioning of the formalism used for determining weathering rates from the study of U-series nuclides in soils and weathering profiles.

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1. Introduction

Reconciling laboratory- to field-derived weathering rates has represented a puzzling issue since the early recognition by Paces (1983) that mineral dissolution rates determined from laboratory experiments overestimate their field counterparts by several orders of magnitude. This so-called “field-laboratory discrepancy” has been subsequently confirmed following various methods and under various contexts (e.g. watershed geochemical mass-balances (Velbel, 1993), changes in solid-state regolith compositions (White et al., 1996; Parry et al., 2015), weight loss of buried mineral test bags (Augusto et al., 2000), decade-long laboratory

column experiments on fresh and weathered rocks (White et al., 2017)), and further reinforced by studies highlighting that silicate weathering rates were negatively correlated to time (Taylor and Blum, 1995; White and Brantley, 2003; Maher et al., 2004; Porder et al., 2007).

Whether this correlation results from an intrinsic gradual loss of mineral reactivity or from other extrinsic factors remains controversial. While some studies suggest that surface aging resulting from the formation of amorphous silica-rich surface layers (ASSLS) contribute to the decrease of silicate dissolution rates (e.g. Nugent et al., 1998; Ruiz-Agudo et al., 2012), others emphasized that the slow precipitation rates of secondary minerals (Zhu, 2005; Maher et al., 2009) and long fluid residence time in natural settings (Maher, 2010) may drive the dissolution reactions at close-to-equilibrium conditions, where the dissolution rates dramatically decrease (Kampman et al., 2009). An illustration of these conflict-

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ing conceptual frameworks can be found in the comparison of the modeling results of Maher et al. (2009), who showed that contemporary and long-term weathering rates were equivalent for the specific site of the Santa Cruz soil chronosequence (CA, United States), as opposed to the recent modeling results of White et al. (2017), who suggested that decreasing the intrinsic plagioclase dissolution rate was necessary to approximate long-term weathering rates.

In a series of papers, we demonstrated that the formation of ASSLS may be responsible for a gradual decline of silicate dissolution rates (Daval et al., 2011, 2013, 2017; Saldi et al., 2015; Wild et al., 2016). However, these studies remained limited to freshly crushed and/or polished starting materials dissolved in simple synthetic solutions, at temperature and/or pH conditions that were not representative of Earth surface weathering, which represents a potential shortcoming for extrapolating our conclusions, since the formation of ASSLS on naturally weathered silicates has been questioned by several studies (Lee et al., 2008 and references therein). To circumvent this issue, here we conducted detailed nanoscale characterizations of the near-surface regions of naturally weathered labradorite feldspar grains that were buried in two different forest soils for several years, and directly compared their reactivity to that of freshly crushed labradorite using mixed-flow reactor set-ups. As opposed to column experiments where stagnant pore spaces may result in slower dissolution rates, the use of mixed-flow reactors ensures that any discrepancy between the reactivity of fresh and naturally weathered minerals is attributable to surface aging. Combining the nanoscale characterizations with the leaching experiments allowed us to propose a model that accounts for the observed reduction of feldspar dissolution rate due to surface passivation by ASSLS. Finally, we discussed some geochemical implications stemming from the mechanism proposed to model the experimental results.

2. Materials and methods

2.1. Starting materials

The labradorite samples used in this study come from Norway, and were supplied by Compagnie Générale de Madagascar, Paris, France. They consist of translucent greyish cm-sized euhedral to anhedral crystals containing ilmenite inclusions ($\leq 0.1\%$ according to Augusto et al., 2000). The structural formula of the labradorite is $K_{0.02}Ca_{0.52}Na_{0.45}Si_{2.49}Al_{1.49}O_8$, based on electron microprobe analyses that can be found in Augusto et al. (2000). Three different batches of labradorite samples were used to conduct the dissolution experiments described in Section 2.2:

The first batch (hereafter referred to as “INI”) was prepared with the following protocol: the cm-sized chunks of labradorite mineral were ground in a jaw crusher, sieved to recover the 100–200 μm sized-fraction, magnetically sorted to remove ilmenite, and finally sonicated in distilled water to remove fine particles. The sonication step was repeated three times. The specific surface area (SSA) of the powder reported by Augusto et al. (2000) is $0.11 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$, as determined from BET measurements.

The second batch (hereafter referred to as “FOU”) consisted of INI labradorite powders that were inserted into nylon bags and buried at ~ 2.5 cm depth for 4 yr (from April 2000 to April 2004) in an 86-yr old beech soil located in the Fougères forest (Brittany, France, $48^\circ 23' \text{N}$, $1^\circ 9' \text{W}$, mean elevation: 150 m), as described in Turpault et al. (2009). The climate in this area is oceanic with an average annual air temperature of 12.9°C and a mean annual rainfall of 868 mm. The pH of the topsoil solution was 3.75 ± 0.05 . In April 2004, the buried samples were recovered, ultrasonically washed to remove soil particles, prior to be gently

dried and weighed to determine the extent of labradorite dissolution. As reported in Turpault et al. (2009), $\sim 1\%$ of the sample was dissolved in 4 yr, corresponding to a mean dissolution rate of $2.5 \text{ mg g}^{-1} \text{ yr}^{-1}$, which corresponds to $2.7 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$. The SSA of the recovered powders is $0.47 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$, as determined from Kr-BET measurements.

The third batch (hereafter referred to as “AUR”) consisted of INI labradorite powders that were inserted into nylon bags and buried at a ~ 2.5 cm depth for 4 yr (from June 2000 to June 2004) in an 85-yr old spruce soil located in Aubure (Alsace, France, $48^\circ 12' \text{N}$; $7^\circ 12' \text{E}$), mean elevation: 950 m). The annual air temperature is 6.3°C and the annual rainfall is 1261 mm. The pH of the topsoil solution was 4.27 ± 0.12 . The samples were ultrasonically washed to remove soil particles at the time of their collection, prior to be dried and weighed to determine the extent of labradorite dissolution. It was calculated that $\sim 0.7\%$ of the sample was dissolved, corresponding to a mean dissolution rate of $1.8 \text{ mg g}^{-1} \text{ yr}^{-1}$, which translates into $1.9 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$. The SSA of the recovered powders is $0.51 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$, as determined from Kr-BET measurements.

2.2. Dissolution experiments and analytical procedures

The three different batches of labradorite were subjected to dissolution experiments conducted at room temperature ($22 \pm 2^\circ \text{C}$) in mixed-flow reactors. The input solutions were stored in polyethylene containers and injected into the reaction vessel using peristaltic pumps. The main experiments were conducted in continuously stirred 15 mL custom-made polypropylene reactors described in Voinot et al. (2013) to run duplicates in short amounts of time, thanks to the short residence time of the solution in such low volume reactors. Some experiments for which the very limited amount of dissolved labradorite lead to Ca concentrations close to the background level were replicated in continuously stirred 60 mL Teflon reactors using greater amounts of powder (~ 1 g vs. ~ 0.2 g for the regular experiments). The solutions were prepared in ultrapure deionized water ($18.2 \text{ M}\Omega \text{ cm}$) and acidified with reagent-grade HCl to $\text{pH } 3.3 \pm 0.1$. The pH of the input solution was purposely adjusted to a value that was slightly lower than that of the soil solutions to maintain conditions of undersaturation with respect to secondary phases such as clays and aluminum (oxy)hydroxides. In total, 12 dissolution experiments were run with the 15 mL reactors and 3 additional experiments were run with the 60 mL reactors.

Because previous studies showed that the passivating effect of ASSLS can be revealed by comparing the dissolution rate of silicate minerals measured in $\text{SiO}_2(\text{aq})$ -free solutions to that measured in $\text{SiO}_2(\text{aq})$ -rich experiments (e.g., Daval et al., 2011, 2013; Johnson et al., 2014; Wild et al., 2016), part of the experiments were conducted in solutions containing elevated concentrations of $\text{SiO}_2(\text{aq})$ ($[\text{SiO}_2(\text{aq})] = 1.5 \text{ mM}$) prepared from reagent-grade sodium metasilicate, whose pH was adjusted to 3.4 ± 0.1 with HCl.

The exit solution from each experiment was collected periodically and acidified to $\text{pH} \sim 2$. The inlet and outlet concentrations of dissolved species (Ca, Na, Al, Si) were measured by ICP-AES (THERMO ICAP 6000 Series) using matrix-matched standards and matrix blanks. The analytical uncertainties, based on repeated analyses of standard solutions and blanks, were estimated to be $\pm 3\%$ for concentrations greater than 100 ppb, and up to $\pm 10\%$ in the 20–50 ppb range.

2.3. Calculations of dissolution rates

The rate of labradorite dissolution based on the concentration of Ca, Al (and Si, when possible) in the exit solution was approximated using the following relation:

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