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#### Notes

# Mechanism of leached layer formation during chemical weathering of silicate minerals

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## ABSTRACT

The dissolution of most common multicomponent silicate minerals and glasses is typically incongruent, as shown by the nonstoichiometric release of the solid phase components. This results in the formation of so-called surface leached layers. Due to the important effects these leached layers may have on mineral dissolution rates and secondary mineral formation, they have attracted a great deal of research. However, the mechanism of leached layer formation is a matter of vigorous debate. Here we report on an *in situ* atomic force microscopy (AFM) study of the dissolution of wollastonite, CaSiO<sub>3</sub>, as an example of leached layer formation during dissolution. Our *in situ* AFM results provide, for the first time, clear direct experimental evidence that leached layers are formed in a tight interface-coupled two-step process: stoichiometric dissolution of the pristine mineral surfaces and subsequent precipitation of a secondary phase (most likely amorphous silica) from a supersaturated boundary layer of fluid in contact with the mineral surface. This occurs despite the fact that the bulk solution is undersaturated with respect to the secondary phase. Our results differ significantly from the concept of preferential leaching of cations, as postulated by most currently accepted incongruent dissolution models. This interface-coupled dissolution-precipitation model has important implications in understanding and evaluating dissolution kinetics of major rock-forming minerals.

## INTRODUCTION

Dissolution is a key process in every fluid-rock interaction, such as in chemical weathering, CO<sub>2</sub> carbonation reactions, metasomatism, and metamorphism. To attempt to quantify and model the rates of reactions involving dissolution, we need to understand the mechanism. Multicomponent silicate minerals are major components of many rocks, and consequently their low-temperature weathering is of paramount importance for understanding a wide range of geochemical processes (Weissbart and Rimstidt, 2000). Many of these minerals dissolve incongruently, as reflected in the observed pattern of element release to aqueous solutions during laboratory dissolution experiments (i.e., the elemental molar ratios measured in the fluid are different from those in the solid, especially at the initial stages of dissolution; e.g., see Casey et al., 1993; Pokrovsky and Schott, 2000; Hellmann et al., 2003; Brantley, 2008; Tisserand and Hellmann, 2008; Daval et al., 2011). This phenomenon results in the formation of so-called leached layers, which are chemically and structurally altered zones at the fluid-solid interface as much as several thousand angstroms thick and depleted in some elements relative to the bulk mineral composition (Casey et al., 1993; Brantley, 2008; Hellmann et al., 2012). The formation mechanism of these layers has been the subject of much research and debate. A widely accepted view is that there is a preferential release of certain elements to the solution (i.e., nonstoichiometric dissolution) due to differences in their bond strengths (Weissbart and Rimstidt, 2000). However, many of the obser-

vations made on experimentally and naturally altered interfaces of silicate minerals (Hellmann et al., 2003, 2012) and glasses (e.g., Geisler et al., 2010) cannot be explained by a leaching or diffusion process. In this sense, the pioneering work by Hellmann et al. (2003) shows that the extremely sharp interface between the parent mineral and the altered layer cannot be modeled assuming an interdiffusion of protons and cations in the leached layer. Our direct observations support Hellmann's conclusions. These observations could be interpreted in terms of an interface-coupled dissolution-precipitation model (see Putnis, 2009, for a review of this reaction mechanism). This model assumes that the dissolution is initially stoichiometric, but is coupled with the precipitation of a secondary phase from a supersaturated boundary layer of fluid, while the bulk solution may remain undersaturated with respect to such a secondary phase.

Most studies reporting leached layer formation lack *in situ* and *in tempore* observations of the reacting mineral surfaces, and thus do not provide unequivocal experimental evidence that confirms any of the hypotheses described above. Most mechanistic interpretations have been based on measurements of total fluxes of dissolved ions and chemical analysis of the reacting surface, mostly by X-ray photoelectron spectroscopy or transmission electron microscopy (see Hellmann et al., 2003; Brantley, 2008). In this study, *in situ* nanoscale atomic force microscopy (AFM) observations of the reacting surfaces and chemical analysis of the output solutions during wollastonite (CaSiO<sub>3</sub>) dissolution at room temperature at acidic pH

are combined in order to establish the mechanism of formation of chemically altered surface layers during mineral dissolution. Wollastonite dissolves incongruently under acidic conditions, forming silica-rich alteration layers (Rimstidt and Dove, 1986; Casey et al., 1993; Xie and Walther, 1994; Weissbart and Rimstidt, 2000; Green and Lüttge, 2006; Daval et al., 2009a, 2009b), and is used here as a model for other multicomponent minerals that are known to dissolve incongruently. We suggest that the experimental strategy of direct observation used in this study is the most effective way to understand the mechanism of incongruent mineral dissolution and leached layer formation.

## MATERIALS AND METHODS

High purity wollastonite crystals from Barberton District (Mpumalanga Province, South Africa) were cleaved with a knife blade to obtain millimeter-size (~3 × 3 × 1 mm) fragments. AFM *in situ* dissolution experiments were carried out by passing acidic solutions (pH 1.5–5.9) over cleavage surfaces. Solutions were prepared immediately before the experiments using double-deionized water (resistivity >18 mΩ cm<sup>-1</sup>) and adjusting the solution pH using HCl. The absence of calcium and silicon in the input solutions ensured constant far-from-equilibrium conditions with respect to the original wollastonite. *In situ* observations and measurements were performed using a Digital Instruments Nanoscope III Multimode AFM equipped with a fluid cell and working in contact mode under ambient conditions (20 ± 1 °C). The solutions flowed continuously at ~100 mL h<sup>-1</sup> from a syringe coupled to an O-ring-sealed fluid cell containing the sample crystal. AFM images were collected using Si<sub>3</sub>N<sub>4</sub> tips (Veeco Instruments, tip model NP-S20) and analyzed with the Nanoscope software (version 5.12b48).

Aliquots of effluent solution were collected continuously (in 4 min batches) and analyzed for Ca and Si using inductively coupled plasma-optical emission spectrometry (Varian Vista proximal) and colorimetry (molybdate blue method; Grasshoff et al., 1983), respectively. Fluxes of dissolved Ca and Si (representing dissolution rates) were calculated as follows:

$$r_i = \frac{[i]_r Q}{A}, \quad (1)$$

where [i] is the concentration of calcium or silicon in the effluent solution (mol m<sup>-3</sup>), *Q* is the

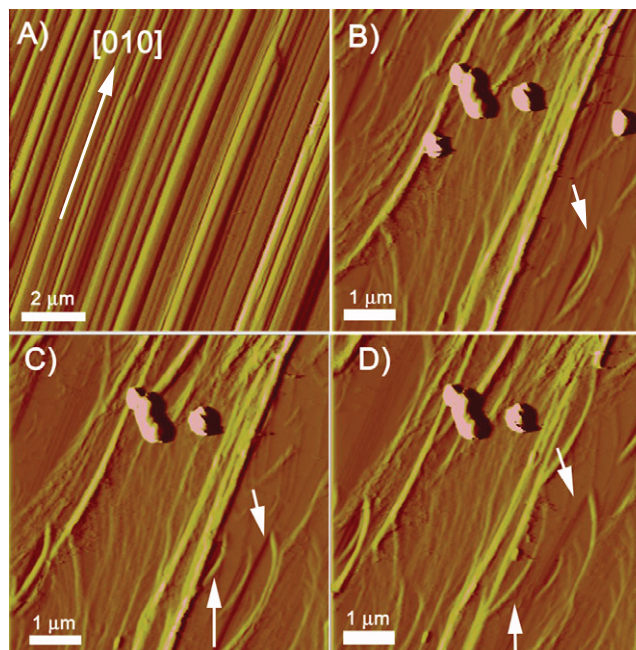
solution flow rate ( $\text{m}^3 \text{s}^{-1}$ ), and  $A$  is the BET (i.e., Brunauer, Emmett, Teller method) surface area of the original crystal exposed to the solution ( $\text{m}^2$ ). To isolate any potential artifact on dissolution rates associated with the interaction between the AFM tip and the mineral surface, parallel flow-through experiments at pH 1.5 were performed, aimed at reproducing the AFM experiments, using Teflon reactors (5 mL volume) containing  $0.1862 \pm 0.0010$  g of solid (BET surface area  $0.45 \text{ m}^2 \text{ g}^{-1}$ ) and using the same solution flow rate ( $100 \text{ mL h}^{-1}$ ) as used for the AFM experiments.

MicroRaman spectroscopy (JASCO NRS-5100, equipped with 532 nm diode laser) and field emission scanning electron microscopy (FESEM; Carl Zeiss Gemini) coupled with energy dispersive spectroscopy microanalysis were used to study the surface of reacted minerals.

## EXPERIMENTAL RESULTS AND DISCUSSION

Most studies reporting incongruent dissolution of wollastonite and the formation of leached layers conclude that this behavior is due to exchange of protons for  $\text{Ca}^{2+}$  ions, which are preferentially released into solution, leaving behind a silica-enriched layer (e.g., Casey et al., 1993; Xie and Walther, 1994; Weissbart and Rimstidt, 2000). This (amorphous) Si-rich layer is proposed to restructure and dissolve releasing silica units with different degrees of polymerization (Casey et al., 1993; Weissbart and Rimstidt, 2000). Casey et al. (1993), as well as most others studying leached layer formation (see review by Brantley, 2008), ruled out any secondary precipitation of amorphous silica because in their experiments the bulk solution was undersaturated with respect to all silica phases. Nevertheless, we find no evidence in our study that supports such a mechanism.

Freshly cleaved {100} wollastonite surfaces show numerous steps parallel to the  $b$ -axis (Fig. 1A). Initially, dissolution at acid pH occurs by retreat of preexisting steps; however, in later stages of the dissolution lens-shaped etch pits, similar to those described on naturally weathered inosilicates (Berner et al., 1980), form on these prismatic faces. At pH 1.5, these etch pits grow by spreading horizontally at a rate of  $9.5 \pm 2.3$  and  $1.4 \pm 0.4 \text{ nm/s}$  along the [010] and [001] directions, respectively (Figs. 1B–1D). The observation of these dissolution features indicates that complete layers dissolve, suggesting surface-controlled normal congruent dissolution (i.e., stoichiometric release of Ca and Si to the solution). Note that for etch pits to spread over a surface, stoichiometric amounts of ions must be released to the solution (Hu et al., 2005). However, dissolution is accompanied by the nucleation of a new phase on the mineral surface (Figs. 1B–1D). This precipitation

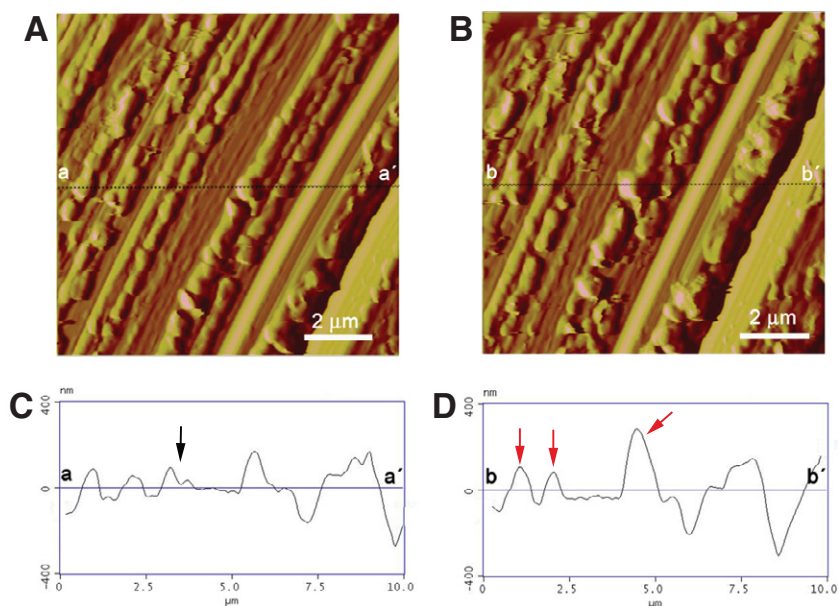


**Figure 1.** Atomic force microscopy deflection images of wollastonite {100} surface. A: Cleaved surface showing step edges parallel to [010] direction. B: Same surface exposed to HCl solution (pH 1.5) 300 s after first injection of acidic solution. C: After 375 s. D: After 465 s. Note formation and spreading of shallow pits elongated along [010] direction.

event is reflected in the height profiles shown in Figure 2, where the newly formed topographic features on wollastonite cleavage surfaces are clearly the result of a growth process. We hypothesize that this precipitate is the leached layer observed in previous studies after exposure of wollastonite to acidic solutions. Hydrothermal AFM observations of anorthite dissolution (Jordan et al., 1999) show that, beneath an altered surface layer, etch pits are present. These

observations are consistent with ours and suggest that the formation of leached layers via secondary mineral precipitation is a general phenomenon. However, Jordan et al. (1999) did not consider that the observed altered layer is a precipitate, as the bulk solution is undersaturated with respect to all silica phases. We discuss this critical issue below.

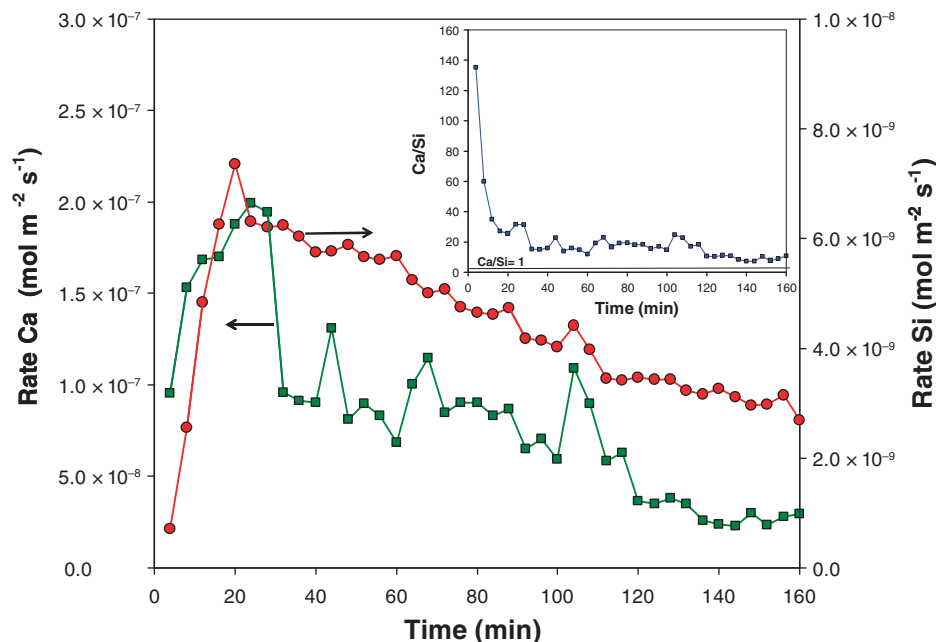
FESEM and MicroRaman spectroscopy analyses of the surface layers formed on wollastonite



**Figure 2.** A, B: Sequential atomic force microscopy deflection images showing formation of surface precipitates during wollastonite dissolution. C, D: Corresponding height profiles. Height profiles show upward and horizontal growth (red arrows) of newly formed precipitates, as well as simultaneous dissolution (black arrows) of this new phase. Time lapse between images is 132 s.

after dissolution at acidic conditions confirm that the surface layer is Ca depleted, and most likely corresponds to amorphous silica (e.g., Casey et al., 1993) (see Fig. DR1 in the GSA Data Repository<sup>1</sup>), which could initially be a silica gel (King et al., 2011). The formation of this surface precipitate explains the fact that elemental ratios in the effluent solution are different from those of the solids, with higher Ca than Si concentration in the outflow, as reflected by the dissolution rates and Ca/Si ratios (Fig. 3). However, thermodynamic calculations performed using PHREEQC (database phreeqc.dat; [http://www.brr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/](http://www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc/)) indicate that effluent solutions are undersaturated with respect to amorphous silica at all pH tested, for both total Ca and the stoichiometric amount of Si, as well as the measured Si concentration (the saturation index with respect to amorphous silica varied from  $-0.3$  to  $-1.23$  during the flow-through experiments; Table DR1 in the Data Repository). We suggest that after an initial transient step of stoichiometric dissolution in which elements are released to the interfacial solution in stoichiometric proportions, the fluid in a boundary layer in contact with the mineral surface becomes supersaturated with respect to a secondary phase that then precipitates. The existence of such an interfacial fluid layer, defined by steep cation concentration gradients close to the surface of the mineral, was observed by Putnis et al. (2005) during mineral replacement reactions using real-time phase-shift interferometry. The formation of a silica surface precipitate results in the progressive coverage of the dissolving mineral surface. This would decrease the reactive surface area of the wollastonite, thus resulting in the observed continuous reduction in calcium flux during the course of the experiments (Fig. 3). Such a trend was also observed in a run where a crystal was subjected to dissolution in the AFM fluid cell at pH 5.9, 3, and 1.5 in successive steps. This, in addition to FESEM observations, confirms that fines or the consumption of highly reactive surface sites such as corners, step edges, or dislocations, often claimed to explain exponentially decreasing dissolution rates, do not fully explain our results. Furthermore, a linear dependence was observed between the logarithm of wollastonite dissolution rates and pH, with a slope of  $-0.48$  at the early stages of dissolution, which is close to the theoretical reaction order (0.50) (see Fig. DR2). However, other published dissolution rates calculated after longer reaction times tend to show lower reaction orders, suggesting that at longer

<sup>1</sup>GSA Data Repository item 2012266, characterization of surface alteration layers, geochemistry of effluent solutions, and characterization of leached layers, is available online at [www.geosociety.org/pubs/ft2012.htm](http://www.geosociety.org/pubs/ft2012.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 3.** Typical evolution of Ca and Si fluxes ( $\text{mol cm}^{-2} \text{s}^{-1}$ ) in outflow solution during wollastonite dissolution experiment performed in Teflon flow-through reactors (Ca/Si ratios versus time in inset). Initial solution pH of 1.5. (Detailed values of composition are in Table DR1 [see footnote 1].)

reaction times a full coverage by a Si-rich surface layer can significantly affect dissolution kinetics. However, our study shows that at decreasing pH values, less-reactive faces begin to participate in the wollastonite dissolution process, as shown by FESEM. Because, like wollastonite, most abundant multicomponent rock-forming minerals are anisotropic, a similar pH-dependent effect should be expected. Furthermore, because most of these minerals form Si-enriched altered surface layers, the initial exponential decrease in dissolution rates typically shown during acid dissolution may be explained, at least in part, by the decrease in the reactive surface area associated with the progressive coverage of the dissolving mineral surface.

It is interesting that fluxes of dissolved elements during wollastonite dissolution experiments show short-term, coupled periodic oscillations superimposed on the longer term overall trends (Fig. 3). Similar findings have been made for other minerals showing nonstoichiometric dissolution (such as dolomite; data not shown), thus suggesting that they do not simply result from errors in the measurements, but are due to a more fundamental process. To our knowledge, these oscillations have not been reported before during similar experiments, mainly because the oscillation period (several minutes) is significantly shorter than typical sampling times. We propose that the observed temporal evolution of the elemental fluxes can be explained assuming that the initial concentration gradient existing at the mineral-solution boundary layer will evolve due to the precipitation of secondary phases,

thereby varying the exposed reactive surface area of the mineral, as well as due to element diffusion toward the bulk solution. After a step of congruent dissolution and subsequent formation of a surface precipitate (reflected in a decrease in the measured elemental fluxes), diffusion from the boundary layer of fluid to the bulk solution results in the boundary layer becoming undersaturated with respect to the precipitating phase. This leads to its partial dissolution, increasing the flux of Si to the solution. Furthermore, this in turn increases the reactive surface area exposed to the solution and thereby fosters Ca release. This is confirmed by AFM observations showing that the newly formed surface layer continuously precipitates and redissolves as the dissolution of the wollastonite substrate progresses, as observed in the case of dolomite (Urošević et al., 2012). Furthermore, this is clear evidence of the coupling between dissolution and precipitation processes in these systems. These considerations lead us to question whether a steady state may be reached in our system (and others), and what would be its nature.

## IMPLICATIONS

We can speculate that the potential importance of our results extends to other multicomponent silicates or glasses in contact with acidic,  $\text{CO}_2$ -rich solutions. Thus, they may have implications for many Earth surface geochemical processes, including weathering and subsequent soil formation, evolution of climate, and the composition of the atmosphere and oceans, as well as important environmental and technological

issues such as the deterioration of concrete and building stone, possible mobilization of nuclear wastes, and CO<sub>2</sub> sequestration. Demonstration that these layers form as a consequence of an interface-coupled dissolution-precipitation process is critical for the correct implementation of such a process in the formulation of codes aimed at quantifying reaction rates. Furthermore, the formation of surface layers on dissolution of multicomponent minerals and glasses may have a significant effect on their reactivity. The fact that altered surface layers developed on silicate minerals are typically made up of a porous amorphous silica phase provides an excellent medium for the diffusion-controlled growth of secondary phases such as phyllosilicates (Zhu et al., 2006), where the actual silica in the surface layer may be eventually incorporated. This may help explain the formation of protective coatings on silicate minerals weathered in nature (Nugent et al., 1998; Hellmann et al., 2012), and contribute to the understanding of the apparent discrepancy, in orders of magnitude, between field and laboratory dissolution rates (Zhu et al., 2006).

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