Unifying natural and laboratory chemical weathering with interfacial dissolution-reprecipitation: a study based on the nanometer-scale chemistry of fluid-silicate interfaces

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ABSTRACT

Chemical weathering reactions of rocks at Earth’s surface play a major role in the chemical cycle of elements, and represent one of the major abiotic sinks for atmospheric CO₂. Because natural chemical weathering reactions occur at different and more complex chemical conditions than laboratory-based weathering experiments, it has long been thought that the underlying fluid-mineral interaction mechanisms are different. In contrast to most previous studies that have relied on ion, electron, and X-ray beam techniques (characterized by µm to mm lateral spatial resolution) to obtain chemical depth profiles of altered mineral surfaces, we have used high resolution and energy filtered transmission electron microscopy (HRTEM, EFTEM) to study mineral-fluid interfaces using TEM foils cut directly across the reaction boundaries. This allowed measurements to be made directly in cross section at nanometer to sub-nanometer-resolution. Our measurements of the surface chemistry and structure of a large suite of laboratory-altered and field-weathered silicate minerals indicate the general presence of surface layers composed of amorphous, hydrated silica. In each case, the boundary between the parent mineral and the corresponding silica layer is characterized by sharp, nanometer-scale chemical concentration jumps that are spatially coincident with a very sharp crystalline-amorphous interfacial boundary. TEM, atomic force microscopy (AFM), and aqueous chemistry data suggest that the surface layers are permeable to fluids. Taken together, our measurements are not in agreement with currently accepted models for chemical weathering, in particular the leached layer theory. Most importantly, our data provide critical evidence for a single mechanism based on interfacial dissolution-reprecipitation. This concept not only unifies weathering processes for the first time, but we also suggest that nanoscale-surface processes can have a potentially negative impact on CO₂ uptake associated with chemical weathering. The results in this study, when combined with recently published research on fluid-assisted mineral replacement reactions, supports the idea that dissolution-reprecipitation is a universal mechanism controlling fluid-mineral interactions (Putnis and Putnis, 2007). Based on this we propose the existence of a chemical weathering continuum based solely on the interfacial dissolution-reprecipitation mechanism.
Keywords: chemical weathering, dissolution-reprecipitation, silicate minerals, transmission electron microscopy (TEM), fluid-solid interfaces, CO₂ sequestration

1. Introduction

1.1. Overview of laboratory and natural chemical weathering processes

Chemical weathering reactions control in large part the chemical cycle of elements in surface and near-surface environments, chemical denudation rates, the quality of potable water resources (e.g., arsenic in SE Asia), soil formation and nutrient availability, and ore genesis. Moreover, the two major abiotic processes that regulate atmospheric CO₂ drawdown are CO₂ uptake in oceans and CO₂ consumption by chemical weathering reactions. Geological radwaste and CO₂ storage are just two examples where weathering processes play a key role in current environmental issues. Because of its global and multidisciplinary importance, chemical weathering has been the subject of laboratory research for more than a century now. However, there is a long-standing assumption that the mechanism(s) controlling weathering in the field are far different from those that operate in simple laboratory experiments. For example, Hochella and Banfield (1995) conceptualize these differences in terms of a broad continuum: one pole is defined by laboratory dissolution reactions (and in some cases natural weathering) that start out being incongruent due to preferential ion exchange, evolve to congruency, and are characterized by the general suppression of secondary phases; at the other end of the continuum are natural weathering reactions that are inherently incongruent overall and occur via direct structural transformation of primary into secondary mineral phases.

In this study we resolve this long-standing controversy by demonstrating that despite differences in environmental and chemical complexity, both field and laboratory weathering are controlled by a single unifying mechanism: interfacial dissolution-reprecipitation. Here, reprecipitation refers strictly to an interfacial process that leads to the formation of amorphous hydrated silica layers on primary silicate mineral surfaces, irrespective of the degree of chemical saturation of the associated bulk solutions with respect to all silica polymorphs. Subsequent precipitation of oxides, oxyhydroxides, and clays from chemically saturated bulk solutions, while evidently playing an important role in weathering processes, are not
specifically addressed in this study. Chemical weathering experiments in the laboratory, both
in the past and at present, generally involve chemically dilute, undersaturated solutions at
temperatures below 100 °C in acid to circum-neutral pH solutions (see extensive compilation
in Bandstra et al., 2008; older compilations in Blum and Stillings, 1995; Brantley, 2003). In
laboratory studies at acid to circum-neutral pH, multi-cation silicates are characterized by the
apparent non-stoichiometric, preferential release of interstitial cations, as well as Al (Garrels
and Howard, 1957; Wollast, 1967; Luce et al., 1972; Paces, 1973; Chou and Wollast, 1985;
Muir et al., 1989, 1990; Inskeep, 1991; Hellmann, 1994, 1995; Schweda et al., 1997; Lee et
al., 2008; Kameda et al., 2009), leading to the formation of chemically distinct surface altered
zones, commonly called ‘leached layers’. Based on both aqueous data and surface sensitive
analytical techniques, it is thought that the leached layer mechanism is primarily controlled by
two separate processes operating simultaneously (schematically shown in Fig.1):

a. charged-balanced, ion exchange via solid-state volume interdiffusion of cations
from the mineral with protons (H⁺ or H3O⁺) from the bulk solution (e.g., Garrels and
Howard, 1957; Wollast, 1967; Luce et al., 1967; Paces, 1973; Muir et al., 1988, 1989;
Casey et al., 1988; Petit et al., 1989; Casey and Bunker, 1990; Banfield et al., 1995;
Hellmann, 1997; Hellmann et al., 1997; Schweda et al., 1997; Yang et al., 2009)
(possibly accompanied by the inward diffusion of water- see Petit et al., 1990)
b. chemical hydrolysis reactions release Si and O into the bulk solution at the outer
interface (Casey et al., 1988, 1993; Petit et al., 1989; Banfield et al., 1995; Hellmann,
1995; Schweda, 1990; Yang et al., 2009).

The rate of retreat of the parent mineral at the inner interface of the leached layer is controlled
by process a, whereas process b controls the rate of retreat of the external interface. Once
rates a and b become equal, a steady-state thickness is achieved.
It is also postulated that leached layers can undergo molecular-scale reorganization,
such as repolymerization (also called recondensation) reactions of silanol groups (Casey and
Bunker, 1990; Arnold et al., 1992; Casey et al., 1993; Hellmann et al., 1997; Schweda et al.,
1997) created by the preferential release of cations (i.e.,
\[ \text{Si–OH} + \text{HO–Si} = \rightarrow \text{Si–O–Si=} + \text{H}_2\text{O} \], recrystallization (Banfield et al., 1995),
restructuring (Casey et al., 1993; Tsomaia et al., 2003), structural collapse (Paces, 1973), and
even porosity creation (Casey and Bunker, 1990). In particular, much work on restructuring processes in surface (altered) layers has been carried out in glass studies (Pederson et al., 1985; Bunker et al., 1988; Casey and Bunker, 1990; Cailleteau et al., 2008). In addition, silica back reactions, as well as readsorption of silica (Banfield et al., 1995), have also been proposed to occur within leached layers.

The more than 50 year-old leached layer theory remains the currently accepted concept for explaining the apparent non-stoichiometric chemical weathering of minerals, as well as glasses. It is interesting to note that the concepts of leached layer formation, as described in recent reviews of mineral and glass dissolution, have not strayed from the classical ideas detailed above (see e.g., Brantley, 2008; Ohlin et al., 2010). Nonetheless, a few studies of laboratory weathering have questioned this theory. To cite just one example, Teng et al. (2001), using X-ray reflectivity and AFM, attributed the apparent non-stoichiometry of orthoclase dissolution to the formation of a surface silica gel.

In contrast to laboratory studies, chemical weathering reactions of rocks on the Earth’s surface and near surface are noted for their chemical and environmental complexity. The chemical saturation states of natural waters and soil pore fluids are extremely variable (Stefánsson and Arnórsson, 2000; Maher et al., 2009). Moreover, the chemistry of natural aqueous solutions is complex, and can include the presence of free metal cations, ligand complexing agents, humic substances, and naturally occurring organic and inorganic acids (Drever, 2003). Mineral grains subject to weathering reactions also do not have pristine surfaces (as in laboratory experiments), since they are often covered with mineral coatings (Nugent et al., 1998; Kawano and Tomita, 2001; Dixon et al., 2002) or clay minerals (Banfield and Eggleton, 1990; Nugent et al., 1998; Zhu et al., 2006). In the critical zone, biota (Barker et al., 1998; Berner et al., 2003; Bonneville et al, 2009) can also adhere to and even penetrate mineral surfaces, thereby directly affecting the dissolution process.

Largely because natural chemical weathering is more complex, there is no unanimity with respect to an intrinsic mechanism (Nesbitt and Muir, 1988; Hochella and Banfield, 1995; Seyama and Soma, 2003; Zhu et al., 2006; see also Table 1 in Lee et al., 2008). Studies advocating leached layers show Si-rich, cation-depleted surface altered layers on naturally weathered minerals (Nesbitt and Muir, 1988; Mogk, 1990; Banfield and Eggleton, 1990;
Nugent et al., 1998; Kawano and Tomita, 2001; Zhu et al., 2006). Several of these studies document sigmoidal cation depletion profiles (Nugent et al., 1998; Nesbitt and Muir, 1988; Mogk, 1990; see also review by Chardon et al., 2006). Alternatively, other studies have failed to find unambiguous evidence for important surface alteration (i.e., very thin surface layers, estimated to be < 2-3 nm in thickness; e.g. Berner and Holdren, 1977; Teng et al., 2001; Lee et al., 2007, 2008), or revealing only clays and/or other neo-formed mineral coatings on the surface (Berner and Holdren, 1977; 1979; Banfield et al., 1995; Dixon et al., 2002). And finally, surface chemical weathering reactions, as well as water-rock interactions at elevated temperature and pressure conditions, can also occur by mineral replacement, which is defined as the direct replacement of a primary mineral by another mineral (Parsons, 1978; Banfield and Eggleton, 1990; Banfield et al., 1995; Lee and Parsons, 1998; Fiebig and Hoefs, 2002; Harlov et al., 2002; Harlov and Förster, 2003; Labotka et al., 2004; Perez and Boles, 2005; Geisler et al., 2007; see reviews in Hochella and Banfield, 1995; Putnis, 2009). Whether mineral replacement occurs directly by solid-state structural transformation, interdiffusion of cations with aqueous species, or surface chemical reactions may be a function of the sample investigated and the analytical technique applied, and therefore remains a subject of ongoing research.

In the present investigation we studied chemical weathering by examining the nanoscale changes in the structure and chemistry of altered silicate mineral surfaces using focused ion beam milling (FIB) to prepare electron transparent foils of uniform thickness across the reaction boundaries. This permitted the altered mineral surfaces to be structurally and chemically characterized directly in cross section using high resolution transmission electron microscopy (HRTEM), energy filtered TEM (EFTEM), high angle annular dark field scanning TEM (STEM-HAADF), and energy dispersive X-ray analysis (EDX). Crucial to our study was EFTEM since it provided chemical maps at 1 nm-spatial resolution.

While many previous studies have used TEM to document structural modifications of altered mineral surfaces (e.g. Banfield and Eggleton, 1990; Casey et al., 1993; Banfield et al., 1995; Kawano and Tomita, 2001; Zhu et al., 2006; see also review in Hochella and Banfield, 1995), the concomitant changes in chemistry of the surface altered layers were not integrally measured with nanometer spatial resolution, or alternatively, were measured indirectly with
surface incident ion, electron, or X-ray beam techniques that have intrinsically poor lateral spatial resolution (i.e., µm to mm-scale beams). The use of these techniques can result in artificially broadened cation depth profiles (Hellmann et al., 2003; 2004), which in turn can lead to erroneous interpretations with respect to mineral weathering mechanisms. To circumvent these analytical problems, Hellmann and co-authors (2003) used a new methodology, based on a combination of ultramicrotomy and EFTEM, to measure in cross section the near-surface chemistry of surface layers on a feldspar. Their surprising and unique set of nano-scale chemical maps and profiles led them to propose that the silica surface layers could best be explained by an interfacial dissolution-reprecipitation mechanism. Furthermore, their results were inconsistent with interdiffusion and leached layer formation.

1.2. Development of dissolution-reprecipitation concept

In the early 50’s, significant research was being devoted to understanding feldspar-feldspar transformation reactions. For example, Goldsmith and Laves (1954) studied the isochemical conversion of microcline (triclinic; disordered distribution of Al, Si) to sanidine (monoclinic, ordered distribution of Al, Si). They argued for a ‘classical’ solid-state diffusive transfer of Si and Al at dry conditions and elevated temperatures, but alternatively, at hydrothermal conditions, they proposed a process comprising the dissolution of microcline and reprecipitation of sanidine. In another study, Wyart and Sabatier (1958) showed that the hydrothermal alteration of labradorite in KClaq led to the formation of distinct, crystallographic domains of orthoclase and anorthite, which requires the rapid migration of Al and Si. To explain this, these authors hinted at the possibility of a dissolution-reprecipitation process, but in the end, they argued for a solid-state diffusion process catalyzed by water. Nonetheless, these authors were perplexed at how water could have this effect without penetrating the crystal structure. Research on oxygen mobility in hydrothermally-altered K-feldspars led Mérigoux (1968) to propose that dissolution-reprecipitation best explains the rapid incorporation of 18O into a secondary Na-feldspar phase.

The pioneering research of O’Neil and Taylor (1967) provided a real conceptual breakthrough in this domain- they suggested interfacial dissolution-reprecipitation as an alternative mechanism to ‘atom-for-atom exchange by solid state diffusion’ to explain K feldspar-Na feldspar mineral replacement under hydrothermal conditions. Most importantly,
they argued that a ‘reaction front sweeps through each crystal grain’, and that the reaction
front is associated with a thin fluid film at the interface between the exchanged and
unexchanged feldspar. Parsons (1978) suggested that the crystallographic transformation of
orthoclase to microcline in plutonic rocks may also occur via the mechanism proposed by
O’Neill and Taylor (1967).

Nonetheless, until recently this mechanism has remained an unproven concept because
sharp chemical fronts could not be measured analytically at high spatial resolution. However,
this changed with the advent of new nano-scale chemical imaging techniques, in particular
EFTEM and EELS, as well as high-resolution (50-100 nm) isotope tracer $^{18}$O
measurements. This has led to far-reaching advances in the understanding of fluid-solid
interfacial processes occurring both in the laboratory and in the field during chemical
weathering of minerals (Hellmann et al., 2003, 2004; Daval et al., 2011; King et al., 2011)
and mineral replacement reactions (e.g. Fiebig and Hoefs, 2002; Lobatka et al., 2004; Putnis
and Mezger, 2004; Putnis et al., 2005; Harlov et al., 2002, 2005; Harlov and Förster, 2003;
Geisler et al., 2007; Hövelmann et al., 2010; see also extensive reviews in Putnis, 2002,
2009). Even the glass dissolution field has seen important advances with the application of
these new techniques (Geisler et al, 2010).

The significance of the present study is that it extends the preliminary results of
Hellmann and co-workers (2003, 2004) with an investigation of a large suite of silicate
minerals, altered both in the laboratory and under natural conditions. One of the most
important results is that we find unambiguous evidence for just one mechanism, irrespective
of whether chemical weathering occurs in the laboratory or in the field. Thus, our findings
serve to unify chemical weathering with a single mechanism, interfacial dissolution
reprecipitation. Very importantly, the results we present ask for a re-interpretation of a great
deal of existing work on chemical weathering, and demand a critical re-evaluation of the old
interdiffusion-leached layer model and the general concept of how chemical weathering
works.

To avoid confusion for the reader, throughout the remainder of the manuscript we use
the term ‘surface layers’ to specifically imply the in situ formation of secondary phases (i.e.
amorphous silica) on primary mineral surfaces by interfacial dissolution-reprecipitation.
Alternatively, use of the term ‘surface altered layers’ refers to the chemical and structural modification of the original mineral lattice, resulting in ‘leached layers’. And finally, when no specific mechanism is implied, we use the term ‘surface (altered) layers’.

2. Materials and Methods

2.1. Laboratory chemical weathering

Using laboratory dissolution experiments we investigated an extensive group of primary silicate minerals having different compositions and structures: the 3-D framework tectosilicates: plagioclase feldspar series (albite: NaAlSi3O8, labradorite: Na0.39Ca0.59Al1.59Si2.41O8, anorthite: CaAl2Si2O8); single chain inosilicates: diopside: CaMg(SiO3)2, wollastonite: CaSiO3; nesosilicates (isolated SiO4 tetrahedra): pyrope garnet: Mg1.982 Ca0.372 Fe0.668 Al1.812 Cr0.118 Si3.023 O12, forsterite olivine: Fe0.168 Mg1.796 SiO4. Cleaved mineral samples, on the order of several mm², were hydrolyzed at ambient temperature (~25 °C) and 1 bar over periods of 2-4 weeks in flow-through systems at far-from-equilibrium conditions; the majority was altered in acidic pH solutions (HCl/H2O) at pH 1-3. In general, acid pH conditions were privileged in order to create surface (altered) layers suitably thick for study. Chemical weathering at acid pH conditions (pH 1-3) occurs in many natural environments, such as acid mine drainage sites, hydrothermal volcanic terranes, soils in water sheds subject to acid rainfall, and geological CO2 storage and sequestration sites. Labradorite feldspar was dissolved over a wider range in pH, from 1 to 13 (KOH/H2O used at basic pH). Surface (altered) layers developed on labradorite at all pHs, but were thinner in the neutral to basic pH range. The cation release rates were measured as a function of time during all of the mineral dissolution experiments. The bulk solutions were always highly undersaturated with respect to potential secondary Si and Al-bearing phases.

2.2 Aqueous chemistry

Aqueous samples were collected at discrete time intervals for all flow experiments. Cation concentrations were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and colorimetry (Si only). All of the minerals displayed initial periods of apparent non-stoichiometric cation release over the first 1-10 days, except for...
wollastonite where dissolution remained non-stoichiometric over the duration of hydrolysis (up to 24 d). Steady-state rates were achieved in all runs. The concentration data were converted to individual cation release rates that were stoichiometrically-normalized with respect to each parent mineral (Hellmann, 1994, 1995). These release rates reflect the global dissolution process (net sum of source and sink processes), and are not always equal to the true intrinsic rate of detachment from the original mineral structure. For each mineral, the cation-specific release rates provided complementary information on the relative thickness and composition of the surface (altered) layer. Solution saturation states (Gibbs free energy of reaction) with respect to the primary silicate minerals and possible secondary phases were calculated with the code EQ3NR (Wolery, 1992), using the LLNL ‘composite’ (com) database and the B-dot equation for activity coefficients of aqueous species. Future publications devoted to each individual mineral will include the corresponding aqueous data and derived rates.

2.3 Sample preparation

Samples were rinsed in alcohol and dried under ambient conditions after each experiment, or after collection in the field. Focused ion beam milling (FIB) was used to prepare electron transparent foils of uniform thickness, such that the altered mineral surfaces could be structurally and chemically characterized directly in cross section using high resolution TEM techniques. The specific protocol that we used consisted of a. sputter coating a protective 50 to 80 nm-thick layer of carbon or gold on the predominant altered cleavage surface, b. in situ preparation of an electron transparent TEM foil (~80 nm thick) by FIB milling perpendicular (vertical) to the altered surface (for more details on FIB, see Wirth, 2004, 2009), c. placement of foil on holey carbon TEM grid.

An important issue with FIB-TEM foil preparation is the implantation of Pt and Ga into the specimen, which potentially creates artifacts (in particular, amorphization; see, e.g. Lee et al., 2007). We addressed this issue by preparing non-altered mineral specimens as controls to identify potential FIB-produced artifacts, such as amorphization or altered chemistry. In addition, routine Ga and Pt EDX line scans across thin surface (altered) layers (e.g. garnet, olivine, diopside) showed these elements to be merely present at the limits of detection.
Moreover, even with respect to the thinnest surface layers investigated in this study (≤ 5 nm, diopside and olivine), HRTEM and EFTEM/EDX, respectively, showed no evidence for local amorphization or changes in the chemistry in the unaltered parent mineral adjacent to the surface layer. Our aqueous chemistry results also provided an independent control on the chemistry and thicknesses of the surface (altered) layers. Based on these criteria, we are confident of the efficacy of the protective C and Au coatings used.

For each laboratory-altered mineral specimen, the FIB-prepared TEM foils were cut perpendicular to the indicated prominent cleavage or parting planes (number of individual specimens analyzed by TEM also indicated): albite {010}: 3; anorthite {010}: 1; labradorite {010}: 7; diopside {110}: 4; wollastonite {100}: 3; olivine {not determined}: 2; garnet {110}: 3. With respect to the naturally weathered K-feldspar {not determined}: 3 and serpentine-lizardite {not determined}: 5, we simply chose prominent flat (weathered) cleavage surfaces under an optical microscope; these same surfaces were then milled by FIB perpendicular to the surface to obtain the cross-sectional ultra-thin sections that were subsequently examined by TEM.

2.4. Solid-state analyses

On each FIB-prepared foil, five to ten different areas of the surface layer were investigated by TEM. Electron irradiation damage was mitigated by first orienting each sample and then recording images and data as fast as possible in adjacent pristine regions; EFTEM and EDX counting times were kept to a minimum to avoid electron beam induced diffusion of mobile elements. Because of the large scope of the study, a total of 4 TEM/laboratories were used (moreover, the choice of instruments was dictated by the technical characteristics of each TEM, in particular, TEM-FEG was used for high resolution EDX line scans): GFZ Potsdam- Philips CM 200 (LaB₆) operated at 200 kV, EDAX Si-Li detector with ultra-thin window; CEA LETI-Minatec Grenoble: Jeol JEM 2010FEF (FEG) operated at 200 kV, 1 nm FWHM spot size, EDX detector: Oxford-Inca Si-Li analyzer with an ultra-thin window; CEA Grenoble- Jeol 3010 (LaB₆) operated at 300 kV, energy dispersion = 0.2 eV/channel, collection angle β = 6.5 mrad; INSA (CLYM) Lyon - Jeol 2010 (FEG) operated at 200kV, with EDX analyses based on 2.4 and 1.0 nm probe sizes using an Oxford-
Inca Si-Li analyzer with an ultra-thin window. FEG-SEM-EDX analyses (serpentine only) were obtained using a Hitachi S-5500 operated at 30 kV (EDX Noran ThermoScientific silicone drift detector), CEA-LETI Grenoble. EFTEM chemical images and EEL spectra were obtained with a post-column Gatan GIF (GFZ, CEA Grenoble) or an in-column Omega (CEA-LETI-Minatec) imaging filter, using the Ca $L_2,3$, O $K\alpha$, K $K\alpha$, Al $K\alpha$, Mg $K\alpha$, and Si $K\alpha$ edges.

EFTEM chemical mapping was based on either the two-window (jump ratio) or three-window (elemental map) method (for details, see Hofer et al., 1997). The energy windows for pre-edge and post-edge images were based on standard settings in the Gatan Digital Micrograph software (typically with a 20 eV slit width). Thickness maps were determined by EELS to verify approximate uniform thicknesses of the FIB thin sections in the areas of interest. All elemental TEM-EDX line scans were obtained using $K\alpha$ X-ray intensities.

Atomic force microscopy (AFM) was based on a Digital Instruments Dimension 3100, ENSEEG (Univ. Grenoble); images were acquired in tapping mode using a Nanosensors Pointprobe-Plus Silicon SPM sensor. SIMS elemental depth profiles were obtained with a Cameca IMS 3f instrument (ASU) using an $^{16}$O$^+$ primary ion beam, 25 nA beam current, 12.6 kV accelerating voltage, 125x125 µm$^2$ raster area, and ion beam incident at 30° to the sample normal.

2.5. Naturally weathered samples collected in field

We chose to investigate two end-member rock types, a granite and a serpentinite. The granite, with an original provenance from the Mt. Blanc granitic pluton, is a glacial erratic boulder that may have been deposited during the last deglaciation on a limestone plateau (Pte. Andey: 46.039 °N, 6.426 °E, 1600 m elevation; Haute Savoie, France). The boulder has an apparent $^{10}$Be exposure age of 14.7±3.7 ka (note that the true age may be considerably greater depending on assumed surface erosion rate). For this study, we chose to specifically investigate naturally weathered potassium feldspars, which are the primary mineralogical component of these granites. Feldspar grains were either extracted from the surface of the boulder (subaerial weathering) or from a depth of ~20 cm in the underlying adjacent soil. The serpentinite sample was collected in the southern part of the Belledonne Massif (45° 07' 55"
3. Results

The most important finding pertaining to all of the laboratory-weathered samples is that the TEM-measured depth profiles show that both the outer and inner interfaces of the surface layers are characterized by sharp (nm-scale), step function-like changes in cation concentrations. The nm-sharp chemical gradients at the inner interfaces are spatially coincident with almost atomically sharp (<2nm) crystalline-amorphous structural transitions. TEM showed all surface layers to be amorphous, less dense, and chemically distinct (silica-rich) compared to the parent minerals, with thicknesses varying from ~5 to 870 nm. In general, the nesosilicates developed the thinnest surface alteration, but in addition, there were significant differences in thickness within single structural groups, e.g. tectosilicates: labradorite >> albite > anorthite; single chain inosilicates: wollastonite >> diopside; nesosilicates: garnet > olivine. This quantification does not take into account the potential effect of anisotropic dissolution with respect to different crystal faces for a given mineral.

Figures 2A-C show nanoscale images and chemical maps obtained for surface (altered) layers that formed on three structurally different minerals after weathering in the laboratory: labradorite, wollastonite, and pyrope garnet. The thick surface layer that formed on labradorite at acid pH displays typical features common to all samples: a crystal lattice terminating abruptly at an amorphous surface layer (Fig. 2A-i, ii) enriched in silica and depleted in other cations (e.g. Ca, Al- see EDX profiles in Fig. 2A-i); the EFTEM profiles reveal very sharp chemical gradients (Ca, Fig. 2A-iii; Si, Fig. 2A-iv). The chemical gradients of Ca and Si are opposite in sign, due to Ca depletion vs. Si enrichment. Hydrogen (Fig. 2A-i inset) and boron (not shown) SIMS depth profiles in the altered layer provide evidence that aqueous species from the bulk fluid permeated all the way to the pristine mineral interface. Alteration at circum-neutral pH (4.0 and 5.7) resulted in much thinner surface layers (≤25 nm). The other feldspars, namely albite and anorthite, possessed significantly thinner surface layers; e.g., those on anorthite were only 2-5 nm in thickness.
Minerals from the other structural groups developed surface layers with additional chemical and structural complexity. Altered wollastonite reveals high porosity throughout the thick surface layer; there is also evidence for localized physical separation of the surface layer from the parent mineral (Fig. 2B-i), indicating a lack of structural continuity between the two phases. In Fig. 2B-i the EFTEM profiles of Ca and Si reveal, respectively, depletion and enrichment associated with very sharp chemical interfaces. Figure 2B-ii shows an atomic force microscopy (AFM) image of the surface of the precipitated silica. The botryoidal topography and large pores are consistent with elevated internal porosity. Diopside alteration produced 10-20 nm-thick Ca and Mg-depleted surface layers. The most complex surface layers formed during garnet alteration. Although thin, they are characterized by three parallel zones of different density that correlate with generalized cation depletion and Si enrichment, but in addition, also correlate with two narrow zones of localized cation enrichment (inset, Fig. 2C). Olivine surface layers were less complex, and relatively thin (\( \leq 5 \) nm).

While the presence of amorphous silica-rich surfaces on naturally weathered silicate minerals is well documented (Banfield and Eggleton, 1990; Kawano and Tomita, 2001; Zhu et al., 2006), we applied the same high spatial resolution chemical mapping techniques to test whether sharp and coincident chemical and structural interfaces also characterize naturally weathered mineral surfaces. Given that the variety of natural weathering environments is tremendously large, for practical reasons we restricted our study to two end-member lithologies (granite, serpentinite) exposed to three distinct weathering environments: mineral-atmosphere, mineral-soil, and mineral-biota.

Several potassium feldspar (\( \text{KAlSi}_3\text{O}_8 \)) grains from the granite that had undergone either subaerial or intra-soil weathering were investigated. Typical results from both environments show that the feldspar crystal lattice ends abruptly at an amorphous surface layer characterized by a spatially coincident and nm-sharp change in chemistry (K depletion). In Fig. 2D the \( \sim 50 \) nm-thick surface layer is composed of two parallel zones with different densities and K concentrations. In contrast to the laboratory-weathered minerals, this thin amorphous layer is overlain by a variably thick (up to 1-2 \( \mu \)m, not shown) over-coating composed of a silica-rich, amorphous matrix containing abundant phyllosilicates.
We also investigated a biota-mineral interface between a several mm-thick, epilithic lichen species (*Rhizocarpon geographicum* gr.) growing subaerially on a serpentinite matrix composed primarily of polycrystalline serpentine (lizardite, Mg$_3$Si$_2$O$_5$(OH)$_4$). Between the lichen and the mineral matrix is a distinct ~150-200 nm-thick amorphous surface layer. The sharp structural boundary between the polycrystalline serpentine and the amorphous layer precisely correlates with an equally sharp change in the chemistry of the layer characterized by both an abrupt increase in Si and depletion in Mg (Fig. 2E).

4. Discussion

The TEM measurements of the field weathered K-feldspar and serpentine demonstrate the natural occurrence of amorphous Si-rich and cation-depleted surface layers having spatially coincident and nm-sharp structural and chemical interfaces. This is indicative of the same weathering mechanism as in the laboratory. The altered K-feldspar revealed additional complexity due to the presence of a thick over-coating on top of the silica layer, which we interpret as a consequence of larger-scale, peripheral chemical weathering (involving abiotic and biotic processes) operating over very long time scales in the presence of fluids at variable, and most probably higher, solution saturation states. These kinds of µm-thick secondary coatings were never observed in our laboratory-weathered samples. In the context of this study, the influence of biota on the overall chemical weathering process remains an open question, as there is no obvious parameter that allows us to discriminate between the effects of abiotic subaerial weathering and lichen-promoted weathering due to, for example, secretion of organic acids.

4.1. Diffusion vs. interfacial dissolution-reprecipitation

The field and laboratory surface layers we investigated never displayed the smoothly varying, sigmoidal cation concentration profiles that would be predicted for leached layers created by interdiffusion (Fig. 1). An interdiffusion-leached layer mechanism is not compatible with surface layers that display nm-scale step function-like changes in cation concentrations. To confirm this, we modeled the binary interdiffusion of protons and cations using a standard volume interdiffusion equation, based on semi-infinite geometry with a planar, non-stationary (i.e. retreating) fluid-solid interface:
\[
\frac{\partial C_H}{\partial t} = \frac{\partial}{\partial x} \left( D^* \frac{\partial C_H}{\partial x} \right) + a \frac{\partial C_H}{\partial x} = 0 \quad (1).
\]

In the above expression \( C_H \) and \( C_{\text{cation}} \) are the normalized concentrations of the inward (H\(^+\) or \( \text{H}_3\text{O}^+ \)) and outward diffusing species (note that \( C_H = 1 - C_{\text{cation}} \)), \( D^* \) is the binary interdiffusion coefficient, \( x \) is the depth into the altered layer measured from the fluid-solid interface, \( a \) is the rate of retreat of the fluid-solid (outer) interface (based on experimental rate of Si release), and \( \partial C / \partial t = 0 \) holds because steady-state conditions were achieved during the experiments. The purpose of the diffusion modeling was to generate theoretical binary cation depletion profiles and compare these to the measured cation depletion profiles on altered labradorite and wollastonite. These minerals were chosen for comparison since they had the thickest surface (altered) layers.

### 4.2. Binary interdiffusion of univalent cations with protons

The binary interdiffusion coefficient is defined as:

\[
D^* = \frac{D_H D_{\text{cation}}}{C_H D_H + C_{\text{cation}} D_{\text{cation}}} = \frac{D_H}{1 + bC_H} \quad (2).
\]

where \( b = (D_H/D_{\text{cation}}) - 1 \). To allow for additional dependence of \( D^* \) on chemical and physical changes in the altered layer, \( D^* \) can be modified with a depth-dependent structural factor (\( \alpha \)) (Lanford et al., 1979; Hellmann, 1997), such that \( D_\alpha \), a modified form of the interdiffusion coefficient, can be defined as

\[
D_\alpha = (1 + \alpha C_H)D^* \quad (3).
\]

Figure 3A shows how the interdiffusion coefficient \( D_\alpha \) varies in a highly non-linear manner as a function of cation concentration (i.e. proportional to depth) in the altered layer; this non-linearity reflects much higher diffusion rates at the outer fluid interface compared to the inner interface, a condition that is consistent with the elevated surface micro-porosity we observed by atomic force microscopy, and as indicated by the large uptake of H (see SIMS profile, Fig. 2A-i, inset) adjacent to the fluid-solid interface. Theoretical interdiffusion depth profiles can be obtained by substituting the expression \( D_\alpha \) (Eqn. 3) for \( D^* \) in Eqn. 2; the modified form of \( D^* \) is then substituted into the general diffusion expression (Eqn. 1), which is then solved with the appropriate boundary conditions.
Figure 3B portrays representative cation diffusion profiles based on $\alpha = -0.9$; this value was chosen since it resulted in depth profiles with steep chemical gradients, analogous to those measured. The three sets of diffusion profiles correspond to $a = 10^{-2}$ Å s$^{-1}$ (measured release rate of Si in solution) and values of $D_H = 10^{-16}, 10^{-15}, 10^{-14}$ cm$^2$s$^{-1}$, and for each value of $D_H$, 4 diffusion profiles were calculated corresponding to different ratios of $D_H/D_{cation}$ ($10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}$; note that $D_H/D_{cation} \ll 1$, a condition verified in many glass corrosion studies (e.g. Smets and Lommen, 1982; and references therein). These particular values of $\alpha$, $D_H$, and $D_H/D_{cation}$ were chosen to produce (univalent) cation diffusion profiles that bracket the 400 to 500 nm-thick surface layers that formed on labradorite reacted at acid pH. The profiles based on $-1 < \alpha < -0.9$ are almost indistinguishable from those shown; profiles using $\alpha > -0.9$ reveal an increasing shift to greater depths and less steep (wider) chemical gradients (hence our choice of $\alpha = -0.9$). Overall, the diffusion profiles in Fig. 3B show the influence of the various parameters listed immediately above; in addition, they serve to clarify certain aspects of the binary interdiffusion profiles for di- and trivalent cations discussed below.

Because we were not able to measure the Na profiles in the altered labradorite (due to electron beam migration of Na), a direct comparison with the theoretical univalent cation diffusion profiles in Fig. 3B was not possible. We assumed, however, that the Na profiles should be identical to those of Ca and Al that were measured by EDX and EFTEM (Figs. 2A-i, iii). We made this assumption because the depths of cation depletion in the present study are in perfect accord with those measured at pH 1 on labradorite in Schweda et al., 1997. Moreover, both studies used the exact same starting material (we thank P. Schweda for the pristine labradorite samples). Because Schweda and co-workers used SIMS, their results also show Na profiles, which are identical to the other depleted-cation profiles in their study.

4.3. Binary interdiffusion of cations ($z = +1,+2,+3$) with protons

The modeling of binary proton-multipvalent cation interdiffusion is more difficult due to the complexity of the $D^+$ term, and thus the existence of an analytical solution remains somewhat speculative. In order to calculate (binary) multi-valence cation (M) depth profiles ($M^{z+}$, with $z = 1, 2, 3$), a numerical solution was developed. Equation 1 was first integrated assuming steady-state conditions and using the previously mentioned boundary conditions, which leads to the following equation:
\[ a = D^* \left( \frac{\partial C}{\partial x} \right) + aC \]  

This equation was then discretized. For an infinitely small interval \( \Delta x \), Eqn. 4 becomes:

\[ C_{i+1} = a \times \Delta x \times (1 - C_i) / D^*_i + C_i \]  

where \( C_i \) is the concentration of \( M^{z+} \) at depth \( x \), \( C_{i+1} \) the concentration at depth \( x + \Delta x \), and the proton-cation \( (M^{z+}) \) interdiffusion coefficient is given by:

\[ D^*_i = \frac{D_{M^{z+}} \cdot D_H ((z-1)C_i + 1)}{z^2 D_{M^{z+}} C_i + D_H (1 - C_i)} \]  

In the relation above, \( D_H \) and \( D_{M^{z+}} \) represent, respectively, the diffusion coefficients of \( H^+ \) and \( M^{z+} \). As was the case for univalent cation interdiffusion, we modified the interdiffusion coefficient with a depth-dependent structural factor, which leads to

\[ D'_i = \left( \frac{D_{M^{z+}} \cdot D_H ((z-1)C_i + 1)}{z^2 D_{M^{z+}} C_i + D_H (1 - C_i)} \right) \times (1 + \alpha (1 - C_i)) \]  

We checked our numerical solutions with the cation depth profiles for proton-univalent cation interdiffusion (Fig. 3B), for which an analytical solution exists.

The modeled cation depth profiles \( (M^{z+}, z = 1, 2, 3) \), shown in Fig. 3C, are based on \( D_H = 10^{-16}, 10^{-15}, 10^{-14} \text{ cm}^2\text{s}^{-1}, D_H/D_{\text{cation}} = 10^{-3}, a = 10^{-2} \text{ Å s}^{-1} \), and \( \alpha = -0.9 \). These values were chosen to facilitate comparison with the Ca and Al depletion profiles measured for laboratory-altered labradorite. Examination of the modeled diffusion profiles reveals that as \( D_H \) increases from \( 10^{-16} \) to \( 10^{-14} \text{ cm}^2\text{s}^{-1} \), the cation depth profiles increasingly diverge from one another as a function of valence. The divergence of the diffusion profiles indicates that the depths of cation depletion depend on the valence (depths increase with decreasing valence). This effect is minor at \( D_H = 10^{-16} \), but becomes much more pronounced with increasing values of \( D_H \) (e.g. \( D_H = 10^{-14} \text{ cm}^2\text{s}^{-1} \)). Taking the case of \( D_H \geq 10^{-14} \text{ cm}^2\text{s}^{-1} \), the depth of depletion of \( M^{z+} (z = 1) \) is greater than that of \( M^{z+} (z = 3) \). On the other hand, for a given value of \( D_H \), the
cation valence does not significantly affect the chemical gradients of the cation depth profiles. Note that in most cases, by simply changing the value of $a$ (Eqn. 1), cation depth profiles simulating surface altered layers on other minerals are easily derived in the same manner- e.g. wollastonite.

Basing a comparison specifically on labradorite surface alteration, the theoretical binary interdiffusion profiles for $M^{z+}, z=1, 2, 3$ in Fig. 3C can be compared to the 400 nm-thick Ca and Al cation depletion profiles that we measured by EFTEM and EDX (Fig. 2A-i, iii). Two points can be made based on these figures:

a. the chemical gradients of the diffusion profiles significantly exceed those measured by EFTEM and EDX, which are sharp on a nanometer-scale
b. the modeled binary diffusion profiles indicate a dependence of the depth of cation depletion on cation valence, and yet the measured Ca and Al depth profiles show equal depths of depletion

These two points thus show that cation interdiffusion is not consistent with our measured cation depletion profiles. Theoretical diffusion profiles corresponding to ≥500 nm-thick near-surface alteration produced during wollastonite hydrolysis yielded similar results and conclusions.

So far we have only considered individual interdiffusion couples for cations of various valences (Fig. 3c). Binary interdiffusion modeling is perfectly adapted to such simple minerals like wollastonite or olivine, as they have only one type of exchangeable cation (i.e., valence +2). On the other hand, more complex silicate minerals containing multivalent cations (e.g. Na$^{+1}$, Ca$^{+2}$, Al$^{+3}$ in labradorite) may behave differently, given that cations with different valences will interdiffuse simultaneously with protons. The question then becomes whether simultaneous, multi-cation interdiffusion will produce the same diffusion profiles that characterize individual binary interdiffusion profiles. The exact response to this question is unknown, but we would expect that simultaneous diffusion profiles would be steeper than their binary counterparts; in addition, the valence should still play a role in terms of their relative diffusion rates (i.e. the higher the valence, the slower the diffusivity- this yielding shallower depths of cation depletion). Solving the appropriate diffusion equations to account...
for simultaneous interdiffusion is far from trivial, and to best of our knowledge, has not yet been developed for leached layers.

4.4. General conclusions of diffusion modeling

In general, the various binary diffusion scenarios that we present produce smooth, sigmoidal cation depletion profiles (depletion depths of 100-1000 nm), with concentration gradients having widths of many tens to hundreds of nanometers, which is significantly greater than those that we measured. Diffusion modeling reveals that \( \alpha \), in conjunction with \( D_{\text{H}} \), are the two most important parameters that control both the depths and the gradients of cation depletion. In addition, the cation valence influences the depth of depletion (depending on the value of \( D_{\text{H}} \)), but has less importance with respect to the chemical gradient. Based on the diffusion model that we used, we conclude that an interdiffusion mechanism is inconsistent with moderate to thick surface layers (> 20 nm) that display step function-like jumps in cation concentrations. Nor is the diffusion model compatible with our measurements that show no dependence of cation depletion depths on cation valence. Moreover, the fact that the measured depths of depletion for Ca and Al are equal in our study is not consistent with the leached layer model, because in general, framework elements like Al diffuse orders of magnitude slower than interstitial cations (see e.g., Freer, 1981; Grove et al., 1984; Smith and Brown, 1988; Brady and Cherniak, 2010). In addition, diffusion models cannot reproduce the complexity of the chemical profiles measured for many of the minerals examined, e.g. garnet, Fig. 2C; also K feldspar, Fig. 2D. And finally, our TEM and AFM observations suggest that surface layers are permeable to the inward and outward fluxes of solution and product species, respectively, and thus transport should not be diffusion limited. This effectively means that alternative pathways, such as interconnected porosity, allow reactants (H\(^{+}\) or H\(_3\)O\(^+\)) to reach the pristine mineral surface much faster than by solid-state diffusion.

Moreover, our observations are in excellent agreement with those from Jordan et al. (1999), who showed that despite the very rapid formation of an interfacial ‘soft surface layer’ on a dissolving anorthite surface, the spreading of etch pits continued unimpeded beneath this altered layer. Taken together, these results confirm that chemical reactions control the
destruction of the crystal lattice (i.e. reactions at pristine mineral interface, see Fig. 4), which is at odds with the leached layer theory.

Diffusion profiles can be simulated that do show sharp concentration gradients, provided that the altered layers are thin (<20nm; see Fig. 3C). In such cases, differentiating the two mechanisms may be challenging. However, the mechanism proposed here explains both thin or thick surface layers. In support of this are characteristic solid-state diffusion rates that are many orders of magnitude too slow at room temperature to produce even thin diffusion profiles, given the short time spans associated with laboratory-based non-stoichiometric dissolution (1-10 days). This point is also borne out in a study by Hellmann et al. (1992) where in situ AFM measurements showed the rapid formation (< 1 hour) of a surface layer on albite feldspar at ambient conditions (compare to, e.g., Jordan et al., 1999).

The dissolution-reprecipitation mechanism we propose is, however, compatible with rapid proton-cation exchange, as long as it is limited to the first monolayer of the mineral surface (see e.g., Fenter et al., 2000).

4.5. Interfacial dissolution-reprecipitation mechanism

We interpret the sharp chemical and structural interfaces measured in our study within the framework of a coupled interfacial dissolution-reprecipitation mechanism, a mechanism first hypothesized (but not proven at the time) for K-Na feldspar replacement by O’Neil and Taylor (1967). Our study, for the first time, provides unambiguous evidence that unifies laboratory and field chemical weathering of silicate minerals within the framework of this concept. The key pieces of evidence that we present in support of this mechanism are:

a. nanometer-sharp chemical interfaces that are spatially coincident with the structural interfaces (crystalline-amorphous boundary), and are present both on laboratory and naturally weathered silicates

b. for any given mineral, the depths and gradients of cation depletion are equal for all elements measured, irrespective of their valence and bonding nature (covalent: framework cations vs. electrostatic: interstitial cations)

c. the short time durations (1-10 d) required to produce surface layers, even with thicknesses of several hundreds of nm, are incompatible with extremely slow solid-state volume diffusion rates at ambient temperatures
d. the precipitation of amorphous silica with high internal porosity- e.g. see Fig. 2B-ii, AFM images of the wollastonite (for details on porosity generation in secondary surface phases, refer to Pollok et al., 2011, see also review in Putnis, 2009)

The important processes of the coupled interfacial dissolution-reprecipitation mechanism, shown in Fig. 4, are:

a. dissolution occurs at a single reaction front in a thin fluid film in contact with the pristine mineral lattice; all constituent atoms are released to the fluid film at the same stoichiometric rate from the crystal lattice, irrespective of the pH, with no diffusion control and no preferential leaching

b. surface layers are formed by the contemporaneous, coupled precipitation of a distinct porous amorphous phase (Fig. 4)
c. precipitation of amorphous silica (i.e. acid to circum-neutral pH) occurs even when the bulk solution is undersaturated, which is perhaps attributable to the properties of thin fluid films in contact with mineral surfaces.

These three characteristics distinguish the dissolution-reprecipitation mechanism from current chemical weathering concepts, and specifically the leached layer model.

The interfacial dissolution-reprecipitation mechanism represents a significant step forward in understanding how chemical weathering works, for it allows for the first time the generalization that silica-rich surface layers can be treated thermodynamically as a single discrete phase. This is an obvious advantage for improved modeling of laboratory and natural chemical weathering reactions. Moreover, this mechanism is also compatible with published measurements that show an abrupt change in the composition of surface layers on altered feldspars from Si to Al-rich at circum-neutral to moderately basic pH conditions (Chou and Wollast, 1985; Nesbitt and Muir, 1988), a phenomenon difficult to explain with the leached layer theory. Related to this is the observation that significant (apparent) non-stoichiometric dissolution can even occur at basic pH (Hellmann, 1995), conditions not relevant for cation-proton exchange. And finally, dissolution-reprecipitation can better explain measurements that show continuous, apparent non-stoichiometric dissolution (e.g. wollastonite: this study; Weissbart and Rimstidt, 2000).
Interestingly, a recent Monte Carlo study also provides evidence in support of the dissolution-reprecipitation mechanism. In their theoretical study of plagioclase dissolution mechanisms, Zhang and Lütte (2009) were able to reproduce the dependence of dissolution rates on composition for the entire plagioclase series when dissolution was modeled via the dissolution-reprecipitation mechanism, and not via thick leached layers.

### 4.6. Properties of thin fluid films and precipitates

A paradoxical aspect of our experiments and the interfacial dissolution-reprecipitation mechanism is that silica-rich surface layers formed on mineral surfaces, even though the bulk solutions were undersaturated with respect to possible secondary phases, in particular the polymorphs of silica. In fact, the experiments took place at far-from-equilibrium conditions, making the analysis of aqueous Si analytically challenging (i.e. low ppb range). Taking as an example labradorite and wollastonite dissolution at acid pH conditions (pH 1 and pH 3, respectively) and 25 °C, and recalling that both developed significant silica-rich surface layers (≥ 400 nm), the highest recorded Si concentrations corresponded to respective solution undersaturations (Gibbs free energy of reaction, \( \Delta G \)) of –4.6 and –6.3 kJ mol\(^{-1}\) for quartz, and –12.0 and –13.7 kJ mol\(^{-1}\) for amorphous silica. It is interesting to note that the problematical presence (from a thermodynamic point of view) of amorphous silica surface layers, formed at conditions of silica undersaturation, has long been recognized (Iler, 1979; see also Casey et al., 1993; Banfield et al., 1995). There are several possible, non-exclusive, explanations for this phenomenon.

One possible reason is that the calculated solution saturation indices (free energy of reaction, \( \Delta G \)) are possibly too low since they are based on pure (anhydrous) amorphous silica, or other pure silica polymorphs (i.e. with respect to the thermodynamic data base of geochemical codes, such as EQ3NR). The solubility of amorphous silica can be decreased by several orders of magnitude by incorporation of foreign ions, especially Al, Ca, and Mg (Iler, 1979; Sposito, 1984). Minor amounts of these elements were always measured in the silica layers formed after dissolution of the relevant minerals (Fig. 2C). In addition to foreign ions, the solubility of amorphous silica has been shown to significantly decrease with increasing degrees of hydration (Iler, 1979). Based on the significant concentration of H in the surface...
layer formed on labradorite (see SIMS H profile, inset to Fig. 2A-i), it is likely that the degree of hydration is generally elevated in surface layers. Another possible reason is based on evidence that fluid molecules have a strong tendency to order over distances of a few molecular layers from surfaces, due principally to reduced orientational and translational entropy (Wang et al., 2006). The consequence of this is that interfacial fluids have thermodynamic and physical properties that differ from those of bulk fluids. Thus, molecular ordering of fluid molecules specifically affects such fluid parameters as diffusion rates, viscosity, solute adsorption, the dielectric constant, and pH (Fenter and Sturchio, 2004; Kerisit and Liu, 2009; see also review in Hochella and Banfield, 1995). These differences, in particular a decrease in the dielectric constant, have been predicted to lead to enhanced solution saturation in thin fluid films (James and Healy, 1972; Putnis et al., 1995), in excess of that due to the electrical double layer and surface adsorption reactions. The nucleation process within the thin fluid film should theoretically not be suppressed by diffusion, due to the extremely short distance between the reaction front and the nucleation sites where eventually the secondary amorphous precipitate forms. We can speculate that the thin fluid film is not thicker than 2-3 monolayers of (ordered) water, which corresponds to approximately 7-10 Å; special fluid properties may even extend to 25 Å, Kerisit and Liu, 2009. In addition, it is possible that the close proximity of the primary mineral surface may serve to lower the nucleation energy barrier, enhancing the stability of nuclei that form within the fluid film. Moreover, it has been experimentally observed that acid pH conditions favor the polymerization of nano-colloidal silica particles that can eventually lead to a highly stable silica gel (Iler, 1979). Nonetheless, there is still much uncertainty about which combination of physical properties eventually allows a stable amorphous silica to precipitate (despite bulk fluid undersaturation with respect to all silica polymorphs), and even whether this is the result of equilibrium or non-equilibrium processes (e.g. Putnis, 1995).

While not possessing any long-range atomic order, it is possible that the short-range order of the amorphous precipitated phase is controlled by the parent mineral structure, in particular the degree of connectedness of the SiO₄ tetrahedra. Thus, the molecular structure of an amorphous silica layer formed on olivine (composed of isolated SiO₄ tetrahedra) may be different than the silica structure that forms on a feldspar (3-D framework of SiO₄ tetrahedra).
Going further, we can speculate that within a single family of minerals (e.g. the feldspar plagioclase series), the differences in the parent structures may be transposed to the respective surface layer structures.

The transfer of structural information from a dissolving crystalline mineral to an amorphous silica precipitate was elegantly demonstrated by Müller et al. (1998). In that study, the amorphous silica layer displayed a micro-lamellar structure identical to that of the parent labradorite. In a similar fashion, carbonation reactions of wollastonite produced thick amorphous silica rinds that perfectly replicated the underlying wollastonite structure (Daval et al., 2009a, b). The generalized occurrence of an epitactic relationship between parent minerals and product phases is one of the key characteristics of interface-coupled dissolution-reprecipitation reactions (Putnis, 2009). Banfield et al. (1995) note that topotactic relations among minerals are suggestive of transport of constituents across interfaces that are thin enough to affect the properties of the fluid. While the mechanism for the transfer of structural information via the fluid film is not fully understood (Putnis, 2002, 2009), it may be related to the close spatial coupling of the reactions, which is in part related to the ordering of fluid molecules controlled by the parent substrate.

4.7. Growth of surface layers and their chemical composition

The overall steady-state thicknesses of laboratory-created surface layers measured in this study are quite variable. The properties of the fluid play an important role; the main parameters that intervene are pH, bulk fluid saturation state, chemical composition, and temperature. In addition to the fluid, the structure and chemistry of the parent mineral control in large part the thickness of the surface layer (e.g. plagioclase feldspar series).

Even though the exact details on the processes generating surface layers are not completely understood, these layers appear to be limited in thickness. The naturally weathered K-feldspars examined in this study (Fig. 2D; exposure age ~ 14.7 ka) revealed surface layer thicknesses on the order of 50 nm. For these samples, we differentiate the thin surface layers (several tens of nm) from the several micron-thick over-layers containing phyllosilicates, whose upper limit in thickness may not be controlled by chemical processes, but rather by mechanical considerations. The exact interface separating the thin surface layer and the thick
over-layer is difficult to determine. In fact, referring to these layers as two separate entities may not be correct, and could be considered subject to debate.

On the other hand, the thickness of the surface layer on the naturally weathered serpentine (~150-200 nm, Fig. 2E) is unambiguous. The weathering exposure age for this sample has not been determined, but is most likely far inferior to the granite (<< 14.7 ka), based on the elevation, the deglaciation history of the Lac Robert area and surroundings (Le Roux et al., 2009), and the fact that a present-day glacier is located just 1-2 km away. Another example concerns K-feldspar grains retrieved from a Jurassic-age sandstone reservoir. These feldspars show evidence of 10-50 nm-thick amorphous surface layers deficient in K and enriched in Si (Zhu et al., 2006).

Considering that surface layers are primarily composed of amorphous silica, with minor amounts of other elements originally present in the parent mineral, the overall thickness of the layer at any point in time should be a function primarily of the Si budget: the time-integrated amount of Si that precipitated in the thin film at the inner interface, less the amount of Si that has been released to the bulk solution at the outer interface (refer to Fig. 4). Considering weathering at far-from-equilibrium conditions (i.e. undersaturated bulk solutions), a steady-state thickness can be achieved when the rate of Si precipitation within the thin fluid film equals the rate of release of Si at the outer interface (i.e. the outer interface is not in thermodynamic equilibrium with the bulk solution due to undersaturation).

Because the surface layer is permeable, the bulk fluid flow rate affects the thin fluid film properties, and therefore the thickness of the surface layer. The fluid flow rate in a flow reactor containing a mineral directly affects the degree of solution saturation of the bulk fluid (i.e. the slower the flow, the higher the fluid residence time, which induces a higher degree of bulk solution saturation). As an example, the wollastonite alteration experiments were conducted at several different flow rates, with the slower flow rates producing significantly thicker silica surface layers. These observations can be interpreted in terms of a retardation of the dissolution rate at the external silica-fluid interface, or an increase in the rate of silica precipitation at the internal interface, or perhaps even both (see also Daval et al., 2011). The effect of fluid flow on surface layer thicknesses has also been observed for orthoclase feldspar. Using X-ray reflectivity, Teng and co-workers (2001) observed the formation of a
very thin silica gel-like surface coating at acidic conditions under slow fluid flow-rate conditions, whereas at high fluid flow-rate conditions, no coating was observed. Taken together, these observations are consistent with the dissolution-reprecipitation mechanism, because they demonstrate a positive feedback between solution saturation and surface layer thickness. On the other hand, considering the leached layer mechanism, one would predict that decreasing the flow fluid flow-rate would increase the build up of product ions at the external interface and decrease the diffusion gradient, thereby leading to thinner leached layers. This is contrary to the results discussed above.

All of the laboratory minerals altered at acid pH displayed surface layers enriched in Si compared to the parent mineral (see Fig. 2). This has also been evidenced in other studies of acid-pH, laboratory-altered silicates (e.g. Mogk and Locke, 1988; Schweda et al., 1997; Nesbitt and Skinner, 2001; Kameda et al., 2009). In the present study, the naturally weathered serpentine also showed Si enrichment in the surface layer, but on the other hand, the K-feldspar from the granite showed essentially no change in Si concentration. Other studies in the literature reporting on natural alteration of silicate minerals in contact with acid pH solutions also show Si enrichment (e.g. Kawano and Tomita, 2001).

We interpret surface layers enriched in Si to be consistent with the dissolution-reprecipitation model. In this study, the normalized concentration of Si in representative parent minerals ranged from 20 to 25 wt. % (i.e. pyrope garnet = 19.6, wollastonite = 24.2, and labradorite feldspar = 25.0 wt %). These Si concentrations can be compared with the theoretical concentration of Si in a precipitated SiO$_2$ surface layer, which equals 46 wt. % (slightly less if hydration is factored in). Therefore, if the surface layer represents a discrete precipitated phase, then one would expect a jump in Si concentration at the inner interface (i.e. the mineral-amorphous layer boundary), which indeed is what we measured (see Figs. 2A, B, C, E). The magnitude of the concentration jumps will be less if it is assumed (from BF and DF TEM images) that the surface layers are lower in density.

Moreover, there is no a priori reason why Si enrichment would be expected for silica-rich surface altered layers formed by preferential cation loss from the mineral structure (i.e. leached layers). The only feasible alternative for a silica-rich relict layer to display an increase in Si concentration (i.e. Si atoms per unit volume) compared to the parent mineral is through
significant structural reorganization, by processes such as condensation and densification. As an example, in their laboratory investigation of chlorite alteration (Kameda et al., 2009), the surface altered region is characterized by elevated Si levels (90-95 avg. EDX counts in silica layer vs. 65 avg. counts in pristine chlorite). The authors attribute this enrichment to hydrolysis-recondensation reactions. While this explanation is plausible, the BF TEM images appear to show that the altered zone is uniformly less electron dense than the chlorite, with no dark, electron dense zones present (as might be expected for layer densification or collapse; e.g. compare to dark banding attributed to densification of altered gel layer on a borosilicate glass, Cailleteau et al., 2008). To resolve this question, one possibility would be to simulate BF TEM images of chlorite in contact with Si layers having variable densities.

With respect to the silica layers observed in our samples, we see no obvious evidence for densification. The aqueous solution data do not show any significant drop in release rates of cations with time, which would be indicative of densification, in particular if the silica layer were to become passivating. The TEM images also do not show any obvious signs of densification, even though we note the presence of some slightly darker bands in some of the HRTEM images (see, e.g. Fig. 2A-ii, C, D). The origin of these darker bands merits a more detailed investigation. In conclusion, even though we cannot completely rule out densification processes in surface layers, at present we do not ascribe the measured Si enrichments measured in our study to such processes.

4.8. Internal porosity of surface layers

A key tenet of the interfacial dissolution-reprecipitation mechanism is that the precipitate does not act as a protective surface layer, such that the transport of aqueous chemical reactants and products between the crystalline reaction front and bulk fluid (inner and outer interfaces, respectively, Fig. 4) is not diffusion controlled (Putnis, 2009). The generation of porosity in secondary crystalline phases is in fact generally observed for mineral replacement reactions (Harlov et al., 2005; Putnis et al., 2007; see also examples in Putnis, 2002, 2009). Development of significant internal porosity within amorphous surface (altered) layers has also been reported (e.g. Casey et al., 1989, 1993; Weissbart and Rimstidt, 2000).
In the present study, the molar volume changes associated with the precipitation of amorphous silica are negative ($V_{\text{amor silica}} / V_{\text{mineral}} < 1$). The Pilling-Bedworth rule predicts the generation of internal porosity within a precipitate when the molar volume ratio of product to parent phase is less than one (see, e.g. Velbel, 1993). More recent work points out that the generation of porosity in the secondary phase depends on both the molar volume change and the difference in relative solubilities of the parent and product phases (Putnis, 2009; Pollok et al., 2011). In the present study, the constant, steady-state cation release rates measured during each mineral alteration experiment are consistent with permeable, non-passivating surface layers (i.e. weathering kinetics were unaffected). Furthermore, the sharp nanoscale chemical gradients measured by EFTEM (Fig. 2) at the mineral-surface layer interfaces, with respect to both laboratory and natural weathering, also indicate that the reactions were not kinetically hindered by solid-state volume diffusion.

Direct evidence for elevated secondary porosity comes from observations of the 3-D surface structures on two of the laboratory-altered minerals, labradorite and wollastonite. Figure 2B-ii shows a tapping mode AFM image of an altered wollastonite surface, composed primarily of amorphous hydrated silica, which is characterized by botryoidal morphology and significant near-surface porosity, with heterogeneous pore spaces ranging from a few tens of nm up to a hundred nm in diameter. Recent molecular dynamics simulations (Kerisit and Liu, 2009) show that self-diffusion coefficients of water and electrolyte ions are not affected by pore size until a critical value of 5 nm is reached; in pore spaces < 5nm in diameter there is a notable decrease with respect to bulk fluid values. The near-surface pores imaged here are largely superior to this critical diameter. In addition, whether the formation of a high porosity, botryoidal surface by the interdiffusion-leached layer mechanism is plausible is highly questionable. We therefore argue that the AFM images support the premise that the surface layers produced in the laboratory experiments did not impede the inward and outward flux of aqueous species.

Even though we have argued that the surface silica layers studied here were not passivating, this may not always be true. A case in point is the study by Daval et al. (2011) on coupled weathering-carbonation reactions on olivine. According to their study, the silica layers (20-40 nm) that originally formed on the olivine surface by dissolution-reprecipitation
became passivating with increasing reaction progress, due to an internal densification process. Their argument is based on the measured reaction rates of olivine that showed evidence for significant retardation, and the fact that the Mg chemical gradients (measured by STEM-EDX) at the internal interface were slightly sigmoidal. Perhaps this particular behavior of olivine was specifically due to alteration in aqueous solutions with high $p\text{CO}_2$. A convincing example of densification and pore closure in surface (altered) layers formed on borosilicate glasses can be found in the study of Cailleteau et al. (2008).

In general, surface precipitates that form during weathering should be considered to be dynamic and subject to structural modification. In his review of mineral replacement reactions, Putnis (2009) states that as long as the porous precipitate is in contact with an aqueous solution, its microstructure will continue to evolve with time via dissolution-reprecipitation reactions (see, e.g. porosity coarsening, Putnis et al., 2005). The in situ nucleation and crystallization of secondary phases, in particular clay minerals, is also commonly observed (e.g. present study, feldspar- see text and Fig. 2D). Silicates reacted at high $p\text{CO}_2$ can result in silica layers that contain in situ precipitated carbonates (Daval et al., 2009b) that may render them passivating.

5. Conclusions and Broader Implications

One of the most important results of this study is that chemical weathering reactions which lead to the generalized occurrence of amorphous surface layers are controlled by interfacial dissolution-reprecipitation. This finding considerably extends the original research on nanoscale alteration of feldspar surfaces by Hellmann et al., 2003. The dissolution-reprecipitation mechanism allows us for the first time to unify simple weathering reactions in the laboratory with complex natural weathering that occurs in the field. We can now take our reasoning a step further and combine our results with recent studies on mineral-mineral replacement reactions, which can be thought of as another type of chemical weathering process. The pioneering research of Goldsmith and Laves (1954), O’Neil and Taylor (1967), and Mérigoux (1968) effectively established the theoretical foundation for a large number of recent analytical studies on mineral replacement, encompassing both laboratory and natural conditions, and at ambient as well as at elevated temperatures. These studies have all
advocated an interfacial dissolution-reprecipitation mechanism (e.g. Fiebig and Hoefs, 2002; Labotka et al., 2004; Putnis and Mezger, 2004; Putnis et al., 2005; Harlov et al., 2002, 2005; Harlov and Förster, 2003; Geisler et al., 2007; Putnis and Putnis, 2007; Hövelmann et al., 2010; see also extensive reviews in Putnis, 2002, 2009, and references therein). Even though the intrinsic mechanism is the same, the major difference between these two types of weathering processes is that in the former the surface layer is an amorphous phase, whereas in the latter the secondary phase is crystalline. When all of these studies are considered together, it can be argued that the interfacial dissolution-reprecipitation mechanism is a universal phenomenon that controls all mineral-water interactions (Putnis and Putnis, 2007).

Because our results concur with the idea of a universal mineral-water alteration mechanism, we therefore redefine the continuum model of weathering described by Hochella and Banfield (1995). In their model, proton-cation exchange characterizes the laboratory end-member (i.e. leached layers, which in some cases can also occur in nature), whereas the natural weathering end-member is characterized by mineral replacement occurring by direct (i.e. solid-state) structural transformation.

Instead, we propose a continuum model that is based on interfacial dissolution-reprecipitation as the principal mechanism of chemical weathering. In this model no distinction is made between laboratory and natural weathering, but rather, the nature of the secondary phase is used to define the two end-members of the continuum. One of the poles defines weathering reactions characterized by the precipitation of amorphous surface phases; the other pole is defined by weathering reactions leading to mineral-mineral replacement reactions. Mineral weathering characterized by amorphous phases that contain in situ-nucleated and crystallized secondary phases (i.e. clays) can be considered as lying between the two poles (see Fig. 4). In the present study, most of the minerals studied fall into the domain characterized by amorphous surface precipitates. The weathering of K-feldspar (Fig. 2D) is an example of weathering where the products are both amorphous and crystalline. In this case, we assume that the amorphous silica contained the precursor nuclei that permitted the in situ crystallization of the phyllosilicates that we observed.

The differences in the physical and chemical conditions associated with specific weathering environments that lead to either amorphous surface layers or mineral replacement
are not precisely known. Given that in the present study amorphous silica layers formed
during laboratory alteration in very dilute aqueous solutions, whereas mineral replacement
reactions commonly occur in the presence of solutions enriched in certain chemical species
(e.g. albite replaced by K-feldspar in solutions enriched in KCl, Labotka et al., 2004), it is
possible that the reprecipitation reactions corresponding to the two poles are controlled by the
chemical saturation state and the chemical composition of the bulk fluids associated with the
weathering process; temperature, and to a lesser degree, pressure, may play subsidiary roles.
These parameters have a direct influence on the physical and chemical properties of the
interfacial thin fluid film (Fig. 4). Kinetic considerations may also play an important role in
the reprecipitation process.

The generalized presence of precipitated silica layers has potential significance with
respect to the global C cycle and the total amount of CO$_2$ consumed during weathering, in
particular for reactive ultramafic rocks (e.g. ophiolites) or industrial CO$_2$ carbonation-
sequestration processes. Even though clays and other neo-formed minerals can affect the CO$_2$
budget, our results show that precipitated surface silica layers retain minor amounts of
divalent metal cations. Their presence potentially reduces both carbonate formation and CO$_2$
consumption. Secondary carbonate precipitates, thermodynamically favored during
weathering in the presence of high HCO$_3^-$ concentrations (i.e. high $p_{\text{CO}_2\text{aq}}$), may even
kinetically hinder chemical weathering due to pore clogging within amorphous silica layers
(Daval et al., 2009a, b), thereby further reducing CO$_2$ consumption.

Our results show the potential of the approach we have used for studying fluid-mineral
and fluid-solid interactions, with potentially diverse applications in the geosciences and in
other fields, such as near- and far-field fluid-solid interactions associated with radioactive
waste repositories (e.g. mechanism of actinide incorporation into surface layers formed either
on glasses or minerals), biomineralization, dental and medical sciences (e.g., periodontal
decay, e.g. Elliot et al., 2005; interaction of bone with biofluids), electrochemistry (e.g.
corrosion reactions at metal-solution interfaces), dissolution and reactivity of natural and
man-made nanomaterials, and tribology (e.g. seismogenic fault behavior related to diminution
of the friction coefficient due to fluid-mineral interactions, e.g. Moore and Rymer, 2007,
and/or the presence of silica gel layers on fault surfaces). Given the current interest in finding
water on Mars, we propose that the potential presence of hydrous, silica-rich surface layers on exposed Martian plagioclases could serve as evidence for chemical weathering reactions in the former presence of free water.

It is interesting to speculate further on the coupled interfacial dissolution-reprecipitation reaction that applies to silicate mineral-fluid reactions, for it may in fact be a more universal phenomenon. Recent experimental findings concerning melt migration through olivine at mantle conditions (Schiano et al., 2006) overturn current thinking by providing strong evidence that this process is not diffusion controlled, but rather occurs via a sharp crystal-melt reaction front whose advance is controlled by partial melting (detachment, analogous to dissolution), followed by crystallization (attachment, analogous to reprecipitation).

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REFERENCES CITED


silica layer formation on the dissolution rate of olivine at 90 °C and elevated $p_{\text{CO}_2}$.


Figure Captions

Figure 1. Amorphous surface altered layer formed by leached layer mechanism (arbitrary scale, view in cross section). The anticorrelated, sigmoidal concentration profiles are created by solid-state volume interdiffusion of preferentially released cations (cation profile- white) with protons from bulk solution (H profile- black)- this represents the core process. The leached layer is a relict structure bonded to the unaltered mineral; the thickness is controlled by two rates: diffusion (inner interface) and surface chemical reactions (outer interface); when the inner and outer interfaces move at the same rate, the layer thickness becomes constant. Leached layers may undergo structural reorganization reactions such as condensation and densification (see text for details).

Figure 2. High-resolution TEM structural images, chemical maps, and cation depth profiles of surface layers formed on silicate minerals after laboratory (A-C) and field chemical weathering (D, E). A: labradorite : (i) BF TEM image with EDX profiles (dark ovals = C contamination from EDX), H SIMS profile in inset (true H profile is sharper-see text); (ii)
HRTEM image; EFTEM chemical maps with Ca (iii) and Si (iv) profiles (Si map obtained in different location, faint white areas in feldspar are an artifact). B: wollastonite: (i) BF TEM image, note fluid-filled pores and physical separation of surface layer from wollastonite (elongated white zone), insets show EFTEM Si and Ca profiles; (ii) AFM image of surface. C: pyrope garnet: HRTEM image, inset shows EDX-cation profiles (inset from different location; true chemical gradients are sharper because of EDX-beam broadening). D: K-feldspar: HRTEM image, superposed EFTEM K profile. E: serpentine: EDX chemical map-Mg (yellow), Si (green), Si-rich and Mg-poor surface layer (dark green), lichen (grey, hole = black).

Figure 3. Interdiffusion modeling of binary cation-proton exchange, simulating leached layers. (A) Variation of binary interdiffusion coefficient log $D_\alpha$ as a function of normalized cation concentration (proportional to depth) and structural factor $\alpha$. (B) Normalized cation concentrations as a function of depth into the altered layer based on univalent (binary) cation-proton interdiffusion (only cation profiles shown). Curves based on $\alpha = -0.9$, $a = 10^{-2}$ Å s$^{-1}$, $D_H$ (H$^+$ or H$_3$O$^+$ diffusion coefficient), and $D_H/D_{\text{cation}}$ ($10^{-2}$, $10^{-3}$, $10^{-4}$, $10^{-5}$; corresponding profiles left to right for each value of $D_H$). Overall, these diffusion curves demonstrate that an interdiffusion process (leached layer mechanism) is not compatible with thick altered surface layers (> 20 nm) having sharp chemical boundaries. (C) Simulated binary, multivalent cation-H$^+$ (H$_3$O$^+$) interdiffusion. Cation depth profiles as a function of $\alpha = -0.9$, $a = 10^{-2}$ Å s$^{-1}$, $D_H$ ($\text{H}^+$ or H$_3$O$^+$ diffusion coefficient), $D_H/D_{\text{cation}} = 10^{-3}$, and cation valence ($z$). The individual, binary cation depth profiles start to increasingly diverge as a function of valence when $D_H \geq 10^{-14}$ cm$^2$ s$^{-1}$, showing strong dependence of cation depletion depths on valence (see text for details).

Figure 4. Coupled interfacial dissolution-reprecipitation mechanism (top), and general concept of chemical weathering continuum (bottom). Cross sectional view of surface layer
separated from crystalline parent mineral by a thin fluid film. Chemical reactions control
stoichiometric release of elements from mineral (inner interface) to thin fluid film; this is
coupled to precipitation of an amorphous, silica-rich surface layer (light grey); step function-
like depletions in certain cation concentrations- yellow dashed line; partial retention of
cations- yellow arrow). Stoichiometric chemical reactions control the release of elements at
outer interface. The continuum concept of chemical weathering, based solely on the
interfacial dissolution-reprecipitation mechanism, has two end-members defined by the nature
of the precipitated phase. This serves to integrate our results, based on the precipitation of
amorphous silica, with mineral replacement reactions, into a continuum concept that
encompasses both laboratory and natural chemical weathering.
Fig. 1  Hellmann et al.

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Figure 2A, Hellmann et al.

- A: Pt + Au layer, surface layer, feldspar, fluid-solid (outer) interface, inner interface.
- ii: [Ca] 8 nm, electron intensity in arbitrary units.
- iii: Surface layer, feldspar, inner interface.
- iv: Surface layer, feldspar, inner interface.
Figure 2B, Hellmann et al.

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Figure 2D, Hellmann et al.
Fig. 2E, Hellmann et al.

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