Water Rock Interaction [WRI 14]

Formation of amorphous silica surface layers by dissolution-reprecipitaton during chemical weathering: implications for CO_2 uptake

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Abstract

Chemical weathering reactions at the Earth's surface and upper crust influence the chemical cycle of elements, chemical erosion rates, the quality of potable water resources, soil formation and nutrient availability, and ore genesis. Chemical weathering is also a major process controlling the regulation of the carbon cycle by CO_2 consumption and sequestration by carbonation reactions. Based on nanometer-resolution TEM measurements, chemical weathering of silicates in both the laboratory and the field was found to result in the development of a distinct interfacial phase that is amorphous, hydrated, and silica-rich. An abrupt, step function-like change in chemistry and structure delimits the interface with the unaltered parent mineral, suggesting a dissolution-reprecipitation mechanism. The existence of these precipitated silica layers has important and so far unrecognized implications with respect to natural and industrial carbon sequestration processes, as surface silica layers may decrease the amount of atmospheric CO_2 consumed during coupled silicate chemical weathering-carbonation reactions.

1. Introduction

   Chemical weathering experiments in the laboratory are generally carried out at conditions that promote the chemical breakdown of minerals, namely in chemically dilute solutions at far-from-equilibrium conditions. Moreover, in order to reproduce natural chemical weathering conditions, experiments are

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commonly conducted at temperatures well below 100 °C in acid to neutral pH solutions. In the laboratory, one of the defining characteristics of multi-cation silicate dissolution behavior is apparent release rates of cations to solution that do not correspond to their ratios in the parent mineral phase. This non-stoichiometric, preferential release of charge-compensating interstitial cations and network-forming Al is thought to be responsible for the formation of chemically-distinct surface 'leached layers'. Leached layers are not true 'layers', but rather are a relict structure composed primarily of Si and O atoms that were part of the original crystal structure. Leached layers are postulated to form by solid-state volume interdiffusion of cations in the mineral structure and protons from the bulk solution [1, 2]. Moreover, leached layers may undergo condensation reactions, thereby rendering them structurally more stable.

As opposed to laboratory studies, chemical and environmental complexity are the hallmarks of chemical weathering conditions that characterize water-rock interactions on the Earth's surface and within the upper crust [3]. Natural waters and soil pore fluids have variable chemical saturation states and complex chemical compositions, often containing free metal cations, ligand complexing agents, humic substances, and naturally occurring organic and inorganic acids. In addition, mineral grains in soils are often covered with mineral coatings, clay minerals, and biofilms and other biota. Because of the more complex nature of natural chemical weathering compared to much simpler laboratory reactions, the existence of an intrinsic mechanism of dissolution common to all chemical weathering reactions has been the subject of vigorous debate.

## 2. Nanoscale TEM measurements of fluid-mineral interfaces

Laboratory experiments were used to chemically alter a large group of primary silicate minerals having variable compositions and belonging to different structural classes at ambient conditions, acid pH, and at far-from-equilibrium conditions. Two field-weathered samples were also investigated, K-feldspar from a granite and lizardite in a serpentinite. Electron transparent foils were prepared vertically in relation to the altered mineral surfaces by focused ion beam milling (FIB). Transmission electron microscopy (TEM) techniques allowed us to measure nm-scale structural and chemical changes of the interfacial regions caused by chemical alteration. For more details on the experimental methods, sample preparation, and analytical techniques, the reader is referred to Hellmann et al., 2012 [4].

Transmission electron microscopy revealed that all of the altered mineral surfaces are characterized by a distinct surface layer that is amorphous, less dense, cation-depleted, and enriched in silica compared to the parent mineral. The nm-resolution chemical profiles show that the surface layers are characterized by sharp, step function-like changes in cation concentrations that are spatially coincident with the amorphous-crystalline interface. These results are not compatible with volume interdiffusion and the formation of leached layers, but rather with an interfacial dissolution-reprecipitation mechanism (see Hellmann et al., ref. [4], and references therein, for details).

3. Amorphous silica-rich surface layers and implications for CO_2 uptake

The formation of altered surface layers by dissolution-reprecipitation during chemical weathering has potentially far-reaching implications for the consumption of CO_2, the global C cycle, and C sequestration processes. It is estimated that up to 63% of the CO_2 consumed during chemical weathering reactions is due to silicate minerals [5]. Mafic silicate rocks (e.g. basalts, amphibolites, serpentinites, peridotites) are particularly relevant for both natural and industrial carbon sequestration because divalent metal cations are liberated during chemical weathering, which combine with aqueous carbonate species to form solid carbonates, thereby locking up CO_2 over geological time spans.
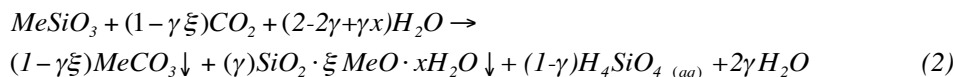
Coupled weathering-carbonation reactions are generally represented by the following relation (Me = Ca^{2+}, Mg^{2+}, or Fe^{2+}):

$$MeSiO_3 + CO_2 + 2H_2O \rightarrow MeCO_3\downarrow + H_4SiO_4 \qquad (1)$$
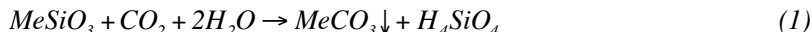
This results in the chemical breakdown of a mafic silicate mineral, consumption of CO_2, release of aqueous silica, and transformation of C to a solid carbonate precipitate ($MeCO_3$). At low water:rock ratios, a thermodynamically stable silica phase precipitates. The carbonate occurs as a thick rind or coating on top of the silica [6], or as veins traversing the original silicate mineral, e.g. weathered ultramafic peridotites, Oman [7].

A key finding of our nanoscale measurements of laboratory and naturally weathered silicates (i.e. the majority were mafic silicates) is that the precipitated silica surface layer sequesters variable amounts of the other constituent cations released from the parent mineral. Moreover, laboratory chemical weathering of mafic silicates at elevated concentrations of $CO_{2\ aq}$ also results in the precipitation of amorphous silica surface layers (with nm-sharp chemical and structural interfaces) containing cations; at these conditions the silica layers are overlain by thick carbonate precipitates [6]. The important consequence of this is that chemical weathering and carbonation are more complex than the reaction given by Eq. 1.

Silica surface layers, a heretofore unrecognized sink for divalent metal cations, directly affect the carbonation process, resulting in decreased consumption of CO_2 because fewer metal cations are available for the formation of solid carbonate. Within the framework of the new chemical weathering mechanism we propose, the presence of a precipitated surface silica layer and competition for available aqueous divalent cations changes the standard weathering-carbonation relation given by Eqn. 1 to:

$$MeSiO_3 + (1-\gamma\xi)CO_2 + (2\text{-}2\gamma+\gamma x)H_2O \rightarrow$$
$$(1-\gamma\xi)MeCO_3\downarrow + (\gamma)SiO_2\cdot\xi MeO\cdot xH_2O\downarrow + (1-\gamma)H_4SiO_{4\ (aq)} + 2\gamma H_2O \qquad (2)$$

In the above reaction, applicable at high water:rock ratios (undersaturated conditions), the silica that is produced by the weathering reaction is partitioned via the γ coefficient between the precipitated silica surface layer (2nd product term) and aqueous silica (3rd product term). In confined environments with low water:rock ratios (bulk and/or pore fluids saturated in silica), the aqueous silica precipitates on top of the silica surface layer, such that the two silica phases become chemically indistinguishable [6], and therefore can be represented as a single, thermodynamically stable silica phase, resulting in:

$$MeSiO_3 + (1-\xi)CO_2 + xH_2O \rightarrow (1-\xi)MeCO_3\downarrow + SiO_2\cdot\xi MeO\cdot xH_2O\downarrow \qquad (3)$$

In reactions 2 and 3, ξMeO is the mole fraction of metal cation that co-precipitates (possibly as a hydrated metal hydroxyoxide) within the silica layer, and therefore is not available to form a carbonate. The importance of the empirical parameter ξ can be deduced by the decrease in both the overall quantity of CO_2 consumed during the weathering process, $(1-\xi)CO_2$, and the amount of carbonate that precipitates, $(1-\xi)MeCO_3$. There is no intrinsic value for the parameter ξ, and it is most likely dependent on many factors, in particular the parent mineral.

We now show that the presence of a silica layer potentially affects the yield of chemical weathering-carbonation reactions, and how this can be applied to either industrial or natural carbon capture and storage (CCS) processes. Taking a hypothetical CCS objective based on conversion of the entire excess amount of CO_2 released into the atmosphere above the pre-industrial revolution baseline (estimated to be $\approx 0.7\cdot10^{15}$ kg) [8] into a solid carbonate, a simple calculation using Eq. 1 shows that this can be achieved

with $\approx 15.9 \cdot 10^{15}$ moles of silicate mineral (MeSiO$_3$); note that this amount represents a negligible fraction of silicates (MeSiO$_3$) in the upper crust. The same calculation using Eq. 3, and using a conservative estimate of $\xi = 0.01$, results in the consumption of $\approx 16.1 \cdot 10^{15}$ moles of silicate mineral. This relative difference, even though small, when converted to reactant mineral mass (e.g. using wollastonite), equals $1.9 \cdot 10^{13}$ kg ($1.9 \cdot 10^{10}$ tons). Moreover, true values for ξ may be significantly higher, such that the reactant mineral masses required may be magnitudes greater than our estimate. This example illustrates that large-scale carbonation reactions require vastly more silicate mineral when the effect of silica surface layers are included.

The above calculations assume that the interconnected porosity inherent to the precipitated silica layers remains open, such that the weathering kinetics of the parent mineral are not affected. However, this may not hold true for weathering-carbonation reactions at low water:mineral ratios. Current studies in our laboratory [6] and elsewhere show that the porous structure of the silica layers can become partially plugged with carbonate nano-crystallites or phyllosilicates, thereby limiting transport of aqueous reactants and products through the silica layers. If partial passivation of chemical weathering reactions turns out to be common-place, then this would have a far more deleterious effect on the extents of reaction using Eq. 3. This has implications both for the natural C cycle on a global scale, as well as the predicted potential of CCS proposals being developed to mitigate rising levels of anthropogenic CO$_2$.

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