

Chemical weathering of silicate minerals: Linking laboratory and natural alteration

R. Hellmann

Environmental Geochemistry Group, LGIT-CNRS, Grenoble Cedex 9, France

R. Wirth

GeoForschungsZentrum Potsdam, Experimental Geochemistry, Potsdam, Germany

J.-P. Barnes

CEA, LETI, MINATEC, Grenoble, France

ABSTRACT: The interdiffusion-preferential cation release mechanism, commonly known as the leached layer theory, has been traditionally invoked to explain the prevalent occurrence of amorphous, silica-rich surface layers on weathered minerals. Based on a new approach using ultrathin Transmission Electron Microscopy (TEM) foils prepared in cross section from weathered mineral surfaces, it is possible to directly examine surface altered layers with analytical probes at the nanometer scale. Results show that the chemical and structural transitions from altered layers to parent minerals are spatially coincident and very sharp, which is not compatible with an interdiffusion mechanism. We argue that a coupled dissolution-precipitation mechanism can better explain the formation of surface altered layers in the context of both laboratory and natural chemical weathering.

1 INTRODUCTION

In order to understand the physico-chemical properties, the reactivity, and the metal and CO₂ sequestration capacity of soils, precise knowledge of nanometer-scale processes occurring at fluid-mineral interfaces is of primary importance. To understand chemical weathering processes, researchers have traditionally turned to laboratory-based experiments. However, a dichotomy has always existed between chemical weathering reactions simulated in laboratory experiments with chemical weathering reactions observed in the field. Because of the inherent complexity of natural weathering, which includes the effects of plants, lichens and microbial organisms, oxyhydroxide metal coatings and/or clays, aqueous organic compounds, higher solution saturation states, and reaction time periods that are orders of magnitude greater than in the laboratory, it has commonly been assumed that chemical weathering in the laboratory and in the field occur by different mechanisms (Nesbitt & Muir 1988, Seyama & Soma 2003, Zhu et al. 2006).

Based on many decades of laboratory experiments, it is widely accepted that aluminosilicate minerals undergo chemical weathering via the 'leached layer' mechanism (Chou & Wollast 1985,

Hellmann 1995, Casey et al. 1988, 1993, Petit et al. 1989, 1990). This mechanism accounts for incongruent and preferential cation release that characterizes the alteration of aluminosilicate minerals. A leached layer represents a surface altered layer that is structurally and chemically distinct from the parent mineral. It forms by way of an interdiffusion process between preferentially released cations from the parent mineral with protons from the surrounding aqueous bulk solution; this occurs at a diffusion front located at the inner interface between the leached layer and the mineral. The amorphous leached layer, which represents a structural relict of the parent mineral, is composed of silica that is 'leftover' after the preferential release of cations by diffusion (silica composition for chemical alteration conditions at acid to circumneutral pH). The leached layer does not attain an infinite thickness because chemical hydrolysis reactions breakdown and release silica into solution at the outer interface of the leached layer.

The leached layer mechanism is based on two simultaneously occurring processes: interdiffusion and hydrolysis. Supporting evidence for the leached layer theory has been provided by diffusion-like, sigmoidal cation depth profiles obtained by surface sensitive analytical techniques that rely on surface bombardment of altered mineral surfaces

with ion, electron or X-ray beams (e.g. SIMS, RBS, RNRA, XPS; see review in Chardon et al. 2006). These techniques, however, are all characterized by poor lateral spatial resolution (i.e. due to μm to mm-sized beam footprints).

Thus, the pertinent question that needs to be addressed is whether natural chemical weathering occurs via the same mechanism of interdiffusion and preferential cation release, or by way of another process. Alternatively, one can also ask the question as to whether laboratory and natural chemical weathering are controlled by an altogether different mechanism.

2 METHODS

Previous investigations of the surface chemistry of weathered minerals have nearly all been based on surface sensitive techniques based on bombarding the surface with ion, electron or X-ray beams that have μm to mm-sized beam diameters; the resultant chemical depth profiles represent indirect measurements at low spatial (lateral) resolution. This analytical methodology results in an artificial broadening of the individual cation depth profiles, and can thus lead to a misinterpretation of the operative mechanism (Hellmann et al. 2004).

A new approach to examine fluid-mineral interfaces is based on cutting or milling weathered mineral surfaces using either ultramicrotomy or focused ion beam milling (FIB). Both techniques provide a cross-sectional ultrathin section (electron transparent) that extends from the outer weathered surface to the unaltered parent. The dimensions of typical FIB thin sections are $15\ \mu\text{m}$ (length) \times $5\ \mu\text{m}$ (height), and $\leq 100\ \text{nm}$ in thickness. The principal advantage of investigating surface altered layers in cross section is that the chemical depth profiles can be measured directly with high spatial resolution probes.

Both ultramicrotomy and FIB can produce artifacts, which is something to be aware of. Thin sections cut by ultramicrotomy have a tendency to be characterized by lamellar fracturing and spatial disordering of the cut mineral (Hellmann et al. 2003). However, this does not necessarily influence the quality of the analytical measurements, provided that large enough intact zones are located for subsequent analyses. In comparison, thin sections are more easily obtainable with the FIB technique. However, this technique has a major weakness in that artifacts are very easily produced. Two fundamental steps of FIB are based on the deposition of a Pt 'strap' (i.e. layer) on the surface area chosen, followed by ion milling of the thin section using a focused Ga beam. Both operations can result in the emplacement of measurable quantities of,

respectively, Pt and Ga into the target mineral, which generally results in amorphization. Therefore, one of the most important preliminary steps is the application of a protective Au or C coating ($\approx 100\ \text{nm}$ in thickness) before the deposition of Pt and subsequent Ga milling (e.g. see Lee et al. 2007). For a thorough description of FIB applied to Earth sciences studies, see Wirth (2004, 2009).

A large suite of silicate minerals has been examined, subject to both laboratory and natural chemical weathering. TEM foils, prepared both by ultramicrotomy and FIB, were examined by various analytical techniques incorporated in transmission electron microscopes (TEM): high resolution TEM (HRTEM), energy filtered TEM (EFTEM), high angle annular dark field TEM (HAADF), electron energy loss spectroscopy (EELS), and energy dispersive X-ray spectroscopy (EDX). All of the above techniques provide either structural or chemical information at the nanoscale.

3 RESULTS

Here we describe two examples in detail. Figure 1 is a bright field (BF) TEM image of a FIB produced TEM foil showing, in cross section, a thick (400–500 nm) amorphous surface altered layer on unaltered crystalline wollastonite. The altered layer formed in response to laboratory chemical weathering. The wollastonite was altered in a flow through stirred reactor at ambient temperature at pH3. The distinctly lighter shade of grey associated with the altered layer indicates an average atomic

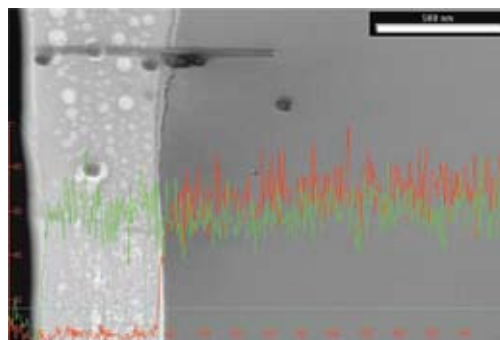


Figure 1. Bright field TEM image of FIB thin section showing cross sectional view of chemically weathered wollastonite; surface altered layer on left (light grey) and unaltered wollastonite on right (darker grey). The two EDX chemical profiles indicate no change in Si and significant Ca depletion in the altered layer. Note the sharp Ca gradient at the interfacial boundary. The bubbles and pits in the image are due to electron beam-solid interactions. The scale bar is $500\ \mu\text{m}$.

density that is less than that of the wollastonite. The superposed EDX chemical profiles reveal that the Si counts are approximately equivalent in both the unaltered wollastonite and the surface altered layer. On the other hand, the Ca counts reveal that the altered layer is depleted in Ca. Note that the change in Ca is abrupt and very sharp (i.e. similar to a step function), and spatially coincides with the interfacial boundary between the wollastonite and the altered layer. The Ca gradient at the interfacial boundary is only a few tens of nm wide. The second example is based on natural chemical weathering of a K-feldspar that was retrieved from a soil immediately adjacent and below a granite boulder.

Figure 2 is a high resolution TEM image that shows in cross section three distinct zones: the unaltered feldspar, a 20 nm-thick amorphous surface altered layer, and a several μm -thick layer containing abundant phyllosilicates oriented roughly parallel with the interfacial boundary separating the feldspar from the altered layer. The 20-nm thick altered layer appears to be made up of two equally thick zones with different densities. EFTEM analyses indicate that altered layer immediately adjacent to the feldspar is composed primarily of silica and is depleted in potassium. As was the case for the laboratory-weathered wollastonite, the chemical and structural boundaries are spatially coincident and very sharp. The width of the K gradient at the K-feldspar-altered layer boundary is estimated to be on the order of 3 nm.

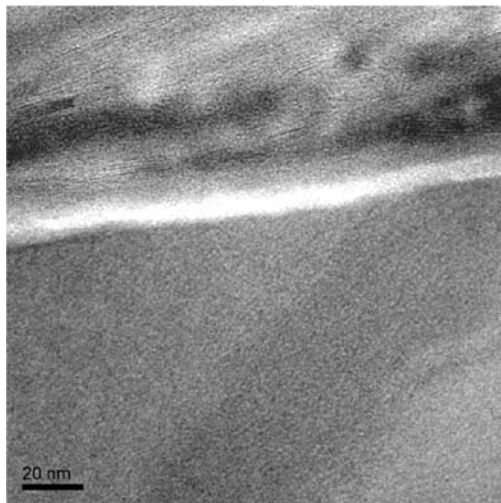


Figure 2. High resolution TEM image showing naturally weathered K-feldspar in cross section. The distinct and sub-horizontal 20 nm-thick band (white and medium grey) is an amorphous surface altered layer that separates the crystalline K-feldspar (below) from a zone comprised of abundant secondary phyllosilicates (above).

4 DISCUSSION

Even though we only have described two examples of silicate chemical weathering, one from the laboratory and one from the field, other silicate minerals that we have investigated are also characterized by similar surface altered layers. In all cases, the structural and chemical boundaries between the parent crystalline phase and the adjacent altered layer are spatially coincident and sharp. The layers are in general composed of silica and depleted in interstitial cations, as well as in Al (when originally present in parent mineral). The main difference between the various weathered minerals is the thickness of the altered layers. The thickness is dependent on the composition and structure of the parent mineral, as well as on the conditions of chemical weathering, i.e., acid pH conditions favor thicker layers compared to circum-neutral pH. The overall physical, chemical, and mineralogical character of the layers is also dependent on whether chemical weathering took place in the laboratory or under natural conditions (i.e. comparison of Figs. 1 and 2). Chemical weathering in the field occurs under conditions that are more complex (numerous abiotic and biotic processes), and over time scales that are generally orders of magnitude greater.

The results that we have shown, in particular the extremely sharp and coincident chemical and structural boundaries, are at odds with a chemical weathering process controlled by interdiffusion and preferential cation release (i.e. leached layer theory). If the surface altered layers had been formed by interdiffusion, the measured cation depth profiles are predicted to be sigmoidal, with much broader chemical gradients. Moreover, diffusion modeling of our results confirm that abrupt changes in chemistry in altered layers greater than 50 nm in thickness (such as in Fig. 1) are incompatible with interdiffusion.

We propose that laboratory and natural surface altered layers form by a process that involves coupled interfacial dissolution-precipitation. This process is compatible with the sharp chemical and structural boundaries that we measured. Dissolution-precipitation implies that the intrinsic dissolution process is characterized by the stoichiometric release of all elements at the reactive interface of the parent mineral. The release of elements from this interface is controlled by chemical reactions, and not by a diffusion process. The release of all constituent elements is followed by the nearly synchronous precipitation of silica within a thin fluid film that contacts the reactive interface of the parent mineral. It is important to note that this process is not directly dependent on the fluid saturation state of the bulk solution. Silica-rich surface altered layers formed on all

laboratory weathered minerals, even though the bulk solutions were completely undersaturated with respect to all polymorphs of silica (crystalline and amorphous).

These novel results call into a question a large body of previously published studies on chemical weathering. The well-entrenched leached layer theory has already been challenged by previous chemical weathering studies that advocate this mechanism (see, e.g. Hellmann et al. 2003), as well as by more recent studies involving carbonation reactions (e.g. Daval et al. 2009a, 2009b). In addition, reactions involving mineral replacement (a subcategory of chemical weathering) may also be controlled by dissolution-precipitation (see pioneering study by O'Neil & Taylor 1967, see also reviews in Putnis 2002, 2009). If the idea of dissolution-precipitation is validated by further research, then this will completely change existing conceptual ideas concerning how chemical weathering really works, both in the laboratory and in the field.

The presence of precipitated silica-rich surface layers has important implications with respect to coupled chemical weathering-carbonation reactions. According to recent studies (e.g., Daval et al. 2009b) carbonation of Ca-bearing silicates such as wollastonite leads to the precipitation of calcium carbonate microcrystallites and phyllosilicates on and within the precipitated silica layer. There is evidence that this leads to partial passivation, thereby slowing down the weathering reaction of the primary mineral. This, of course, has important implications with respect to the efficacy of CO₂ sequestration, both in the field as well as with respect to industrial processes.

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