Chemical Geology 294–295 (2012) 203–216

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

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

Roland Hellmann [a,*], Richard Wirth [b], Damien Daval [c,1], Jean-Paul Barnes [d], Jean-Michel Penisson [e,2], Delphine Tisserand [a], Thierry Epicier [f], Brigitte Florin [d], Richard L. Hervig [g]

[a] ISTerre, University of Grenoble 1, Observatory for Earth and Space Sciences (OSUG), F-38041 Grenoble Cedex 9, France
[b] GeoForschungsZentrum Potsdam, Telegrafenberg, D-14482 Potsdam, Germany
[c] Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720 USA
[d] CEA-Leti, MINATEC Campus, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
[e] DRFMC, CEA Grenoble, F-38054 Grenoble Cedex 9, France
[f] INSA Lyon-MATEIS: UMR CNRS 5510, F-69621 Villeurbanne Cedex, France
[g] School of Earth and Space Exploration, Arizona State University, Tempe, Arizona, 85287-1404 USA

ARTICLE INFO

Article history:
Received 27 September 2011
Received in revised form 3 December 2011
Accepted 5 December 2011
Available online 13 December 2011

Editor: J. Fein

Keywords:
Chemical weathering
Dissolution–reprecipitation
Silicate minerals
Transmission electron microscopy (TEM)
Fluid–solid interfaces
CO_2 sequestration

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 CO_2. 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 CO_2 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.

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 CO_2 drawdown are CO_2 uptake in oceans and CO_2 consumption by chemical weathering reactions. Geological radwaste and CO_2 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

* Corresponding author.
E-mail address: roland.hellmann@obs.ujf-grenoble.fr (R. Hellmann).
[1] LHyGeS, Université de Strasbourg/EOST-CNRS UMR 7517, 67084 Strasbourg, France.
[2] Retired.

0009-2541/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2011.12.002

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 (Nash and Marshall, 1956; Garrels and Howard, 1957; Wollast, 1967; Luce et al., 1972; Paces, 1973; Chou and Wollast, 1985; Muir et al., 1989, 1990; Inskeep et al., 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 H_3O^+) from the bulk solution (e.g. Garrels and Howard, 1957; Wollast, 1967; Luce et al., 1972; Paces, 1973; Muir et al., 1989, 1990; Casey et al., 1988; Muir et al., 1989; 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; Schweda et al., 1997; Banfield et al., 1995; Hellmann, 1995; Yang et al., 2009).

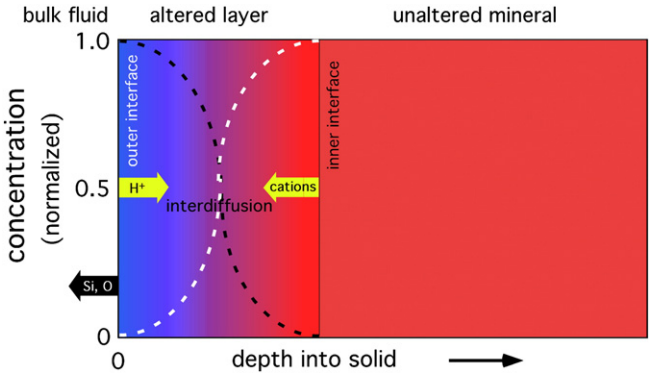

Fig. 1. Amorphous surface altered layer formed by leached layer mechanism (arbitrary scale, view in cross section). The anticorrelated, sigmoidal concentration profiles are created by solid-state volume interdiffusion of preferentially released cations (cation profile—white) with protons from bulk solution (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).

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., $\equiv Si-OH + HO-Si\equiv \rightarrow \equiv Si-O-Si\equiv + H_2O$), 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., 1986; 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; Banfield and Eggleton, 1990; Mogk, 1990; Nugent et al., 1998; Kawano and Tomita, 2001; Zhu et al., 2006). Several of these studies document sigmoidal cation depletion profiles (Nesbitt and Muir, 1988; Nugent et al., 1998; 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,