

Reactions of feldspar surfaces with aqueous solutions

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Abstract

Reactions involving feldspars are of great importance in the environment, influencing geochemical cycles in many ways. Dissolution of feldspars has been widely studied in the laboratory, with attempts being made to reproduce and understand the processes of “weathering” as seen in the environment. It has long been recognised that weathering of feldspars involves the attachment and detachment of atoms at the surface of the mineral. A wide range of factors influences the reactions involved, from the composition of the feldspar to the nature of the solution, but it is generally accepted that weathering leads to the presence of a leached layer, with a composition different from both the bulk mineral and the fluid. The aim of this paper is to review recent work carried out on feldspars, focusing particularly on developing an understanding of the leached layer using both spectroscopic methods (including Secondary Ion Mass Spectroscopy and X-ray Photoelectron Spectroscopy), and microscopic imaging techniques (including Atomic Force Microscopy and Scanning Electron Microscopy) to follow changes at the mineral/solution interface. Contrasting models of surface evolution are discussed.

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1. Introduction

Environmental transport of nutrient elements and contaminants is influenced by their partitioning between solid and solution phases, so that understanding interaction with mineral surfaces is an essential foundation for understanding transport processes. Silicates in general, and feldspars in particular, are the most common minerals in the Earth’s crust and, although sorption on feldspars is minor in comparison with

sorption on clay minerals and oxyhydroxides, understanding the reactivity of feldspar surfaces in contact with low temperature aqueous solutions and their interactions with solutes is essential. Reaction of feldspars is of specific importance in agriculture because they can be a source of inorganic nutrients in soils, modifying fertility. They can also limit the acidification of soils and waters through neutralizing acidity by cation exchange, and on a larger scale, can have an effect on global climate change by buffering atmospheric CO₂ and thus modifying the balance between the volcanic input from the Earth’s interior and the output through chemical weathering of silicates (Berner, 1995).

The feldspars have been extensively studied over many decades and the literature concerning their

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chemical reactions with aqueous solutions (“weathering”), both at laboratory and field scale, is considerable. The term “weathering” is specifically used to describe the outcome of interactions with the biosphere, hydrosphere and atmosphere. Comprehensive reviews of previous work on the mechanisms and kinetics of feldspar dissolution are provided by Blum (1994), White and Brantley (1995), and Blum and Stillings (1995). However, recent improvements in techniques offer new prospects for understanding the dissolution of feldspars, and the development of surface analysis and spectroscopic tools now enables direct measurement of the modifications of the mineral surface taking place during dissolution, at least within the limitations of the various techniques. The primary aim of this paper is to review the work that has been done using newly developed spectroscopic and imaging tools in the context of our current knowledge of feldspar dissolution. Here, we concentrate on the determination by different spectroscopic methods, particularly Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS), of the surface chemical composition of feldspars after weathering, and on characterisation of microstructure and surface microtopography using techniques such as Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Other aspects, such as details of dissolution kinetics and of the influence of organic acids on dissolution, or the use of *ab initio* calculations to describe dissolution mechanisms, have not been dealt with in detail here because they are comprehensively covered in White and Brantley (1995) and references therein. Some of the studies mentioned here give incompatible results, partly perhaps because of instrumental artefacts. Many, including XPS, SIMS and Transmission Electron Microscopy (TEM) require the use of high or ultra high vacuum and, therefore, do not allow the study of *in situ* conditions at the solid–liquid interface. In addition, surface charging and poor depth resolution may affect the quality of the data. Techniques that can be used *in situ*, such as AFM or X-ray Reflectivity probably give the truest picture of what is happening at the surface. A summary of the strengths and limitations of the techniques mentioned in this paper is given in Table 1.

It has long been known that the addition of powdered feldspar to an aqueous solution modifies the pH and composition of the solution, releasing cations as the result of ion exchange and dissolution (Wollast, 1967; Helgeson, 1971; Busenberg and Clemency, 1976; Busenberg, 1978; Chou and Wollast, 1984; Holdren and Speyer, 1985a). Several factors can

modify the rates and mechanisms of such dissolution, including:

- (1) the pH of the original solution (Wollast, 1967; Holdren and Speyer, 1985b; Knauss and Wolery, 1986; Casey et al., 1988; Brady and Walther, 1989; Casey et al., 1989b; Blum and Lasaga, 1991; Casey et al., 1991; Fenter et al., 2003);
- (2) the temperature (Petrović et al., 1976; Hellmann et al., 1990; Casey and Sposito, 1992; Hellmann, 1994; Fenter et al., 2003);
- (3) the precise composition of the initial solution (Blum and Lasaga, 1988; Muir and Nesbitt, 1991);
- (4) the composition of the feldspar (Busenberg, 1978; Siegel and Pfannkuch, 1984; Brady and Walther, 1989; Shotyk and Nesbitt, 1992; Franke and Teschner-Steinhard, 1994; Oelkers and Schott, 1995);
- (5) the initial grain size of the feldspar (Holdren and Speyer, 1987; Amrhein and Suarez, 1992);
- (6) the composition of the atmosphere in contact with the reacting system (Wollast and Chou, 1992).

Numerous previous studies have proposed different mechanisms of dissolution at acidic, neutral and basic pH, involving formation of a leached layer, the composition and depth of which varies with the pH of the initial solution and the mineral composition. It has been generally accepted that bulk dissolution at room temperature is incongruent at acid pH and congruent at alkaline pH, with a “transition” phase at near neutral pH (see Blum and Stillings, 1995; and references therein; see also Wollast, 1967; Casey et al., 1988; Alekseyev et al., 1997; Gout et al., 1997; Kobayashi et al., 2001; Teng et al., 2001; Seyama et al., 2001), although in some cases, minor but measurable incongruency at high pH has been observed (see Chou and Wollast, 1984, 1985). In addition, high levels of incongruency have been observed at both low and high pH under high temperatures (Hellmann, 1995). However, because feldspar composition and structure vary in such a complex fashion, the dissolution mechanism can also vary with mineral composition. For instance, comparisons between the dissolution of labradorite, a plagioclase with variable contents of anorthite, and pure anorthite show that in acidic conditions the more anorthite component present in the feldspar, the more congruent the dissolution (see Section 1.1). This is due to the fact that pure anorthite contains equimolar Al and Si. Therefore, hydrolysis of Al–O–Si bonds results

Table 1
Strengths and limitations of surface analysis and imaging techniques discussed in this paper

Technique	Strengths	Limitations
Secondary Ion Mass Spectrometry (SIMS)	<ul style="list-style-type: none"> –Depth profiling up to several microns into the sample –All elements can be analysed down to trace levels (ppb) –Isotopic ratios can be measured 	<ul style="list-style-type: none"> –UHV technique –Insulating samples often hard to analyse / surface charging problems –Differential sputtering can happen –Destructive technique
X-ray Photoelectron Spectroscopy (XPS)	<ul style="list-style-type: none"> –Analysis depth from a few to over 100 Å, depending on the mineral surface –Gives compositional, oxidation state and species information –Can provide semi quantitative near-surface compositions 	<ul style="list-style-type: none"> –UHV technique –Analyses of H and He not possible –Spatial resolution limited around 10 µm
Rutherford Backscattering (RBS)	<ul style="list-style-type: none"> –Non-destructive depth profiles obtained –Very quantitative method 	<ul style="list-style-type: none"> –UHV technique –Requires particle accelerator –Needs a priori knowledge of the surface chemistry of the sample to interpret results –Poor depth resolution
Elastic Recoil Detection Analysis (ERDA)	<ul style="list-style-type: none"> –Quantitative analysis of light elements, especially H –Non-invasive method –Maximum depth range around 1 µm, detection limit around 20 ppm 	<ul style="list-style-type: none"> –UHV technique –Accuracy around 10% –Depth resolution around 100 Å
Resonant Nuclear Reaction Analysis (RNRA)	<ul style="list-style-type: none"> –Provides depth profile for H in the near-surface of minerals 	<ul style="list-style-type: none"> –Poor depth resolution (several tens of Å)
X-ray Reflectivity	<ul style="list-style-type: none"> –Analyses the near-surface structure at depths down to several 1000 Å –Depth resolution below 10 Å –Can be used in situ 	<ul style="list-style-type: none"> –Flat samples needed
Scanning Electron Microscopy (SEM)	<ul style="list-style-type: none"> –Large depth of field –Image resolution from light microscope capabilities down to 10–20 Å –Large magnification range –Gives elemental information when used in combination with Energy-Dispersive X-ray spectrometer (EDX) 	<ul style="list-style-type: none"> –Images are rather large (tens of sq. Å)
Atomic Force Microscopy (AFM)	<ul style="list-style-type: none"> –Gives good images of surface microtopography –Surface microtopography can be observed down to molecular scale (atomic scale in the vertical direction) –Can be used in situ –Can be used on conducting and non-conducting surfaces 	<ul style="list-style-type: none"> –Quality of image very dependent on quality of tip –No chemical information provided
Transmission Electron Microscopy (TEM), including its variants High-Resolution TEM (HRTEM) and Energy-Filtered TEM (EFTEM)	<ul style="list-style-type: none"> –Gives ultra-high magnification images of surface –Can also be used to study surface atomic structure 	<ul style="list-style-type: none"> –UHV technique –Very small area analysed –Tedious preparation of the sample

in isolated Si which is not incorporated in the structure so that dissolution is close to congruent.

Two contrasting though not incompatible models, the surface reaction model and the leached-layer diffusion model, have been used to describe the feldspar dissolution mechanism in acid conditions. The surface reaction model involves dissolution occurring predominantly at sites of high energy on the surface, such as kink sites or defects (Lasaga, 1995) and the existence of etch pits and roughening of the

surface after dissolution is used to support this hypothesis. On the other hand, the leached-layer diffusion model (Casey et al., 1988; Hellmann et al., 1989; Casey and Ludwig, 1995) postulates the preferential release of alkali cations from the mineral into solution during the non-stoichiometric, early stages of acid dissolution, leading to the formation of a leached layer. In this case, the slowest and therefore limiting step for reaction is the release of Si and O at the surface (Oelkers, 2001). The development of

powerful new spectroscopic tools has given a better understanding of this layer. However, both these models have their limitations (Adriaens et al., 1999) and a correct view of the process may be a combination of the two. Indeed, it has been established that etch pit formation and preferential dissolution occur at high energy sites, whether in the presence of a leached layer or not. In addition, Lasaga and Lutge (2001) have shown using Monte Carlo simulations that dissolution stepwaves emanated from the presence of etch pits, enabling the removal, layer by layer, of material from the dissolving surface. This has led a number of workers (Petrović et al., 1976; Holdren and Berner, 1979; Casey et al., 1988; Teng et al., 2001; Hellmann et al., 2003, 2004) to develop an approach for describing feldspar dissolution using a dissolution/precipitation mechanism. This approach uses a unique stoichiometric dissolution mechanism at both acidic and basic pH (see Section 3 below). However, this model has so far only been used to describe labradorite dissolution at very low pH (pH=1).

2. Determination of surface chemical composition, structure and morphology of feldspars after dissolution

Numerous techniques have been used over the last 40 years to study the composition of feldspars before, during, and after dissolution. The information provided is usually specific to a given technique, so it is often useful to use them in combination. These techniques can generally be categorised in two groups: techniques for determining surface chemical composition, and techniques for determining surface microtopography and crystal structure. In the study of feldspars, the techniques used for the determination of surface composition have been mainly SIMS, XPS, Resonant Nuclear Reaction Analysis (RNRA), Elastic Recoil Detection Analysis (ERDA), Rutherford Backscattering Spectroscopy (RBS), and TEM including its High-Resolution and Energy-Filtered “variations” HRTEM and EFTEM. X-ray Reflectivity has also been used to a certain extent. For the study of surface topography, the main techniques used have been Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), the latter being used both in air and in situ.

2.1. Secondary Ion Mass Spectroscopy (SIMS)

SIMS has been used to measure depth profiles in the leached layer and these profiles provide information

about the first few microns beneath the sample surface. Since the technique is very sensitive, trace (down to parts per billion) as well as major elements can be detected. Nesbitt and Muir (1988) and Muir et al. (1989) have been the main investigators using SIMS to study feldspars.

For 10 to 15 years, it has been accepted (e.g. Muir and Nesbitt, 1992) that the first step in the formation of a leached layer during dissolution at acid pH is the exchange of Na^+ or Ca^{2+} in the feldspar framework for H^+ or H_3O^+ , resulting in replacement of an eight-coordinated Na^+ or Ca^{2+} ion by a singly coordinated H^+ and thus weakening the framework (Muir and Nesbitt, 1992, 1997). In a study of the dissolution of labradorite at pH between 3.5 and 5.7 over periods of up to 90 days, Muir et al. (1989) have shown, when looking at the ratios of elements relative to contents of ^{28}Si , that the profile obtained for Na is unusual in showing a higher $^{23}\text{Na}/^{28}\text{Si}$ ratio near the surface than in the bulk (see Fig. 1). Similar observations were made by Nesbitt and Muir (1988) for weathered and unweathered plagioclase. This was interpreted as being an artefact arising from charge-induced migration rather than reflecting the real profile of the element. XPS results from other studies (Chou and Wollast, 1984; Berner et al., 1985; Chou and Wollast, 1985; Hochella et al., 1988; Hellmann et al., 1990) as well as other SIMS results (Streit et al., 1986) tend to confirm this hypothesis. Thus, it is believed that the behaviour of Na is similar to that of Ca and Al, and that it is depleted in the near-surface layer; the composition of the mineral at greater depths appears to be similar to the unweathered material. The behaviour of Si is generally more difficult to assess, as most studies show depth profiles in terms of ratios of leached element to Si. However, in the study by Hellmann et al. (2003), EFTEM chemical maps of Ca, Al, Si and O at an interfacial boundary separating an acid-altered and unaltered zone of a labradorite feldspar show evidence of depletion in Al and Ca, and enrichment in Si and O in the altered layer. Other methods, in addition to SIMS, are therefore needed to establish fully the behaviour of Na.

The results reported by Muir et al. (1989) on labradorite and on other feldspars (albite and oligoclase) show a thicker depleted layer being developed on reaction with solutions at low pH (600 to 1200 Å depth for both Ca and Al depletion; see Fig. 2) compared with that found at near neutrality. In double-distilled water (pH=5.7), the depletion reaches depths of less than 120 Å for Al and 300 Å for Ca. However, one can ask what the real influence of the contact time in solution is

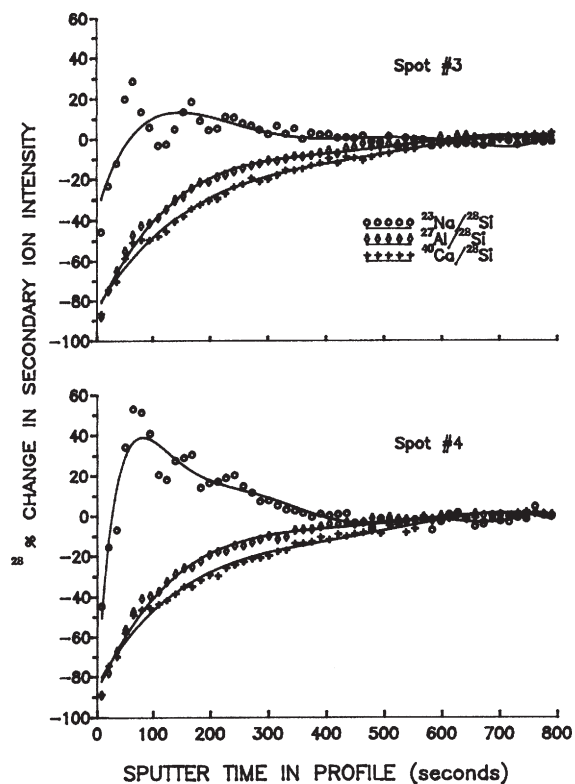


Fig. 1. SIMS depth profiles for $^{23}\text{Na}/^{28}\text{Si}$, $^{27}\text{Al}/^{28}\text{Si}$ and $^{40}\text{Ca}/^{28}\text{Si}$ (normalization for two points of analysis) after leaching of labradorite in pH=3.5 solution for up to 90 days. Data show the good reproducibility of the SIMS technique. The normalization is calculated as a percentage according to the equation:

$$\left(\frac{(^{23}\text{Na}/^{28}\text{Si})_{\text{surface}}}{(^{23}\text{Na}/^{28}\text{Si})_{\text{bulk}} \times \left(\frac{(^{23}\text{Na}/^{28}\text{Si})_{\text{surface}}}{(^{23}\text{Na}/^{28}\text{Si})_{\text{bulk}} \right)_{\text{control}}} - 1 \right) \times 100$$

where ^{23}Na is replaced by ^{27}Al or ^{40}Ca for the other points of analysis. The time scale represented on the x axis can be related to depth by using a profile meter measuring the depth of the crater formed after bombarding the surface. Reproduced from Muir et al., 1989. Reprinted from *Geochim. Cosmochim. Acta*, 53, Muir I. J., Bancroft G. M. and Nesbitt H. W., Characteristics of altered labradorite surfaces by SIMS and XPS. 1235–1241, Copyright (1989), with permission from Elsevier.

on the depth of leaching, as one sample was left in contact with the solution for longer than the other (90 vs. 60 days). In later studies (Muir and Nesbitt, 1991, 1997), similar profiles were obtained after 72 days of leaching, suggesting that the trend seen here is indeed valid.

Similar results were obtained by Goossens et al. (1989) on sanidine, where an amorphous layer depleted in aluminium, potassium and sodium and enriched in hydrogen appears after reaction at pH 1 in

HCl/H₂O solution. The thickness of the layer increases with the reaction time and the temperature (see also Adriaens et al., 1999). The use of deuterium combined with SIMS and Fourier Transform Infrared Spectroscopy (FTIR) has enabled study of the nature of the hydrated layer. It seems that hydrogen is mainly present as adsorbed water because, when the experiment is carried out with deuterium, a small signal indicates the presence of only Al–OD bonds, and no peak for Si–OD bonds can be detected. However, it is possible that rapid exchange of D for H could occur during the short period of time when the sample is in contact with air.

In the presence of a powdered SiO₂ suspension (giving a dissolved silica concentration below the saturation value), the surface layer obtained is drastically depleted in Al, Na and K compared to similar experiments conducted without SiO₂ (Adriaens et al., 1999). This could be explained by the existence of a leached layer, as already described, or could be the result of a repolymerization mechanism leading to the formation of a precipitated layer of SiO₂. The use of further analytical methods has not enabled Adriaens et al. (1999) to decide between these mechanisms, but it seems that a combination of the two mechanisms would best describe the dissolution. Indeed, the use of SIMS, FTIR, XPS, TEM or SEM (see below) has not provided definitive results in support of one or the other hypothesis. Even the use of $^{30}\text{SiO}_2$ powder instead of $^{28}\text{SiO}_2$ by Adriaens et al. (1999) in order to decide between the leached and precipitated layer hypotheses does not provide conclusive evidence for one or other mechanism. In these experiments on sanidine, values of ^{30}Si in the layer were higher than values in the mineral before dissolution, but lower than the spike values. Moreover, values of ^{30}Si in solution after dissolution have changed when compared to the initial values, indicating some kind of exchange between the solution and the mineral. Although exchange between solid and solution has been demonstrated, direct precipitation of Si onto the surface cannot be completely ruled out, given the higher values of ^{30}Si in the layer.

Experiments carried out on labradorite by Muir and Nesbitt (1991) and involving different free cations in solution, have also shown the importance of the cation concentration gradient at the solid/solution interface on the dissolution process. In their experiments, the addition of free aluminium in solution produced greater depletion of the leached layer in Ca than in Al, and made it thinner. Different behaviour was observed by Goossens et al. (1989) where addition of Al₂O₃ in

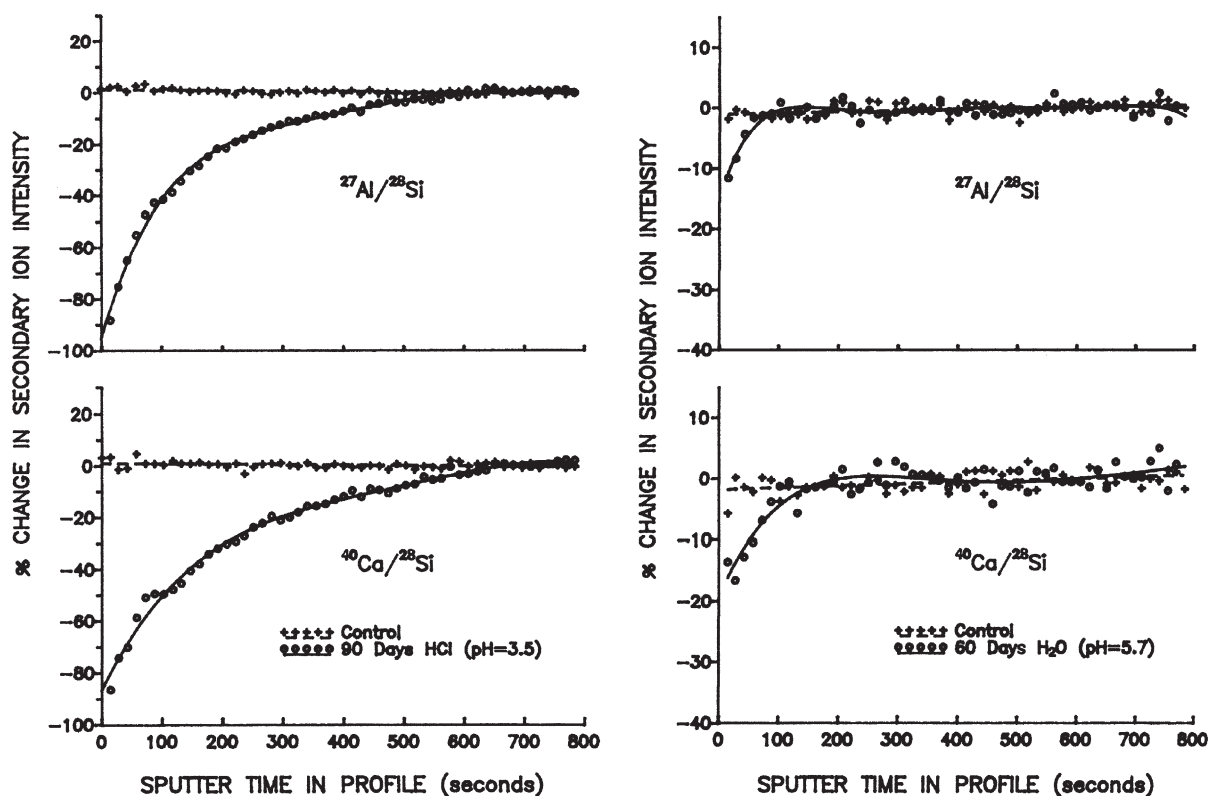


Fig. 2. SIMS depth profiles showing the percentage change in secondary ion intensity as calculated in Fig. 1 for the reacted labradorite (open circles and solid lines; pH=3.5, 90 days on the left; pH=5.7, 60 days on the right) and the unweathered labradorite (+ signs and dash line). The percentage change in secondary ion intensity (ordinate) is plotted against time in seconds of sputtering. Reproduced from Muir et al., 1989. Reprinted from *Geochim. Cosmochim. Acta*, 53, Muir I. J., Bancroft G. M. and Nesbitt H. W., Characteristics of altered labradorite surfaces by SIMS and XPS. 1235–1241, Copyright (1989), with permission from Elsevier.

solution did not lead to observation of a leached layer on sanidine, but this result needs to be considered carefully as contact times were very different (2 days at 150 °C in Goossens et al. (1989), and 72 days at room temperature in Muir and Nesbitt (1991)). Addition of Mg^{2+} in solution (an ion which, unlike Al, is not present in the mineral) does not lead to any preferential cation removal, whereas addition of Ca^{2+} in solution does not affect the Al/Ca ratio of the depleted layer but does reduce its thickness. From these results, it can be concluded that the main factors affecting the thickness of the altered layer are a competitive sorption of the cations present in solution at the solution/solid interface, and a diffusion of Al through the leached layer.

Further experiments by Muir and Nesbitt (1997) have examined the influence of different anions and cations in solution at pH \approx 4 on labradorite, in either HCl, HF or oxalic acid. They show that the presence of aqueous cations in solution reduces the leaching of certain cations (Al, Na and Ca) from the surface relative to Si,

by affecting the diffusion gradients for the metals released to solution, whereas introduction of certain aqueous anions has the opposite effect. Introducing ligands that can form complexes with those cations both in solution and at the surface also affects the rate of leaching and, thus, the overall reaction rate is dictated by the composition of the reacting solutions. Previous SIMS results (Muir and Nesbitt, 1992) have shown that the Al–O bonds are more likely to be hydrolysed than the Si–O bonds, for which reaction rates are slower. Thus, after the initial release of Na^+ or Ca^{2+} , which creates an excess of negative charge and its compensation by H^+ or H_3O^+ , release of Al^{3+} is the next step. The concentrations of free Al^{3+} , Ca^{2+} and Na^+ in solution are then important factors, as they can cause variations in the concentration gradients through the layer (the concentration gradient of an ion is clearly greater if none of that ion is in solution at the beginning of the experiment). Hence, the presence in solution of complex-forming ligands enhances the formation of the

leached layer by lowering the concentration of free cations in solution. In these circumstances, complexed cations cannot compete for the active sites on the mineral surface, enabling H_3O^+ to penetrate more easily and thus enhancing diffusion of further Na^+ , Ca^{2+} and Al^{3+} ions through the layer. Put another way, the presence in solution of free cations limits the extent of formation of an altered layer, whereas the presence of complex-forming ligands enhances it.

Similar results were found by Schweda et al. (1997) and Muir and Nesbitt (1991), revealing a deeper depletion in Ca than Al, but a uniform H concentration in the layer once it is formed. Estimates of the cation mass balance (see also Casey et al., 1988; Hellmann et al., 1997) also support the proposition that all hydrogen in the leached layer is present in the form of H^+ . It can then be concluded that the release of Al^{3+} happens either by a ligand-exchange reaction with water, implying the formation of Si–OH and HO–Al–O–Si groups at the surface, or by ion-exchange with protons (see also Hellmann et al., 1990 and below).

Shotyk and Nesbitt (1992) and Nesbitt et al. (1991) have studied the nature of this leached layer and its dependence on bulk mineral composition using two different labradorites and an anorthite sample. They also studied the leached layer as a function of the acid present in solution, introducing HF and oxalic acid to replace HCl. In the case of labradorite, a leached layer depleted in Al, Na and Ca, and enriched in Si is always found. The form of acid used is an important influence on the presence and composition of the altered layer, although dissolution is incongruent in all cases (see Fig. 3). Leached layers formed after contact with HF are much thicker than those formed after contact with oxalic acid which, in turn, gives a thicker layer than HCl. Also, the more calcic the labradorite, the thicker the layer. In addition, rates of dissolution increase with the anorthite content of the feldspar (Casey et al., 1991) This suggests that the complexation of Al in solution with oxalate or fluoride encourages diffusion of Al through the layer, leading to an increase in thickness. Because plagioclase has a sufficiently extensive Si network to maintain a surface layer even after depletion of Al in the framework, the dissolution observed is incongruent (see below). Also, the differences observed following reaction with HF and oxalic acid can be explained by looking at the sizes of the anions involved. As F^- is much smaller than the oxalate ion it can penetrate much more easily through the surface layer, attack Al and Ca sites in the feldspar and form strong aqueous complexes with both cations that can, in turn, facilitate their detach-

ment, thus enhancing the rates of release of those ions.

The results obtained are slightly different in the case of anorthite (see Fig. 4) for which dissolution under acidic conditions seems to be almost congruent and, even though a leached layer is apparent, it is about 50% thinner (about 1600 Å in thickness compared to up to 3000 Å for the labradorite). However, the residual solutions contain more Si and Al than is the case for labradorite, indicating a greater reactivity under acidic conditions. This can be explained by the fact that the Al/Si atomic ratio is close to 1:1 in feldspars from the anorthite end and nearer to 1:3 in labradorite. Therefore, an attack on Al in labradorite is less likely to affect the silicate framework of the feldspar, whereas the same attack on a more calcic feldspar damages proportionately more Si–O–Si bonds, which are already present in inferior number, bringing about the collapse of the framework and, thus, congruent dissolution. To summarise, the greater the An content of a feldspar, the more reactive it is, even though changes in depletion and thickness of the leached layer can also be influenced by the speed of the reaction. Oxburgh et al. (1994) have proposed, after studying the dissolution kinetics of three different plagioclases in dilute HCl (pH 3 to 7), that the rate of dissolution can be expressed by an equation combining surface complex reaction theory with the Arrhenius law. According to them, the rate of dissolution can be expressed by the equation:

$$\text{Rate} = \chi_a A \exp(E_a/kT) (C_{\text{H}}^{\text{s}})^n$$

where C_{H}^{s} is the concentration of protonated surface sites, χ_a is the mole fraction of activated protonated sites, A is the Arrhenius pre-exponential factor, E_a is the activation energy of the reaction and n is the order of the reaction. The rate of dissolution is then proportional to the order of the reaction which is, itself, proportional to the number of protonated sites involved in the dissolution. As the number of those sites increases with the mole fraction of anorthite in the plagioclase, due to the relatively high reactivity of Al–O–R bonds, so does the rate of the reaction and this is also consistent with the leached layer being thinner.

2.2. Ion beam techniques

In addition to SIMS, several techniques have been used to provide a better understanding of the dissolution process. Amongst them, ion beam techniques such as Resonant Nuclear Reaction Analysis (RNRA), Elastic Recoil Detection Analysis (ERDA) or Rutherford

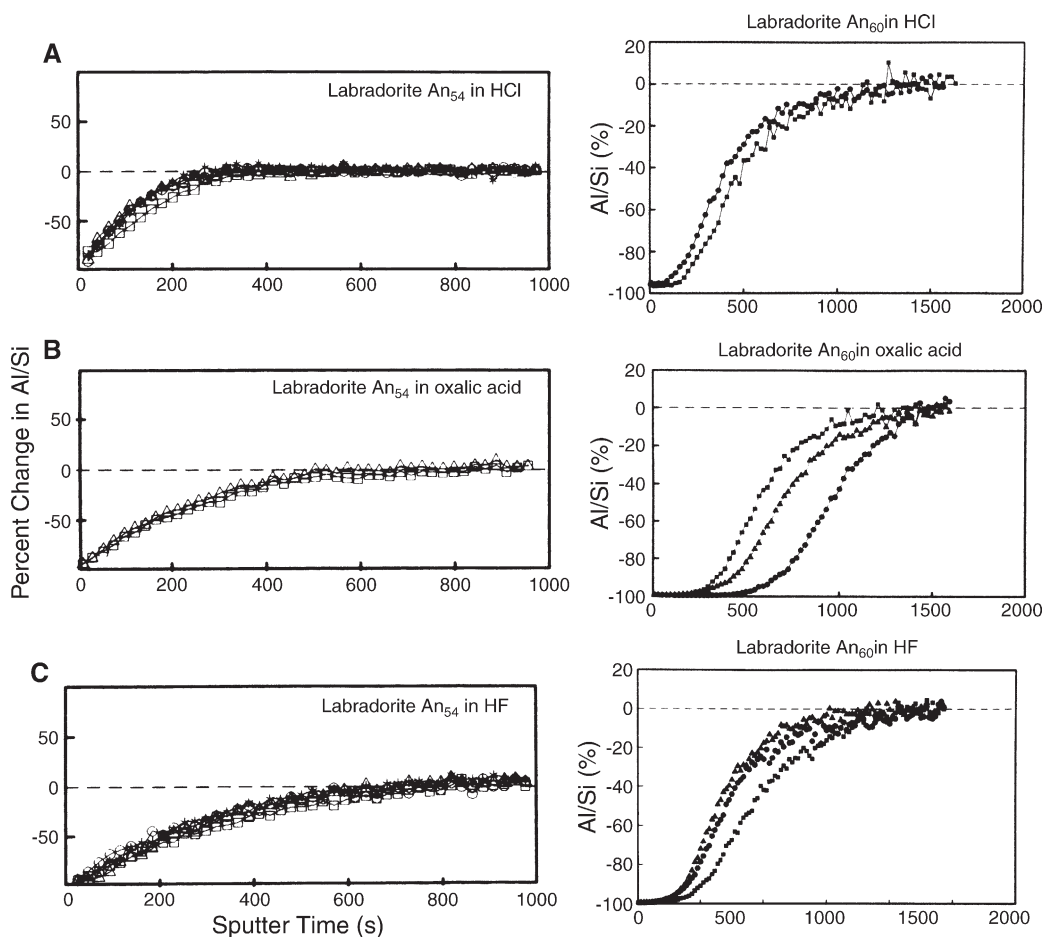


Fig. 3. SIMS depth profiles showing the percentage changes in Al/Si (calculated as in Figs. 1 and 2) of labradorite An₅₄ (left) and An₆₀ (right) after reaction at pH=4, 72 days in (A) HCl, (B) oxalic acid or (C) HF. These data reflect the deeper loss of Al compared to Si in the leached layer of the An₆₀ labradorite than the An₅₄ labradorite. The leached layer formed in the case of An₅₄ after contact with HCl (about 600 Å) is thinner than after contact with both oxalic acid and HF (about 1000 Å). The leached layer produced in the case of An₆₀ after contact with HF (about 5000 Å) is thicker than after contact with both HCl and oxalic acid (about 3000 Å). Compare with unweathered labradorite and labradorite reacted for 90 days at pH 3.5 (see Fig. 2). Reproduced from Shoty and Nesbitt, 1992. Reprinted from Geoderma, 55, Shoty W. and Nesbitt H. W., Incongruent and congruent dissolution of plagioclase feldspar: effect of feldspar composition and ligand complexation. 55–78, Copyright (1992), with permission from Elsevier.

Backscattering Spectrometry (RBS) have been of great use in giving information on the composition of the surface after dissolution under various conditions and providing depth profiles of H, Si, Al, Ca and Na. Casey et al. (1988, 1989b), Petit et al. (1989) and Hellmann et al. (1997) have used these techniques on labradorite and albite treated at different pH values and temperatures. In all cases, incorporation of H in a near-surface layer was observed at acid and neutral pH, and to a greater extent in acid conditions. A leached layer of variable depth was also present. In theory, the cation depletion profile can be described by a concentration gradient for which the boundary conditions are a 100% depletion at the fluid/leached layer interface and a 0% depletion at the leached layer/solid interface. However, it is generally observed

that the profile is more sigmoidal than that seen by SIMS. The hydrothermal conditions (300 °C, 170 bars) used by Hellmann et al. (1997) caused incorporation of H at the surface that is so deep that the thickness of the H permeation layer is beyond that detectable using the instrument, but comparison with previous experiments still suggests a sigmoidal profile with the concentration of H tending toward zero at a depth undetectable by RNRA and ERDA (respectively, penetrating to about 6000 and 10,000 Å). In addition, under these experimental conditions (high temperature and pressure, acid to neutral pH) the Na profiles detected by RNRA are sigmoidal, showing depletion at the solution/surface interface. However, the calculated thickness of the depleted layer appears to be overestimated compared

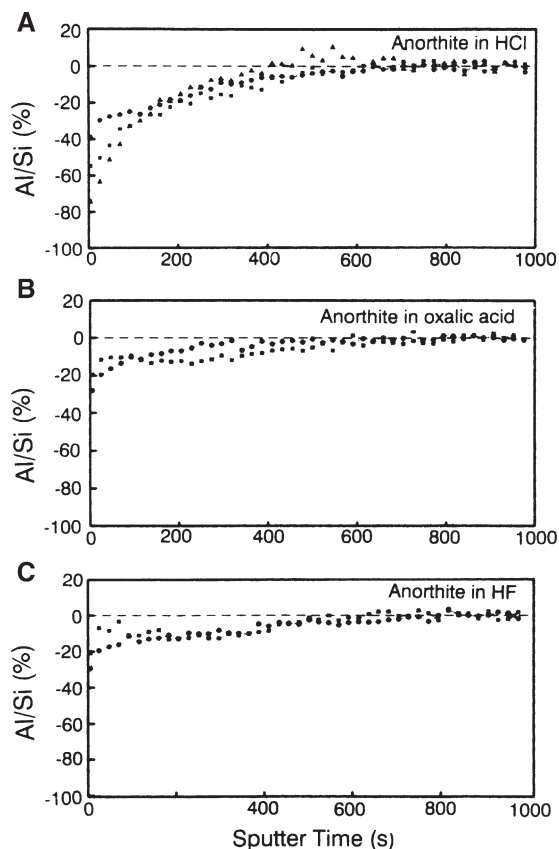


Fig. 4. SIMS depth profiles showing the percent changes in Al/Si (calculated as in Figs. 1 and 2) of anorthite after reaction at pH=4, 72 days in (A) HCl, (B) oxalic acid or (C) HF, and reflecting the loss of Al compared to Si in the leached layer. The percentage change in Al/Si is much smaller than for the labradorites shown in Fig. 3. Both leached layers produced in presence of oxalic acid and HF are thinner than the leached layer produced in the presence of HCl. Reproduced from Shotyk and Nesbitt, 1992. Reprinted from Geoderma, 55, Shotyk W. and Nesbitt H. W., Incongruent and congruent dissolution of plagioclase feldspar: effect of feldspar composition and ligand complexation, 55–78, Copyright (1992), with permission from Elsevier.

with that determined using ion beam techniques (see Hellmann, 1995). A mass balance calculated using Na loss, preferential leaching of Al, and H permeation at acid pH shows a slight charge imbalance. H incorporation is a function of the rate of Na^+/H^+ ion exchange, but also depends on the speciation of the Si–OH and Al–OH groups and, thus, on pH. Ab initio calculations (Kubicki et al., 1996) have shown that the bridging bond between either a Si or an Al and an O atom at basic pH is weakened, forming Si–O⁻, Al–OH or Al–O⁻ groups. The formation of hydrogen bonds between these bridging oxygens and water molecules is also favoured, thus encouraging the hydrolysis reaction at high rather

than at neutral pH. This matches observations by numerous workers (see Brady and Walther, 1989; Hellmann, 1994, 1995; see also Hellmann et al., 1997) that the rate of reaction increases with increasing pH from neutral to basic. At basic pH, deprotonation of the Si–OH and Al–OH groups causes a decrease in the amount of H permeating the near-surface layer, and the Na^+ ions are probably replaced by other species in solution. Indeed, dissolution carried out in a KOH/H₂O solution (pH 8.3 at 300 °C; pH 11 at 25 °C) shows an enrichment in K at the surface, countering the charge imbalance (Hellmann et al., 1997). Similar experiments carried out with Ba(OH)₂ solution (pH 8.6 at 300 °C; pH 11.3 at 25 °C) also show enrichment of the surface in Ba (see Fig. 5, bottom), although part of this enrichment can be attributed to the precipitation of a Ba silicate at the surface, and part to incorporation of Ba in the structure (Hellmann et al., 1997). Thus, and as noted above, the behaviour of hydrogen is different at low and at high pH, leading us to distinguish between H retention and H permeation. Retention is mainly a feature of acid pH, when hydrogen in the form of H⁺ cations can remain in the structure, as well as being exchanged with Na⁺. At higher pH, hydrogen is mostly in the form of H₂O or OH⁻, but since Si–O⁻ and Al–O⁻ are predominant rather than the protonated forms, the hydrogen present after hydrolysis will not remain in the framework but will permeate the leached layer zone

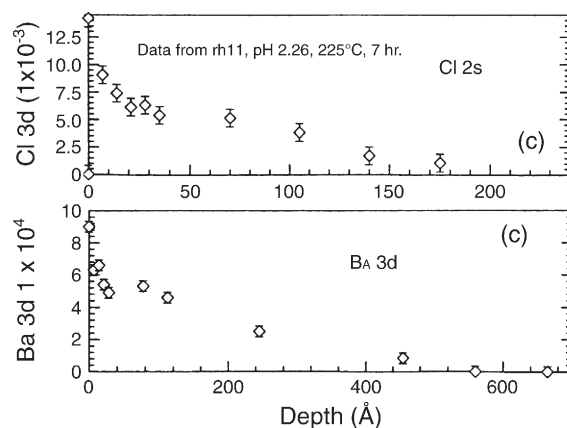


Fig. 5. Top: variations of Cl 2s peak intensity with depth after contact of albite with pH 2.26 solution for 7 h at 225 °C. Cl content gradually decreases over a range of approximately 200 Å. Bottom: variations of Ba 3d peak intensity with depth after contact of albite with a pH 10.1 solution for 3.6 h at 225 °C. Ba infiltration is due to pH adjustment of solution with Ba(OH)₂. Reproduced from Hellmann et al., 1990. Reprinted from Geochim. Cosmochim. Acta, 54, Hellmann R., Eggleston C. M., Hochella M. F., Jr and Crerar D. A., The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions, 1267–1281, Copyright (1990), with permission from Elsevier.

(hence the concept of H permeation). Thus, the charge imbalance mentioned above arises from the almost complete absence of free H species in the structure after dissolution.

The use of X-ray Reflectivity by Fenter et al. (2000) to study the acid dissolution of orthoclase under atmospheric conditions, also reveals depletion in cations (K^+ in this case) of the first layer at the surface. No depletion of the deeper layers was observed, consistent with previous results (Busenberg and Clemency, 1976; Chou and Wollast, 1984; Blum and Lasaga, 1991; Stillings et al., 1995). Again, entry of H_2O into the structure is observed, and the sorption here is believed to be dissociative: OH^- is believed to attach to dangling silicon atoms (i.e. silicon atoms at the surface that are not attached to four oxygens) forming a silanol group (Si–OH) at the surface of the mineral, while the remaining H^+ is exchanged for K^+ ions. Theoretical calculations carried out by Kubicki et al. (1996) have confirmed the possibility of losing cations from the framework after attack by H_2O molecules. It has been established (Kubicki et al., 1996) that bridging oxygen atoms in $(Si_3)Al-OH_2$ and $Na^+(HSi_3)Al-OH_2$ groups are nearly coplanar with the aluminium atoms, thus allowing attack by a further H_2O molecule and formation of a fifth bond to give a pentacoordinated Al^{3+} . If, at a given Al on the surface, two Al–O–Si bonds are hydrolysed to form two Al– OH_2 groups (the prevalent group at acid pH), nucleophilic attack of the aluminium atom is then possible leading to such a change in the coordination of the cation on the surface. Further hydrolysis of the remaining Al– O_{br} bond would then lead to the release of Al^{3+} into solution.

RBS and RNRA measurements carried out after dissolution in basic solutions and under similar (hydro-thermal) conditions to those employed by Hellmann (1995) lead to completely different results, as also observed by many workers from titration experiments. Under these conditions (300 °C, 170 bars, $pH \approx 8.6$ –8.9 in KOH or $Ba(OH)_2$), Hellmann et al. (1997) report no change in the RNRA spectra of H for albite after reaction, as compared with the spectra for a fresh sample. Moreover, the spectra observed for Na only show limited depletion over a few hundred Ångstrom units depth of penetration. These differences in dissolution behaviour have been investigated by modelling studies (Xiao and Lasaga, 1996; Hellmann, 1997) and it is now believed that the rate of release of Na and the rate of sorption of H are dependent on each other. Their dependence can be described using a single interdiffusion coefficient, D , reflecting mainly temperature and operational pH. The composition of the leached layer is

also dependent on the pH, and its depth is dependent on the temperature (Hellmann, 1995; Hellmann et al., 1997).

The use of SIMS and other ion beam techniques has provided a better understanding of the reactions of feldspars under well controlled conditions. However, other spectroscopic techniques can give complementary results, and ion beam experiments are generally used in combination with XPS and a range of imaging techniques.

2.3. X-ray Photoelectron Spectroscopy (XPS)

Since its development about 30 years ago, XPS has allowed major advances in the understanding of surface chemistry and has been valuable in studying the modification of mineral surfaces after dissolution (Hochella and Brown, 1988; Hochella et al., 1988; Muir et al., 1989, 1990; Hellmann et al., 1990; Inskip et al., 1991; White and Hochella, 1992; Seyama et al., 1996; Chen et al., 2000; Kobayashi et al., 2001; Nesbitt and Skinner, 2001). A summary of relevant experiments carried out using XPS is given in Table 2.

Studies by Petrović et al. (1976), Berner and Holdren (1979), Holdren and Berner (1979), Fung and Sanipelli (1982) and Berner et al. (1985) on dissolution of feldspars have suggested that under laboratory conditions (ambient temperatures to 100 °C, 1 atm pressure, pH from 2 to 8), no leached layer is detectable and the dissolution appears to be stoichiometric, suggesting a surface reaction mechanism rather than one involving the formation of a leached layer depleted in alkali ions. However, there is some preferential dissolution observed at step edges and defects, leading to the formation of etch pits after prolonged contact with solution. In addition, formation of particulates containing high levels of Al was observed on the surface during the first stages of dissolution (Holdren and Berner, 1979; Fung and Sanipelli, 1982). This could reflect reprecipitation of Al from solution, preventing the solution from becoming saturated with this element, but this is not believed dramatically to affect the rate constants. However, it has been difficult to explain the non-linear rates of dissolution in the early stages of reaction, which are then followed by constant rates. It is now generally established that the parabolic dissolution rate curve obtained initially reflects enhanced dissolution of small particles (<1 µm diameter) remaining at the surface of the solid from grinding. These particles may be different due to their very small size, presenting different surface areas and defects at the surface, resulting in different dissolution behaviour from the

Table 2
Summary of experiments carried out on feldspars using XPS

Author	Year	Mineral	pH	Major findings
Holdren and Berner	1979	Albite	6 to 8	No obvious existence of protective coating. Dissolution promoted at crystal defects
Eggleston and Hellmann	1989	Albite	0.57–10.1	Modelling of depolymerisation / repolymerisation at the surface Na, Al depletion. Depletion decreases with increasing pH in acid range, and increases with increasing pH in basic range.
Hellmann et al.	1989/1990	Albite		
Hellmann et al.	1997	Albite	3.4, 5.7, 10.9–11.3	H enriched / Na depleted layer
Chen et al.	2000	Albite	2.9	Preferential leaching of Al and Na at $T < 50$ °C, stoichiometric dissolution at $T = 90$ °C. Thickness decreases with increasing T
Hochella et al.	1988	Labradorite	6.64	Layer enriched in Al (thickness 20 Å), depleted in Na, Ca, Si
Muir et al.	1989	Labradorite	3.5 to 5.7	Na, Al, Ca depletion
Muir et al.	1990	Labradorite	3.5	Si enrichment, Ca and Al depletion. Thickness of the layer increases with Ca content of feldspar. Existence of etch pits.
Inskeep et al.	1991	Labradorite	4	Ca and Al depletion, Si and slight Na enrichment (due to method)
Schweda et al.	1997	Labradorite	1 to 3	Na and Ca depletion at first, followed by Al depletion. Layer enriched in Si and H
Nesbitt and Skinner	2001	Labradorite	2	After 2 days, enrichment in Si and depletion in Al, Na, Ca.
Farquhar et al.	1999	Oligoclase	3.1 to 7	Rapid Na depletion
Berner and Holdren	1979	Na-plagioclase	1	Presence of etch pits at acid pH. No apparent protective coating, but existence of an Al-rich coating.
Seyama et al.	2002	Plagioclase	1 to 5	Na, Ca, Al depleted surface layer, less depleted at higher pH and enriched in Al at almost neutral pH.
Kobayashi et al.	2001	Orthoclase, Albite and anorthite	2	Si-rich layer (poorly developed for anorthite)
Petrović et al.	1976	Sanidine	4 to 8	No evidence of altered layer (if any, then thickness < 17 Å)
Fung and Sanipelli	1982	Microcline	2 to 7	Existence of aluminosilicate particles on surface, especially at acid pH. Etch pits and channels along crystal defects at very acid pH
Althaus and Tirtadinata	1989	Sanidine	Mildly acid	Penetration of H into the structure, deeper than the thickness of the depletion of K and Al
Goossens et al.	1989	Sanidine	1	Depletion of Na, Al and Ca, enrichment of H and Si. Thickness increases with reaction time and temperature.

rest of the mineral. However, these results were obtained with the first generation of XPS instruments, much less powerful than the latest machines, and have to be viewed with caution. Later experiments have shown that the non-detection of a leached layer was more likely due to a lack of resolution of the instruments used rather than to the absence of this layer (Goossens et al., 1989; Adriaens et al., 1999).

Several workers (Hochella et al., 1988; Althaus and Tirtadinata, 1989; Eggleston and Hellmann, 1989; Hellmann et al., 1989, 1990) have studied the dissolution of feldspars at temperatures above 200 °C and pressures above 300 bars. The presence of a leached layer up to 1000 Å thick (depending on the particular feldspar mineral studied), and depleted in Al, Na and O but enriched in Si, has been detected by XPS. The top few layers are drastically depleted in Al and Na, accentuating the incongruent character of the dissolution. Once again, the thickness of this layer is dependent on pH, decreasing with increasing pH in the acid range,

but increasing with pH in the basic range. However, the real power of XPS measurements is in their ability to give both species information and elemental composition of the material at the surface. Angle Resolved XPS (ARXPS) carried out by Hellmann et al. (1990) on albite samples after contact with solutions of different pH at 225 °C has provided numerous insights into possible dissolution mechanisms. As in previous studies, they showed the presence of an altered layer depleted in Na and Al across the whole pH range considered (between 0.57 and 10.1), the thickness of which depends on the pH of the experiment. However, XPS shows that Al is removed from deeper in the surface than Na, except at near-neutral pH. In addition, the Si 2p and Al 2p peaks were distorted towards low binding energies relative to the spectrum of the freshly cleaved albite, perhaps reflecting a change in the number of chemical environments for those elements. Adriaens et al. (1999) obtained XPS data for sanidine after acid treatment at 200 °C for 2 and 21.5 h, with reaction carried out both

with and without added SiO_2 powder. Slightly different results from Hellmann et al. (1997) were found, but still showed a layer depleted in Na, Al and K. In the presence of SiO_2 , none of these elements could be detected by XPS after contact for 21.5 h, but a preferential release of Na and K over Al was observed after only 2 h of treatment. Na and K concentrations were below the limit of detection of the instrument, whereas the Al signal could still be observed although it was much reduced compared to the untreated sample. The differences between the Hellmann et al. (1990) and Adriaens et al. (1999) studies are likely to be due to the nature of the mineral samples used, but similar arguments can be used to explain dissolution: in both cases, Na and K are removed faster from the surface than Al, but Al is removed from deeper in the solid than the other elements.

The XPS spectra of Hellmann et al. (1990) reveal the presence of Cl^- in the first few monolayers of the surface, a species also detected by Schweda et al. (1997) using SIMS on samples prepared under non-hydrothermal conditions. Ba^{2+} was also detected in samples prepared at pH values both below and above the pH_{pzc} (see Fig. 5). The Cl^- and Ba^{2+} come from the addition of HCl to lower the pH or $\text{Ba}(\text{OH})_2$ to raise the pH. The intensities of the Cl and Ba peaks detected by ARXPS are too high to suggest penetration of these elements only via cracks or crystal defects, although they are concentrated at such sites. This provides direct evidence that metal ions in solution can penetrate into the bulk structure of the leached layer and, thus, contribute to the mass and charge balances, implying a mechanism much more complex than the simple ion exchange model used earlier to interpret the leaching of cations out of the surface and the uptake of H^+ or H_3O^+ . In addition, at low pH, the breakage of $\text{Si}-\text{O}-\text{Al}$ or $\text{Si}-\text{O}-\text{Si}$ bonds by hydrolysis leads to the formation of $\text{Si}-\text{OH}$ or $\text{Al}-\text{OH}$ groups (see Fig. 6). However, these groups are amphoteric with points of zero charge ($\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$) values of 2.5, -2.0 , 7.0 for $\text{Si}-\text{OH}$ (Huang and Stumm, 1973) and 8.5, 7.9 and 9.1 for $\text{Al}-\text{OH}$ (Schindler and Gamsjäger, 1972). Hence, over the pH range considered ($2 \leq \text{pH} \leq 7$), they are predominantly in the form of $\text{Si}-\text{OH}$ or $\text{Al}-\text{OH}_2^+$. This would also explain the broadening of the Si and Al peaks in the XPS spectra. In order to compensate for this excess of positive charge (more H^+ being consumed than cations released) penetration of charge-balancing, negatively charged, ions into the layer is required; hence the presence of a Cl peak in the XPS spectrum after contact with an acid (HCl) solution. A similar argument can be used to explain the presence of a Ba peak in the spectra

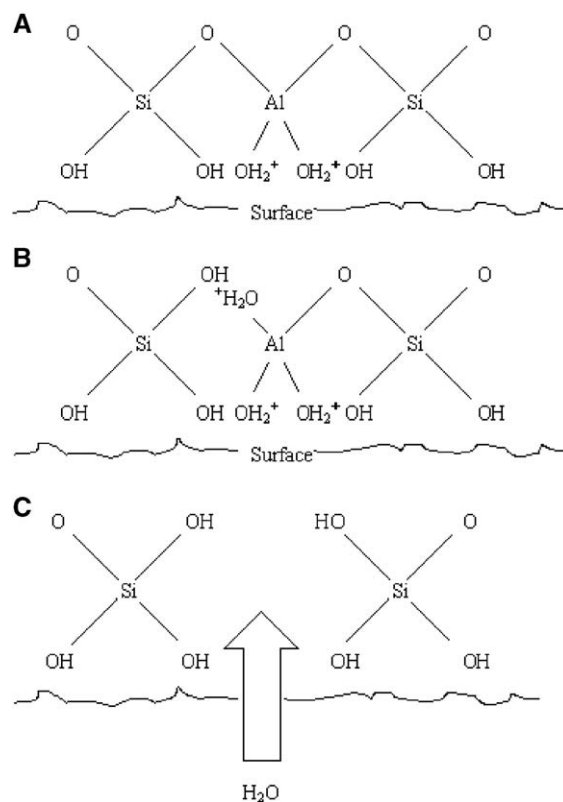


Fig. 6. A diagrammatic representation of the albite surface in contact with an acid aqueous solution ($2 \leq \text{pH} \leq 7$): (A) a $\text{Si}-\text{O}_{\text{br}}-\text{Al}$ bond is preferentially hydrolysed, resulting in uptake of H^+ and creating $\text{Si}-\text{OH}$ and $\text{Al}-\text{OH}_2^+$ groups; (B) further hydrolysis of the Al group occurs until the last $\text{Al}-\text{O}_{\text{br}}$ bond is broken, resulting in the detachment of Al from the structure; (C) this yields free $[\text{Al}^{3+} \cdot 6\text{H}_2\text{O}]_{\text{aq}}$, and leaves behind another silanol. In addition, the detachment of Al leads to restructuring and allows the influx of water deeper into the structure. Redrawn from Hellmann et al., 1990. Redrawn from Geochim. Cosmochim. Acta, 54, Hellmann R., Eggleston C. M., Hochella M. F., Jr and Crerar D. A., The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions, 1267–1281, Copyright (1990), with permission from Elsevier.

obtained after dissolution and uptake of OH^- at $\text{pH} > \text{pH}_{\text{pzc}}$. However, it would have been interesting to examine the spectra obtained when using a non-penetrating anion, paralleling the experiments done using HF and oxalic acid and employing SIMS. Further hydrolysis of the $\text{Al}-\text{OH}_2^+$ groups can lead to the release of hydrated Al^{3+} into solution, thus explaining a preferential removal of Al over Na and the greater depletion depth for Al than for Na (see also Lasaga, 1995; Hellmann et al., 1997).

Improvements in techniques combined with the development of new methods have led to alternative hypotheses which are superseding the long-established view of a surface reaction mechanism involving a

leached layer. It is now believed that feldspar behaviour at room temperature and pressure could be similar to that previously observed under hydrothermal conditions. Goossens et al. (1989) have used XPS and other techniques to study the dissolution of sanidine at pH=1 and at room temperature. Whatever the reaction conditions, a layer of varying thickness, depleted mainly in Na and K and to a lesser extent in Al, can be observed. Moreover, layer thickness increases with reaction time as well as temperature, eventually reaching more than 10 atomic layers. Muir et al. (1989, 1990) have obtained similar results from the dissolution of different plagioclase specimens at acidic pH values (3.5 and 5.7). The XPS spectrum of Si is unchanged after 60 days contact time, while changes are observed in the Al, Na and Ca spectra for which the signals are less intense than those observed for the freshly cleaved sample (see Fig. 7). Experiments carried out on orthoclase, albite and anorthite at pH 2 by Kobayashi et al. (2001) give the same results, i.e. the formation of a Si-rich layer depleted in Na, Ca, K and Al, and thicker for albite and orthoclase than for anorthite where dissolution can be considered as almost congruent (as discussed above; Shotyk and Nesbitt, 1992). However, the XPS results are not sufficiently clear-cut to give definitive information about the chemical state of the silicate in this altered

layer, as the shifts in binding energies are quite small between the freshly cleaved and the treated sample in this case.

In a similar attempt to understand dissolution, Inskeep et al. (1991) combined XPS and other imaging techniques with sputter depth profiling to study the dissolution of labradorite at pH 4. Relatively high depletion in Ca (between 30% and 50%) and slight depletion in Al (less than 15%) compared to the freshly cleaved sample was observed at the surface and up to a depth of 500 Å, consistent with the results of Muir et al. (1989, 1990). However, enrichment in Na by up to 15% compared to the unaltered mineral was observed, contrary to the results reported by Muir et al. (1989) and Hellmann et al. (1990). One possible cause of this could be differences in the way that calcic and sodic phases are exposed to the detectors in such experiments (Fig. 8). If the beam is not exactly perpendicular to the crystal face, or if the sample texture and composition are not uniform, the X-ray analyses may not be representative of the bulk mineral (see Inskeep et al., 1991), suggesting a need for ARXPS studies (Hellmann et al., 1990). Given this explanation, the results from Inskeep et al. (1991) can be considered as in agreement with those from Muir et al. (1990), and the formation of an altered layer depleted in cations by leaching under

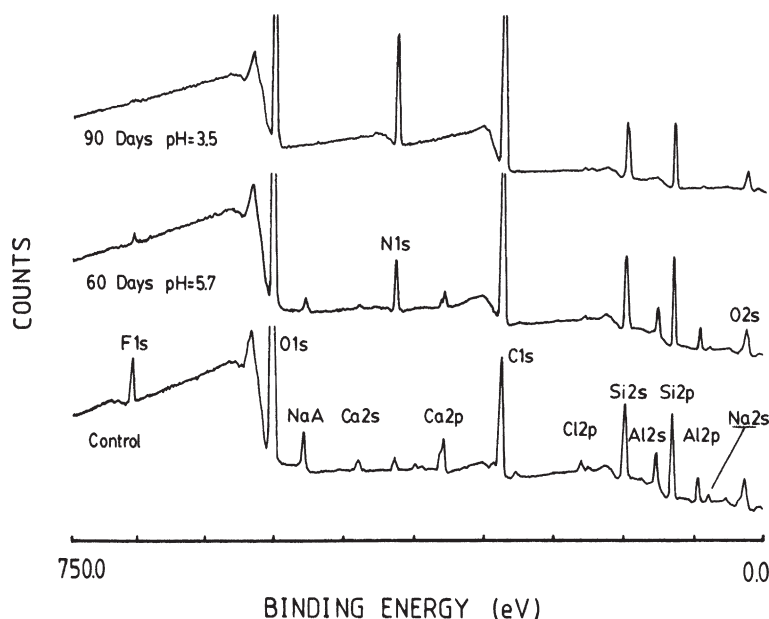


Fig. 7. XPS spectra for unreacted labradorite (bottom), labradorite after 60 days in contact with deionised water (pH 5.7; middle) and after 90 days in HCl solution (pH 3.5; top), showing the photoelectron counts on the ordinate vs. binding energy on the abscissa. The reduction in peak areas for Na, Al and Ca in the reacted samples compared to the non-reacted sample provides evidence of depletion of the surface in these elements. Reproduced from Muir et al., 1989. Reprinted from *Geochim. Cosmochim. Acta*, 53, Muir I. J., Bancroft G. M. and Nesbitt H. W., Characteristics of altered labradorite surfaces by SIMS and XPS. 1235–1241, Copyright (1989), with permission from Elsevier.

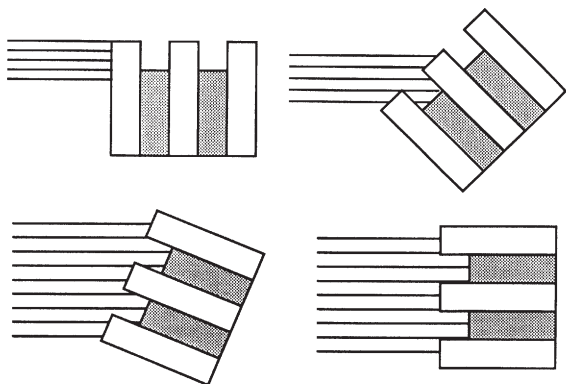


Fig. 8. Representation of orientation of the surface to the detectors after preferential dissolution of the calcic phase in a labradorite sample (open: sodic phase, stippled: calcic phase). If the surface analysed is not virtually flat and smooth, as in the case of preferential dissolution shown on the figure, and if the surface is not uniform and exhibits non-random or systematic differences in relative elevation between the two phases, the X-rays will hit one phase more than the other (see left hand side and top right hand figures). In this case, the results of the XPS spectra will be biased towards one phase or the other because one phase will absorb part of the photoelectrons produced from the other phase. Therefore, in order to obtain results that are representative of the surface, the incident X-rays need to be perpendicular to the surface and hit both phases to the same extent (see bottom right hand figure). Reproduced from *Inskeep et al., 1991*. Reprinted from *Geochim. Cosmochim. Acta*, 55, Inskeep W. P., Nater E. A., Bloom P. R., Vandervoort D. S. and Erich M. S., Characterization of laboratory weathered labradorite surfaces using X-ray Photoelectron Spectroscopy and Transmission Electron Microscopy, 787–800, Copyright (1991), with permission from Elsevier.

ambient as well as under hydrothermal conditions is still possible. Moreover, recent experiments carried out by *Farquhar et al. (1999)* using low-angle X-ray Reflectivity on oligoclase, revealed the rapid formation of a Na-depleted layer after contact with deionised water, while analyses carried out on grains of labradorite after laboratory weathering show that the core structure of the mineral is not dramatically changed, confirming that dissolution is essentially a surface process.

Chen et al. (2000) and *Nesbitt and Skinner (2001)* have studied the development of the leached layer on plagioclase feldspars (albite and labradorite) with time and as a function of temperature. Mainly using XPS, and under acidic conditions (pH values of 2.9 and 2), they have shown that major changes occur over several thousand hours. On increasing the temperature from 5 to 90 °C, the dissolution of albite shifts from being highly non-stoichiometric, with a preferential release of Na and Al over Si, to being stoichiometric. Moreover, calculations using the results obtained by XPS and using previous values found in the literature suggest that the activation energy for the leaching of the cations from the

mineral is lower than the activation energy of the dissolution of the mineral by about 10 kJ/mol. This argument is also used by *Nesbitt and Skinner (2001)* to explain the change in behaviour of the surface after long periods of contact with solution. During the first stage of dissolution, Al and Ca are believed to leach out by “moving” rapidly from vacant site to vacant site, from the area with the highest concentrations (the bulk mineral) to the area with the lowest concentration of cations (the solid–solution interface). Thus, the release of Al and Ca should lead quickly to a steady state (in a few hours to a few days), followed by much slower reactions such as repolymerization, or the development of surface defects such as etch pits and porosity.

To summarise, a diagram showing the various stages of leached layer formation is provided in *Fig. 9*. The two interfaces (solution/ altered layer and altered layer/ fresh surface) are represented as moving at different rates, the inner one being controlled by diffusion of cations, and the outer one controlled by chemical reaction (bond-breaking).

3. Study of the surface microtopography

In the last decade or so, the development of imaging methods has enabled a better understanding of surface dissolution processes by, for example, allowing reactions to be followed with real-time imaging. Thus, the existence of etch pits and the formation of an altered layer at acid pH have been confirmed, validating

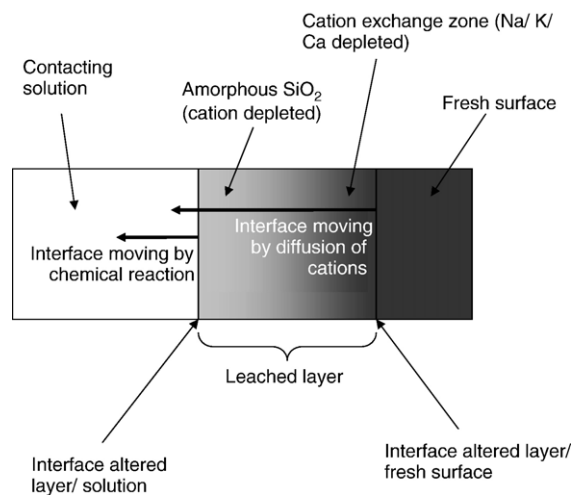


Fig. 9. Schematic representation of the various stages in leached layer formation. The leached layer/fresh surface and solution/ leached layer interfaces are moving at independent rates, the inner one being controlled by diffusion of cations through the layer, and the outer one controlled by chemical reaction involving the breakdown of the aluminosilicate framework.

previous interpretations. Indeed, the availability of Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and, more recently, Atomic Force Microscopy (AFM) have provided very good quality images of the feldspar surface and its structure (see for example Casey et al., 1989a; Hochella et al., 1990; Drake and Hellmann, 1991; Inskeep et al., 1991; Hellmann et al., 1992; Higgins et al., 1998). Their use, combined with ion beam and spectroscopic techniques, has led to a better understanding of the dissolution process. A summary of experiments carried out using various imaging tools can be found in Table 3.

For a long time, it has been assumed that the presence of defects at the surface of a mineral influence the rate and mechanism of its dissolution (Lee and Parsons, 1995; Lee et al., 1998). The use of simulations, and in particular of Monte Carlo modelling, allows prediction of the formation of etch pits and even of their morphology (Lasaga and Blum, 1986; Murphy, 1989). However, recently developed tools can now match such model predictions with reality. Earlier experiments led to the same conclusions as discussed above; SEM and TEM showed the presence of an amorphous layer at the surface of the feldspar after contact with an acidic solution (Goossens et al., 1989) and in situ Scanning Force and Atomic Force Microscopy (SFM and AFM) under ambient conditions (Hellmann et al., 1992) and hydrothermal conditions (100 to 145 °C, 6 to 6.8 bar; Higgins et al., 1998; Jordan et al., 1999) showed roughening of the surface.

However, by examining the rate of dissolution of different cleavage surfaces, Suzuki et al. (1994, 1996) demonstrated that the reaction rate was proportional to the density of pits on the surface of the feldspar. Also, imaging of the surface during and after dissolution at room temperature and pressure has shown preferential formation of etch pits along certain axes, depending on the cleavage of the mineral (Lee and Parsons, 1995; Lee et al., 1998; Fenter et al., 2000; Teng et al., 2001). In the case of the labradorite feldspar studied by Suzuki et al. (1996), the dissolution rate of the (100) face is much faster than (010) or (001) faces, which react at similar rates to each other. Since all of the cleavage planes present the same density of Si–O and cation–O bonds, the crystallographic orientation of the mineral is unlikely to have a major effect on the rate of dissolution. Therefore, the microtexture of the surface and the presence or absence of etch pits are the key factors determining the rate of the reaction. This hypothesis is also supported by Nugent et al. (1998) and Lee and Parsons (1995). Moreover, experiments carried out on orthoclase by Cremeens et al. (1989), as well as

theoretical calculations by Lasaga and Blum (1986) and Lasaga and Lutge (2001), suggest that creation of new etch pits is energetically less likely than enlargement of existing ones, implying that the more defects there are on the surface, the quicker the dissolution.

A strength of some imaging techniques is the possibility of following the reaction and observing structural changes at the surface in real time. In situ AFM images (Dove and Platt, 1996), and AFM images obtained on samples reacted with fluids for different lengths of time, can be examined and the morphologies compared to those of freshly cleaved samples. The presence of an altered layer on the surface has generally been confirmed by these studies (Casey et al., 1989a; Inskeep et al., 1991; Hellmann et al., 1992; Jordan et al., 1999; Sturchio et al., 2001; Teng et al., 2001). Jordan et al. (1999) carried out AFM studies on three different plagioclase feldspars (albite, labradorite An₆₀ and anorthite An₉₆) in a fluid cell under hydrothermal conditions. As previously observed for powdered samples, the results depend substantially on the composition of the feldspar. Thus, although a slight roughening of the surface can be seen on albite during acid dissolution, the difference from the fresh sample is not significant. As observed previously, the more An content in the core structure, the more reactive the surface; hence the low reactivity of albite and the only slight changes during its acid dissolution (also see Section 1.1). Results for labradorite and anorthite are similar. For labradorite, at low temperature no changes can be detected after a short period of time. However, as soon as the sample is heated to 125 °C, roughening of the surface can be observed to a depth of about 40 nm within 5 h. Moreover, the surface not only becomes rough but also soft and, if a greater force is applied by the AFM tip, the soft layer can be removed to expose a surface of comparable hardness to the freshly cleaved sample (Fig. 10). This behaviour has also been observed during the dissolution of albite by Hellmann et al. (1992) and of orthoclase by Teng et al. (2001), and removal of the soft layer can also be achieved by increasing the fluid flow rate over the mineral (see Fig. 11). These observations can be related to the results from other techniques, such as XPS, as they give evidence of the existence of a leached layer whose chemical composition has been previously determined. However, it is interesting to note that the rapid formation of a gel layer (in less than a few hours) is incompatible with the slow interdiffusion process associated with leached layer formation.

Anorthite seems to be more reactive than labradorite, as already noted in Section 1.1. The roughening is very

Table 3
Summary of experiments carried out on feldspars using surface imaging methods

Author	Year	Mineral	pH	Imaging technique used	Major findings
Hochella et al.	1990	Albite	N/A (in air)	AFM (with LEED)	Imaging of some small reactive sites: etch pits and steps, that might play an important role during dissolution
Hellmann et al.	1992	Albite	2	AFM	Rapid dissolution of the surface in a few minutes.
Higgins et al.	1998	Albite	2	SFM	Roughening of the surface after contact for 4 h, suggesting leaching of the surface in Al and Na.
Nugent et al.	1998	Albite	4.3	SEM/TEM/AFM	Weathering in acidic natural environments shows similarities with laboratory dissolution. Leached layer obtained is likely to be due to reprecipitation on the surface, and can probably inhibit rate of reaction in soils.
Casey et al.	1989a	Labradorite	1 to 4	TEM/SEM	Possible repolymerization on the surface after ion-exchange and depolymerization reactions leading to a porous Si-rich layer, amorphous to electron diffraction.
Inskeep et al.	1991	Labradorite	4	SEM/TEM	Non-uniform etching and surface alteration detected by SEM. Presence of exsolution lamellae detected by TEM
Suzuki et al.	1994/ 1996	Labradorite	3–4.5	SEM	Etch pits formed along 2 directions in (100) plane and along cleavage directions in (010) and (001) planes.
Jordan et al.	1999	Labradorite/ anorthite	2	HAFM	Roughening and softening of the surface for both minerals. Presence of etch pits on anorthite on the surface underneath the leached layer.
Hellmann et al.	2003/2004	Labradorite	1	EFTEM/ HRTEM	Layer depleted in Ca, Na, K, Al, enriched in Si, O and B. Very sharp concentration gradients at the interface between the mineral in contact with solution and the unweathered mineral.
Lee and Parsons	1995	Alkali feldspars	Acid	SEM/TEM	Complex microtexture influencing the weathering of the mineral. However, mineralogical and crystallographic factors cannot be omitted to describe influence on weathering rates.
Lee et al.	1998	Alkali feldspars/ sanidine	2	SEM/TEM/AFM	Dissolution rates increasing with dislocation density. Preferential dissolution at dislocation outcrops and albite exsolution lamellae, but not influencing the overall rate of reaction.
Goossens et al.	1989	Sanidine	1	SEM/HRTEM	No evidence of precipitation of silicon layer observed by SEM: layer observed is more likely due to removal of Na, Al, K than reprecipitation of SiO ₂ . Increasing number of etch pits with temperature
Adriaens et al.	1999	Sanidine	1	SEM/TEM	Collapsed structure observed rather than epitaxial growth. Layer enriched in SiO ₂ is not uniform on the surface.
Creemeens et al.	1989	Orthoclase		SEM	Dissolution results in smaller and more numerous etch pits rather than enlargement of existing ones in poorly drained soils.
Fenter et al.	2000	Orthoclase	Neutral (DIW)	AFM	Surface essentially flat with presence of unit-cell height step.
Sturchio et al.	2001	Orthoclase	1.1–12.9	In situ AFM	Terrace roughening at low pH and step motion at high pH.
Teng et al.	2001	Orthoclase	1.1 and 12.9	In situ AFM	Gel-like surface at acid pH, disappearing if the flow rate is increased. Minimal non-stoichiometric dissolution at acid pH, stoichiometric at basic pH.

rapid, even at room temperature, and although the behaviour seems to be quite similar to that of labradorite, dissolution occurs to a greater extent and

much faster. If part of the soft layer is removed, a new layer reforms almost instantly on the fresh surface. It is believed that this layer, rather than being the result of

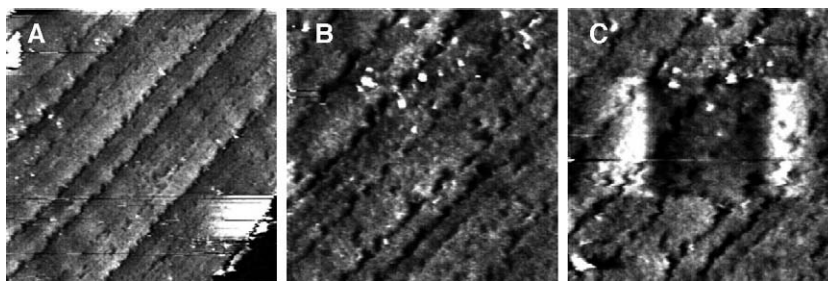


Fig. 10. AFM images of labradorite at 125 °C after contact with an acidic solution (HCl in deionised water, pH 2): (A) after 98 min contact (size: $17 \times 17 \mu\text{m}^2$) roughening of the surface and cleavage steps are observed; (B) after 105 min, lines of small pits are observed (size $9 \times 9 \mu\text{m}^2$); (C) after 118 min and removal of the soft layer by the tip, the morphology of the surface is similar to the morphology of the surface before removing the layer (size $9 \times 9 \mu\text{m}^2$). Reproduced from Jordan et al., 1999. Reprinted from *Geochim. Cosmochim. Acta*, 63, Jordan G., Higgings S. R., Eggleston C. M., Swapp S. M. and Janney D. E., Acidic dissolution of plagioclase: in situ observations by Hydrothermal Atomic Force Microscopy, 3183–3191, Copyright (1999), with permission from Elsevier.

repolymerization of the whole surface, is the result of repolymerization only on the fresh surface. Indeed, after removal of part of the soft layer, the difference in thickness between the soft layer already present and the one re-formed decreases with time; after one hour, no major differences can be seen, showing that the soft layer “heals” where it has been damaged. This suggests that a steady state is reached and the thickness of the leached layer remains constant.

It is likely that the removal of preferentially leached elements takes place at the interface between the fresh surface and the altered layer, and not at the interface between the altered layer and the solution, implying mass transport through the altered layer. Indeed, Jordan et al. (1999) have also shown with in situ Hydrothermal Atomic Force Microscopy (HAFM) on anorthite that, as etch pits form, the changes in the scan field only affect the vertical positions of pits, but not their morphology at the edges. The analogy given by Jordan et al. (1999) of an object moving under a blanket, represents well what

is happening: the morphology of the altered layer does not change once it is formed, but the vertical position of the features created by dissolution does. Thus, it can be envisaged that the removal of leached elements occurs between the fresh surface and the altered layer, and not between the altered layer and the solution. This mechanism had already been proposed following experiments carried out on powders, although the use of AFM does not give enough information to determine whether mass transport through the layer is rate-controlling. However, the removal of Si and O is believed to take place at the interface between the altered layer and the fluid, therefore explaining why the thickness of the altered layer on ancient feldspar does not increase indefinitely with time (see Zhu et al., 2004).

AFM carried out on a sample dried after reaction (see Fig. 12) provides more information because the surface changes during drying. The surface shows roughening features when in situ AFM is carried out at 52 °C for 6 h, but imaging the air-dried, reacted surface shows that the

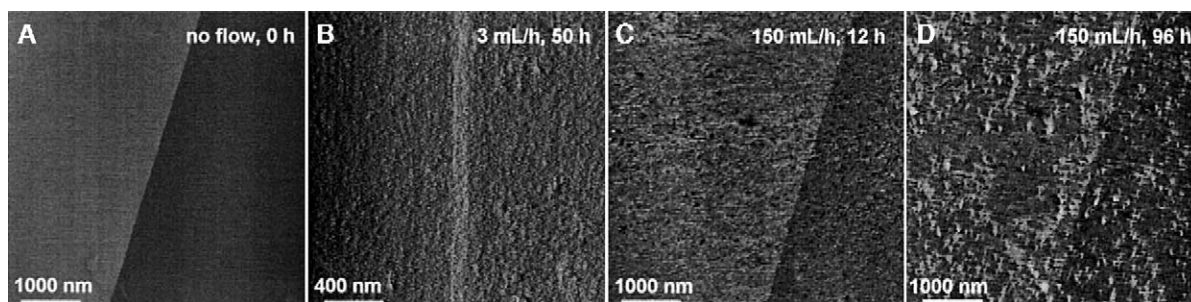


Fig. 11. AFM images of: (A) freshly cleaved orthoclase; (B) Orthoclase after contact with pH=1.1 solution for 50 h at low flow rate (3 mL/h) showing a soft layer on the fresh surface, and (C) and (D) after contact with pH=1.1 solution for 12 and 96 h at high flow rate (150 mL/h), when no coating is observed. Reproduced from Teng et al., 2001. Reprinted from *Geochim. Cosmochim. Acta*, 65, Teng H. H., Fenter P., Cheng L. and Sturchio N. C., Resolving orthoclase dissolution processes with Atomic Force Microscopy and X-ray Reflectivity, 3459–3474, Copyright (2001), with permission from Elsevier.

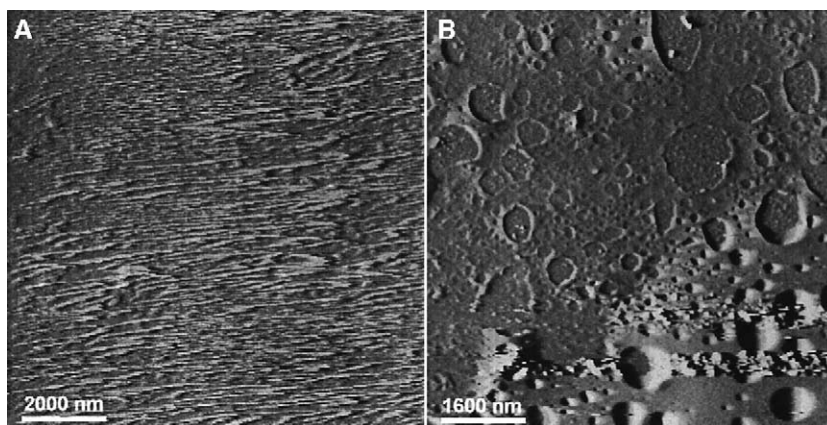


Fig. 12. AFM images of orthoclase after: (A) contact at $T=52\text{ }^{\circ}\text{C}$ with $\text{pH}=1.1$ solution for 12 h, imaging in deionised water, and (B) drying in air. Image (A) shows the coating sticking to the AFM tip indicating a soft, gel-like layer. Image (B) shows spalling of the surface coating under dry conditions. Reproduced from Teng et al., 2001. Reprinted from *Geochim. Cosmochim. Acta*, 65, Teng H. H., Fenter P., Cheng L. and Sturchio N. C., Resolving orthoclase dissolution processes with Atomic Force Microscopy and X-ray Reflectivity, 3459–3474, Copyright (2001), with permission from Elsevier.

coating tends to crack and spall upon drying. This suggests that dehydration of the surface occurs, but cracking of the surface could also be due to repolymerization of the soft silica gel layer with residual material on the surface on drying, eventually covering only part of the surface. Comparison with previous studies (Casey et al., 1989a; Brantley and Stillings, 1996) suggests that this soft layer is enriched in Si and depleted in alkali cations, although this obviously cannot be confirmed by AFM. Experiments carried out on naturally weathered feldspar (Lee et al., 1998; Nugent et al., 1998) lead to the same conclusions. In summary, even though anorthite has a lack of bridging Si–O–Si bonds in its structure, the results described by Jordan et al. (1999) imply that an altered layer is involved in the dissolution process and is readily formed. Moreover, the rapid reappearance of a soft layer after its initial removal suggests that a steady state rate of formation of such a layer is achieved within minutes.

In order to investigate further the formation of this soft layer and its composition, Fenter et al. (2000, 2003), Sturchio et al. (2001) and Teng et al. (2001) have used in situ AFM and X-ray Reflectivity to compare dissolution of the (001) surface of orthoclase feldspar in both acid and alkaline conditions. As discussed earlier, at acid pH values and low solution flow rates in a liquid cell, a viscous gel-like layer appears which can easily be removed by applying a greater force with the AFM tip, or by increasing the rate of flow. The formation of this layer leads to roughening of the flat areas seen between big steps on the freshly cleaved surface, and to “rounding” of the steps. If left to dry in air, the coating

appears to crack, then showing completely different features. If the altered layer is removed, the surface below shows numerous etch pits, also referred to as nanopores (see Figs. 11 and 12). Dissolution in alkaline solution produces different features, with no gel-like coating but with preferential leaching at step edges, leading to the appearance of split steps instead of single ones and etch pits in flat areas (see Fig. 13). These differences have been interpreted in terms of the mechanisms of dissolution. As already described, dissolution is apparently non-stoichiometric at acid pH, with the preferential release of cations and incorporation of H^+ in the structure, but is stoichiometric at alkaline pH. However, the results from in situ X-ray Reflectivity studies under both acid and alkaline pH conditions suggest that the mechanisms may be more complex than is implied by a simple stoichiometric versus non-stoichiometric description. Indeed, except for the presence of a non-stoichiometric layer of 1-unit cell depth at acid pH, the dissolution of orthoclase seems to be essentially stoichiometric, whatever the pH. Compositional changes in feldspar are often accompanied by structural differences and, therefore, different behaviour is expected for the various feldspar minerals (most studies have focused on plagioclase rather than on the alkali feldspars); however, such a change seems unlikely to be due just to the feldspar composition. Instead, a new mechanism has been suggested by Teng et al. (2001); here, the differences in rates of dissolution at acid and alkaline pH are explained by differences in reactivities of particular reacting sites. If a sample previously reacted in acid solution is put in contact with

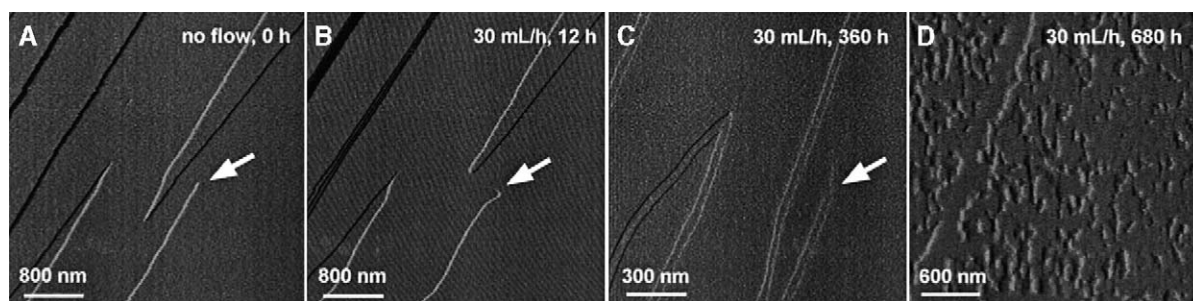


Fig. 13. AFM images of: (A) freshly cleaved orthoclase and (B–D) after contact for 12, 360 and 680 h with a pH=12.9 solution at a flow rate of 30 mL/h. No coating is observed, but split steps can be seen in (C). A patchy surface is observed in (D), resulting from nucleation of etch pits. Reproduced from Teng et al., 2001. Reprinted from *Geochim. Cosmochim. Acta*, 65, Teng H. H., Fenter P., Cheng L. and Sturchio N. C., Resolving orthoclase dissolution processes with Atomic Force Microscopy and X-ray Reflectivity, 3459–3474, Copyright (2001), with permission from Elsevier.

an alkaline solution, the dissolution rates observed after the change of pH are very high. By contrast, if the freshly cleaved sample is put in contact with the same alkaline solution without initial exposure to an acid solution, the rates of dissolution are much lower. Teng et al. (2001) explained the high rates observed initially at alkaline pH as due to the presence of numerous undercoordinated sites, formed at low pH and highly reactive at high pH. Thus, surface reaction would be mainly observed at etch pits and involves roughening of terrace areas at low pH values, whereas it is mainly observed at step edges and defects under alkaline conditions. The results obtained from X-ray Reflectivity by Teng et al. (2001) also suggest that the operation of different mechanisms under acidic and basic pH conditions cannot provide a complete explanation of the observed phenomena. Instead, they suggest that dissolution can be understood as the result of two mechanisms: a mechanism more active at terraces and step defects at high pH and that does not affect the surface roughness or stoichiometry, and a mechanism that is less site-specific at acidic pH with dissolution occurring more randomly on the surface. Thus, although more work needs to be carried out to determine if this hypothesis is generally valid, especially in neutral conditions, it seems that the dissolution rates need to be described as a combination of two activation energies.

Recent results on labradorite published by Hellmann et al. (2003, 2004) also suggest that the previously accepted model involving different mechanisms at acid and alkaline pH may be inadequate, and that a model of repolymerisation at the surface as proposed by others (Petrović et al., 1976; Holdren and Berner, 1979; Casey et al., 1988; Teng et al., 2001) may be more realistic. Hellmann et al. (2003, 2004) have analysed labradorite

samples after acid dissolution using High-Resolution and Energy-Filtered TEM (HRTEM and EFTEM) and SIMS. An altered layer, depleted in Al and interstitial cations (Na, Ca and K) is observed. However, HRTEM shows that the changes in the concentrations of these elements occur exactly at the altered layer/mineral interface, and that there seems to be no leaching of elements from the mineral into the altered layer or from the altered layer into solution. This would indicate that the model of a single mechanism involving leaching of elements through an altered layer is also inadequate. The concentration gradients of the elements, although varying with the element considered (but probably an artefact due to instrument drift or electrical charging of the sample) are always very sharp, occurring within a few nm (see Fig. 14) and perfectly coincident with the structural altered/ non-altered layer interface. This can be better explained by a mechanism involving dissolution/precipitation than by a leached layer model. Further results by Fiebig and Hoefs (2002) also suggest that the albite layer detected on the surface of plagioclase used in their experiments is due to precipitation of dissolved plagioclase, with a restructuring of the initial framework. In order to explain the sharpness of the concentration gradients Hellmann et al. (2003, 2004), used theoretical models of steady state dissolution combined with binary interdiffusion, as previously used by Doremus (1975) and Lanford et al. (1979) to describe the dissolution of glasses. However, in the case of feldspars, it seems that these models are unable to reproduce the experimental results. Given the sharpness of the gradients observed, it is impossible to describe the penetration of H^+ ions and simultaneous cation depletion over a few hundred nanometres by the model of preferential leaching of cations and interdiffusion with H^+ often used at low pH values. Instead, they

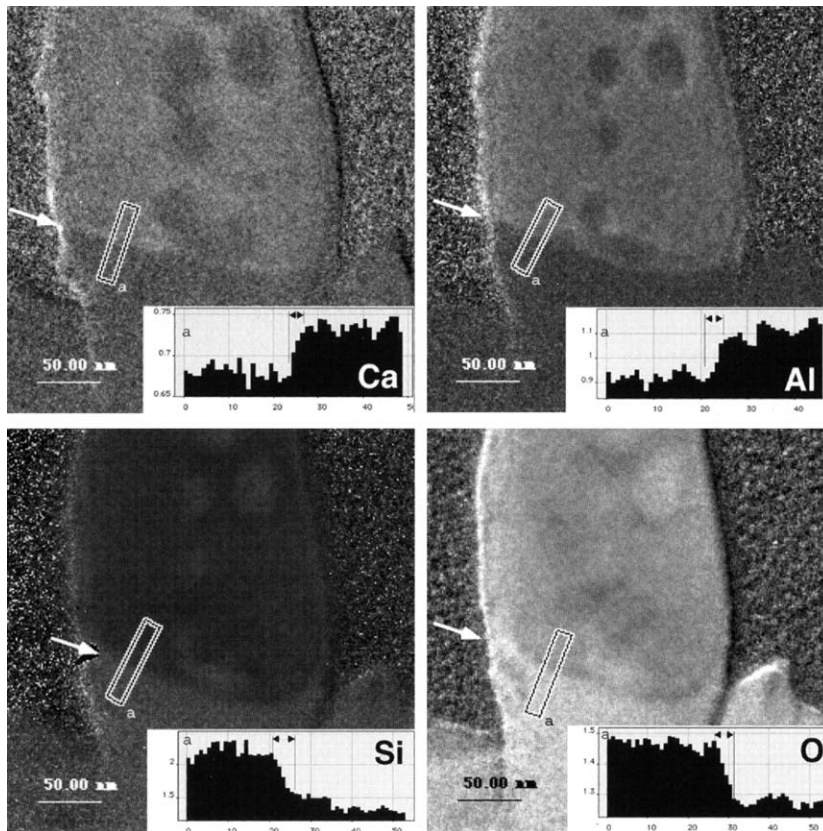


Fig. 14. EFTEM chemical maps of Ca, Al, Si and O at the interfacial boundaries (horizontal lines highlighted by white arrows) between the altered mineral (part of the sample below the interface shown by the white arrow) and the unaltered mineral (part of the sample above the interface shown by the white arrow) for a labradorite feldspar after contact in pH=1.1 solution. Lighter tones represent higher concentrations. The chemical profiles are also shown as insets, based on the diagonal rectangular areas (left to right: altered mineral to freshly cleaved), and showing depletion of the altered layer in Ca and Al and enrichment in Si and O. Small black arrows in insets indicate the estimated widths of interfacial regions (abscissa units are in pixels, ordinate units are arbitrary), which are always very sharp, leading to chemical gradients values ranging from 3.8 nm for Ca, 4.9 nm for O, 5.1 nm for Al and up to 6.8 nm for Si. Reproduced from Hellmann et al., 2003. Reprinted from Phys. Chem. Min., An EFTEM/HRTEM high-resolution study of the near surface of labradorite feldspar altered at acid pH: evidence for interfacial dissolution–reprecipitation, Hellmann R., Penisson J.-M., Hervig R. L., Thomassin J.-H. and Abrioux M.-F., 30, 192–197, Fig. 2a, Copyright (2003), with permission from Springer.

propose a single mechanism, termed interfacial dissolution/reprecipitation. In this mechanism, bond-breaking and release of cations occurs directly at the interface between the fluid and the mineral, similar to the dissolution process observed at alkaline pH, and is then followed by reprecipitation of an amorphous secondary phase at the surface (see also Putnis, 2002). Both processes, dissolution and reprecipitation, occur in a thin film at the interface between the solution and the mineral. This would explain both the results obtained by Teng et al. (2001) and Fenter et al. (2000, 2003) who found that depletion in K^+ is only one unit cell deep, and who also observed the presence of a layer enriched in Si. Indeed, the secondary precipitate would be composed of Si, O and H, and be essentially a hydrated silica gel layer. Such a layer would be porous, and ion transport through it would be achievable, in accordance with

many studies including those discussed above (in particular Nesbitt and Skinner, 2001; see Section 1.3). In addition, this model of interfacial precipitation can be applied to naturally weathered feldspars, as the precipitation of a secondary phase is usually observed under the conditions prevalent during natural weathering (Nugent et al., 1998). This model, if it is valid for all feldspars, would mean that the breakdown is stoichiometric at every pH, and that the non-stoichiometry observed at acid pH is actually due to later precipitation onto the surface.

4. Comparisons between laboratory experiments and naturally weathered feldspars

Most of the studies discussed above have focused on the reactions of feldspars under well-defined laboratory

conditions. However, it is important to consider the extent to which natural processes can be reproduced in the laboratory and, thus, whether the models proposed here are applicable to naturally weathered minerals. A review of field and laboratory studies can be found in Hochella and Banfield (1995). The methods used to characterise naturally weathered feldspars are similar to the methods used in laboratory “weathering” studies. Thus, variations in the surface area of samples have been largely studied by the BET method, especially to explore the role of microtextures and microstructures. In order to follow dissolution at the mineral/solution interface, the imaging methods described above have also been used. HRTEM have produced results of particular interest and, although the method has only been used relatively recently, it has already provided important information (Hellmann et al., 2003, 2004; Zhu et al., 2004). It is particularly useful for obtaining information on microtextures. Indeed, the determination of the effects of microstructures and microtextures on weathering turns out to be fundamental. Essentially, if their influence on surface reaction is minimal, then the reactivity of a given mineral should be independent of its environmental history. On the other hand, if microtextures and microstructures play a role in natural weathering, then reaction rates and mechanisms for a given mineral reacted under the same conditions will be different, depending on the geological history of the mineral. In this context, HRTEM is especially powerful in the study of plagioclases that very commonly show exsolution lamellae, and thus have variable compositions at their surfaces. However, one of the major drawbacks of HRTEM is the very small area analysed, which may not reflect the overall composition of the mineral. This problem may be more pronounced in naturally weathered feldspars, as these minerals are more likely to show inclusions and impurities than those carefully chosen for laboratory experiments. Lee and Parsons (1995) and Lee et al. (1998) have assessed the role of microtextures in the natural and laboratory weathering of alkali feldspars. Different environments have been studied, representing the whole “life” of a grain of alkali feldspar, from initial exposure of the “mother rock” to solution, to weathering processes in soils. According to these studies, the correlation between naturally-weathered and laboratory-weathered minerals depends critically on the nature of the solution in contact with the mineral. Where the solution is unsaturated in the elements present in the mineral, the dissolution rates observed are similar to the ones observed for a laboratory-weathered mineral, indicating that microtexture and microstructure do not play a

significant role in the dissolution. However, where a saturated solution contacts the sample, as would occur in the weathering in soils or in an internal zone within crystals (such as defects for example), sites such as etch pits and dislocations with a low activation energy for dissolution will be more likely to react. In this case, the microtexture of the mineral will play a major role in weathering. Nugent et al. (1998) have used AFM to study a naturally weathered albite from an acidic soil, and have shown preferential etching of albite (010) twins and albite and oligoclase lamellae (see Fig. 15). Moreover, in the case of naturally weathered minerals, defects and etch pits can host bacteria or organic substances, the presence of which is also likely to affect dissolution rates. In the case of laboratory-weathered minerals, the cleaning of the grains prior to reaction, commonly carried out in an ultrasonic bath, eliminates such contaminants and may also change the microtexture at the surface of the mineral.

Most laboratory dissolution experiments show reaction rates up to 4 orders of magnitude greater than the rates calculated for natural weathering (Velbel, 1993; Blum and Stillings, 1995). However, experiments carried out on albite also show that the mechanisms of dissolution are similar for naturally-weathered and laboratory-weathered

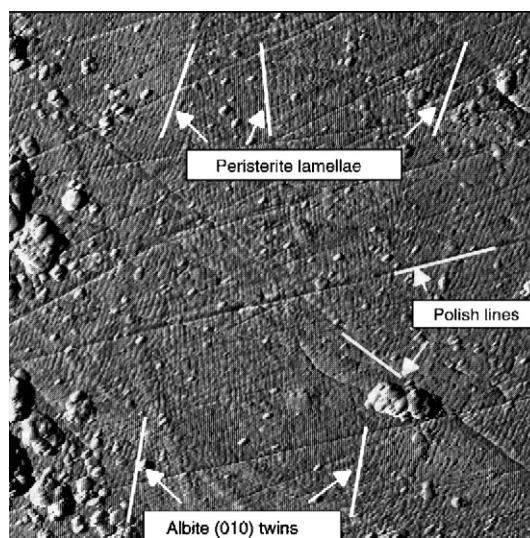


Fig. 15. AFM image of albite weathered for 3 years in an acidic soil (size $2.5 \times 2.5 \mu\text{m}$), showing preferential etching of albite (010) twins and albite and oligoclase lamellae. Polish lines are present both before and after weathering, and the grooves created by the peristerite lamellae are at least 1.5 nm deep. Reproduced from Nugent et al., 1998. Reprinted from Nature, 395, Nugent M. A., Brantley S. L., Pantano C. G. and Maurice P. A., The influence of natural mineral coatings on feldspar weathering, 588–591, Copyright (1998), with permission from Nature Publishing Group.

samples. Although previous experiments have shown that the reactivity of albite under hydrothermal conditions is much lower than that of anorthite-containing feldspars (see Section 2 and references therein), Nugent et al. (1998) have studied the differences between laboratory and naturally-weathered albite at low pH. A protective coating is observed by AFM after contact with an acidic soil for a time between one month and 3.5 yr, with the thickness of the coating increasing with contact time and reaching up to 80 Å. SIMS and XPS of these samples have also shown that this protective coating is present from the very early stages of weathering (already being detected after one month). It is always depleted in Na, but only depleted in Al if the sample has been left in contact with the solution for 6 months or less, and enriched in this element otherwise (Fig. 16).

This appears to be the main difference between the laboratory-weathered and naturally-weathered minerals. As discussed above, in acid conditions in the laboratory, the leached layer formed is usually depleted in both Na and Al, and enriched in Si (Nesbitt and Muir, 1988; Blum and Lasaga, 1988; Lasaga, 1995; Brantley and Stillings, 1996; Mukhopadhyay and Walther, 2001). However, a mass balance estimated by Nugent et al. (1998) has shown that the amount of Al and Si found in this layer after natural weathering is greater than the

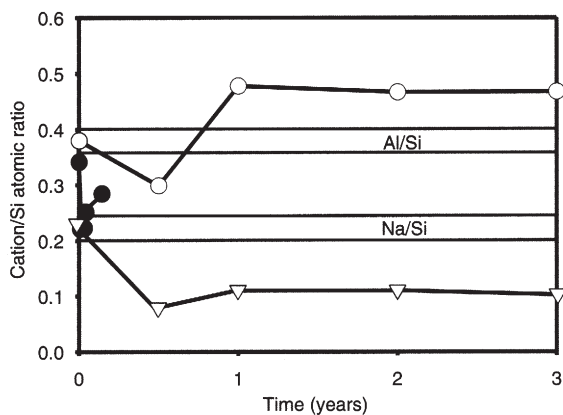


Fig. 16. Atomic ratios for albite after weathering in acidic soil, versus time, measured by XPS. The empty circles and triangles represent respectively Al/Si and Na/Si atomic ratios for albite weathered in an acidic soil, and filled circles represent Al/Si atomic ratio for albite treated with pH 4 acetate/lithium acetate buffer laboratory solution. The boxes are defined by the high and low values of Al/Si and Na/Si ratios measured on unweathered albite blanks. All the weathered samples are Na-depleted, whereas only the 6-month sample is Al-depleted. Samples weathered for more than 6 months are Al-enriched. Reproduced from Nugent et al., 1998. Reprinted from Nature, 395, Nugent M. A., Brantley S. L., Pantano C. G. and Maurice P. A., The influence of natural mineral coatings on feldspar weathering, 588–591, Copyright (1998), with permission from Nature Publishing Group.

amounts of these elements released from the surface. This suggests that elements from the soil solution phase in contact with the mineral are involved in the formation of the coating, and that the epitaxial growth of secondary phases, observed under laboratory conditions, also occurs in naturally weathered systems (Casey et al., 1993; Casey and Ludwig, 1995).

This conceptual model of elements in solution taking part in the formation of the altered layer has, in the last few years, also been used to interpret the surface reactions of laboratory-weathered feldspars. Hellmann et al. (2003) were amongst those to question the apparently non-stoichiometric dissolution of laboratory-weathered labradorite at acid pH, and to suggest an alternative mechanism. Indeed, experiments carried out on labradorite in HCl/H₂O solution at pH=1 for 500 h revealed a leached layer depleted in cations but enriched in H, Si and B (Hellmann et al., 2003, 2004), the boron being present only as an impurity in solution. Measurements by SIMS and HRTEM/EFTEM provide results that are not completely consistent with the generally used model of preferential leaching of cations from the surface and enrichment in Si, O and H. Although a coating depleted in some structural elements and enriched in Si and O is observed, the sharpness of the concentration gradients obtained through this layer (see Section 2, Fig. 14) is difficult to explain by the conventional mechanism. The altered zone is several tens to several hundreds of Å thick, whereas the concentration gradients between the weathered and unweathered part of the mineral are always very sharp (less than 10 Å) indicating that the composition of the surface on both sides of the interface between the fresh mineral and the altered layer is almost homogeneous, even very close to the interface. Moreover, the concentration values obtained here are only values relative to the bulk composition and, therefore, absolute enrichment in Si and O near the mineral/solution interface is unlikely to be seen in the case of the presence of an altered layer (although the altered layer is enriched in Si and O relative to the bulk composition). At best, in the case where only cations leach out of the mineral, conservation of the amount of those elements in the layer would be detected. Finally, the presence of boron, an impurity from the solution used and detected by SIMS in the experiments carried out by Hellmann et al. (2004), also supports the alternative mechanism. Dissolution can now be seen as stoichiometric, with equal release rates for all elements from the solid–solution interface. Interfacial reprecipitation of a silica layer, eventually concomitant with precipitation of secondary phases from elements present in solution,

could then happen at acidic pH. The layer formed would obviously be enriched in Si and, eventually, in other elements as observed in naturally weathered feldspars, but the dissolution itself would follow a single mechanism for the whole range of pH. However, very few experiments have been carried out so far, all on labradorite, and this hypothesis has yet to be confirmed at $\text{pH} > 1$. Clearly further experiments would be valuable, both for naturally-weathered and laboratory-weathered feldspars.

5. Summary and overall conclusions

We have reviewed here many papers dealing with dissolution of feldspars, in both the natural and the laboratory environment. Very acid to acid ($\text{pH} = 1$ to 4), neutral, and very alkaline ($\text{pH} = 12$ to 13) conditions have been used in different experiments, although most studies concentrate on acid to neutral conditions. The focus on these low pH conditions reflects the fact that most natural weathering processes occur in acid solutions. This is due to both the presence of microorganisms in soils, which decompose soil organic matter, increasing the concentration of CO_2 in soilwater and making it acidic, and due to the acidity of rain water. Several models have been put forward to describe the dissolution of feldspars, mainly depending on the pH of the reaction. Until recently, different mechanisms were proposed to explain the behaviour of the mineral at different pH values. Stoichiometric dissolution was thought to be occurring at high pH, whereas a preferential removal of cations, both interstitial (Na, Ca and K) and from the framework (Al) was observed at low pH, leading to the formation of an altered layer usually enriched in Si, O and H. However, it has also been suggested that only a single stoichiometric mechanism operates over the whole range of pH, the leached layer then forming by reprecipitation at the surface. This approach can potentially rationalise weathering under both laboratory and natural conditions, and can also be used to explain results from previous experiments, under both hydrothermal and atmospheric conditions. The variations observed in the leached layer, depending on the external conditions, can also be explained. Specifically, this approach can explain why:

- (1) the layer is more depleted in Al and K when SiO_2 is present in solution (Goossens et al., 1989; Adriaens et al., 1999);
- (2) the layer is less depleted in Ca and Al if Ca and Al are already present in solution (Muir and Nesbitt, 1991);

- (3) impurities (Cl and Ba), only present in solution at the beginning of the experiment, are found in the surface layer (Hellmann et al., 1990, 1997);
- (4) there are very sharp concentration gradients of elements in the leached layer (Hellmann et al., 2003, 2004).

However, other observations are more difficult to explain with this dissolution/reprecipitation model. Specifically, it is difficult to explain why:

- (1) some elements are removed from deeper in the surface than others (Al vs. Na; Hellmann et al., 1997);
- (2) the leached layer is generally homogeneous over the surface whereas preferential sites of precipitation would normally be expected;
- (3) the presence of Mg is not detected in the leached layer when Mg is present in solution (Muir and Nesbitt, 1991);
- (4) the congruence/incongruence of dissolution depends mainly on the composition of the mineral; anorthite usually shows congruent dissolution, whereas labradorite shows incongruent dissolution (Shotyk and Nesbitt, 1992);
- (5) etch pits and preferential dissolution at defects occurs (these are more difficult to explain with an entirely stoichiometric reaction mechanism).

To summarise, there is the prospect of developing a single model for feldspar dissolution, although more experimental data obtained under a greater range of conditions would be helpful. This is starting to appear (for example, through the combined use of AFM and X-ray Reflectivity techniques) and, increasingly, attention is turning to the application of such a model to the natural weathering of feldspars. AFM and SEM have long been used to describe changes in surface morphology, but recent developments in TEM, especially the variations HRTEM and EFTEM, are now providing unique insights into the interface between mineral and solution. The greater resolution of the modern TEM, and its ability to provide analytical information, should facilitate its contribution to a greater understanding of interfacial processes.

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