

SECONDARY ION MASS SPECTROMETRY (SIMS) AND ITS APPLICATION TO CHEMICAL WEATHERING

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Abstract. Secondary ion mass spectrometry (SIMS) is the mass spectrometry of atomic species which are emitted when a solid surface is bombarded by an energetic primary ion beam. By continually bombarding the surface of the sample with the ion beam, the atoms making up the material being studied are sputtered away. The secondary ions emitted from the surface are continually analyzed and their intensities recorded over time. The secondary ion intensities are proportional to the concentration of elements in the sample, thereby producing a semiquantitative concentration depth profile. The depth profile provides an illustration of the chemical composition of a sample as a function of depth through the surface. The SIMS technique has been applied to a wide variety of surface analytical problems and can easily be used to analyze reacted glass and mineral surfaces which have been

exposed to weathering solutions. Traditional experimental studies of chemical weathering were based primarily on the analyses of aqueous solutions generated during leaching experiments. Such studies have provided valuable information concerning rates and stoichiometry of mineral dissolution reactions but have led to some confusion and much speculation regarding the mechanisms of surface processes. SIMS analyses of the surfaces of dissolving glasses and plagioclase feldspars have recently been used to help resolve a number of unanswered questions. For example, SIMS analyses of dissolving feldspars have shown how the chemical composition of reacted surfaces and depth of attack vary, depending on the composition of the mineral, the pH of the leaching solution, and the presence of dissolved salts and complex-forming organic ligands.

1. INTRODUCTION: SIMS, CHEMICAL WEATHERING, AND SOILS

1.1. SIMS

Secondary ion mass spectrometry (SIMS) is the mass spectrometry of atomic species which are emitted when a solid surface is bombarded by an energetic primary ion beam [Vickerman, 1987]. Continually bombarding the surface of the sample with the primary ion beam is a process known as "sputtering." Most of the particles which are sputtered away are uncharged, but a small fraction consists of atomic or molecular ions. Either the positive or negative "secondary" ions ejected from the sample are separated according to their mass/charge ratio and analyzed in a mass spectrometer. Thus the atoms making up the material being studied are continually ejected and analyzed, with secondary ion intensities recorded as a function of time. The secondary ion intensities are proportional to the concentration of elements in the sample, thereby producing a semiquantitative concentration depth profile.

The depth profile reveals the chemical composition of a sample as a function of depth through the surface.

For example, consider a typical SIMS depth profile of fresh (unweathered) labradorite (An_{54}) feldspar with the following bulk composition (wt %): SiO_2 , 55.31 ± 0.21 ; Al_2O_3 , 28.84 ± 0.20 ; CaO , 10.95 ± 0.10 ; Na_2O , 4.72 ± 0.07 ; K_2O , 0.19 ± 0.02 . Shown on the ordinate in Figure 1a is the logarithm of secondary ion intensity, which is proportional to the atomic concentration of elements in the sample. The most intense signals are ^{27}Al and ^{28}Si , followed by ^{40}Ca and ^{23}Na , reflecting their abundance in the feldspar. The ^{39}K and ^{88}Sr signals are less intense, reflecting their lower abundance in the mineral (i.e., trace elements). Shown on the abscissa is the sputtering time in seconds. Measurements of crater depth as a function of sputter time have shown that the primary ion beam penetrates labradorite at a rate of approximately 1–2 Å/s. Thus the SIMS depth profile of the fresh labradorite shows that the concentrations of Al, Si, Ca, and Sr do not change significantly from the surface of the mineral over the distance profiled (approximately 500–1000 Å).

The SIMS depth profile of the same labradorite leached in HCl at pH 4 reveals a significantly different picture. The intensities of Al, Ca, and Sr are signifi-

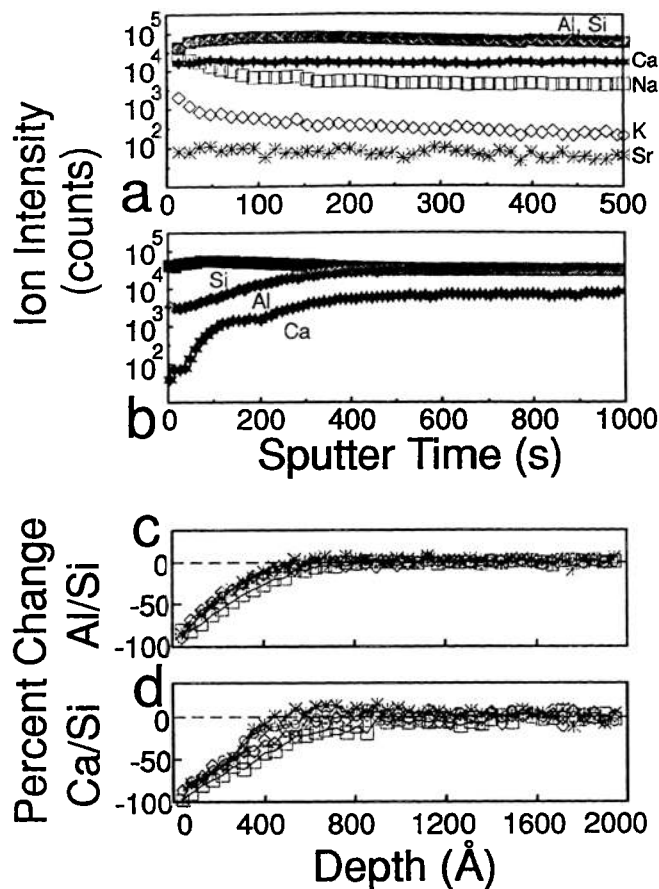


Figure 1. (a) SIMS depth profile of fresh labradorite feldspar (An_{54}). Notice that the secondary ion intensities of Al, Si, Ca, and Sr do not vary significantly with sputtering time. The intensities of ^{23}Na and ^{39}K are higher at the surface of the mineral than in the interior. This feature is unique to SIMS depth profiles of Na and K and does not accurately reflect the true metal concentration profiles. Instead, both profiles are affected by the charge-induced migration of Na^+ and K^+ in response to the negative primary beam [Streit *et al.*, 1986]. (b) SIMS depth profile of labradorite leached at pH 4.0 in 10^{-4} M HCl for 72 days at room temperature. The intensities of Al and Ca are significantly lower at the beginning of the profile than they are after 500 s. (c) Percent change in Al/Si of labradorite (An_{54}) leached for 72 days in HCl. Four spots on the surface of the sample were depth profiled. (d) Same as Figure 1c except for Ca/Si.

cantly lower at the surface of the mineral than in the interior (Figure 1b). For example, the ^{27}Al ion intensities at the surface of the feldspar (5×10^3 counts per second) are 1 order of magnitude lower than the intensities at 1000 s (5×10^4 counts per second). The relative change in ^{40}Ca ion intensity from surface to the bulk specimen is even greater. Notice that the intensities of ^{28}Si are either unchanged or perhaps slightly higher at the surface of the mineral in comparison to the interior.

In order to emphasize the changes in relative abundance with depth through the samples, the ratios Al/Si and Ca/Si may be normalized to bulk values (unaltered

zone of the leached mineral) and then to control specimens (no leaching). These ratios show the percent change in Al/Si and Ca/Si of the reacted feldspar with depth (Figures 1c and 1d). Aluminum and Ca are clearly depleted relative to Si, from the surface of the mineral toward the interior. The SIMS depth profiles, therefore, provide direct evidence that an Al- and Ca-depleted layer approximately 500–1000 Å thick has formed on the surface of the dissolving feldspar.

The formation of such cation-depleted leached layers on the surface of feldspars dissolving in HCl was first predicted by Correns and colleagues [Correns and von Engelhardt, 1938a, b; Correns, 1940] more than 50 years ago. However, the possible existence of such layers could not be confirmed and remained controversial for a long time (see Petrovic *et al.* [1976], Holdren and Berner [1979], Aagaard and Helgeson [1982], Helgeson *et al.* [1984], Tole *et al.* [1986], Muir *et al.* [1989], Mogk [1990], and Schweda [1990] for reviews). A number of investigators used SIMS depth profiling to identify significant hydrated, cation-depleted layers on the surface of dissolving glasses (see the reviews by Gossink [1980] and Lodding *et al.* [1985]). Once the value of the SIMS for depth-profiling dissolving glasses was realized, it was successfully applied to aluminosilicate weathering. In the last few years, direct evidence for the formation of leached layers on the surface of dissolving feldspars has been obtained, to a large extent as a result of using SIMS. The value of SIMS analyses for helping to understand chemical weathering as it takes place at the solid-water interface is now well established.

The SIMS has found a variety of applications in the Earth sciences [Shimizu and Hart, 1982; Reed, 1984; Havette, 1985; Metson *et al.*, 1985; Williams, 1985]. Silicates, carbonates, sulphides, biominerals, and biological materials have all been analyzed for major and trace elements from H to U, including the platinum group elements and rare earth metals (Table 1). The emphasis of this review is on the use of SIMS to study processes taking place at the surface of dissolving glasses and minerals.

The purpose of this review is threefold: to outline some of the outstanding problems in chemical weathering, including an introduction to their historical development; to explain the SIMS technique and compare it with other methods of surface analyses; and to show how the SIMS may be used to help answer some of the unresolved questions concerning chemical weathering in soils and sediments.

1.2. Chemical Weathering of Minerals in Soils

The long-standing interest in the rates and mechanisms of mineral dissolution in soils is rooted in the need to understand the development and maintenance of soil fertility. For example, the classic textbooks on agriculture from the eighteenth and nineteenth centuries by Home [1762], Davy [1815], Liebig [1843],

TABLE 1. Some Recent Applications of SIMS in Earth Sciences

<i>Material</i>	<i>Application</i>	<i>Reference</i>	
Silicates	REE	<i>Crozaz and Zinner</i> [1986]	
		<i>MacRae</i> [1987]	
		<i>Muir et al.</i> [1987]	
		<i>Bottazzi et al.</i> [1991]	
		<i>Vanucci et al.</i> [1991]	
		<i>Bottazzi et al.</i> [1992]	
		<i>MacRae et al.</i> [1993]	
		<i>Yurimoto et al.</i> [1989b]	
		<i>Gijbels</i> [1987]	
		<i>Yurimoto et al.</i> [1991]	
(Fluid inclusions) Carbonates Sulphides	major, trace, REE	<i>Hervig and Williams</i> [1988]	
	REE, Th, U	<i>Yurimoto et al.</i> [1989a]	
	Ni	<i>Lorin et al.</i> [1990]	
	H	<i>Hervig</i> [1992]	
	Biominerals Biological materials	oxygen isotopes	<i>Hervig et al.</i> [1992]
			<i>Lorin</i> [1992]
			<i>Diamond et al.</i> [1990]
		Na, K, Ca	<i>Swart</i> [1990]
		Fe, Mg, Mn, Sr	<i>Lindsay and Sellschop</i> [1988]
		Au and Pt	<i>Vandentop et al.</i> [1989]
Ag, Cu, Ni, Zn		<i>Chryssoulis</i> [1990]	
Ag and Au		<i>McFarlane and Shimizu</i> [1991]	
sulphur isotopes		<i>Arehart et al.</i> [1993]	
		<i>Lodding et al.</i> [1990]	
	<i>Linton and Goldsmith</i> [1992]		
	<i>Ripoli et al.</i> [1992]		

REE denotes rare earth element.

Johnston [1847], *Dana* [1858], and *Thaer* [1860], all discuss the chemistry of soil mineral weathering. In addition to the importance of chemical weathering to plant nutrition, we now realize that chemical weathering regulates the chemical composition of natural waters [*Stumm and Morgan*, 1981; *Berner and Berner*, 1987; *Drever*, 1988] and provides the long-term acid-neutralizing capacity of soils [*Sverdrup*, 1990]. Although pedology and geology continue to drive research efforts, much of the interest in chemical weathering today is stimulated by two global environmental problems: the desire to understand the effect of acid rain on soils, natural waters, and building materials [*Drever*, 1985; *Colman and Dethier*, 1986; *Kittrick*, 1986], and the need to predict the long-term fate of vitrified nuclear waste [e.g., *Brookins*, 1984].

Chemical weathering is the alteration process which rocks and minerals undergo as they approach chemical equilibrium with their surroundings [*Merrill*, 1921; *Chesworth*, 1992]. Under the conditions of their formation, all minerals are thermodynamically stable in relation to their reactants. For example, igneous minerals are stable under conditions of high pressure and temperature. At the surface of the Earth these primary minerals are thermodynamically unstable and so they decompose, releasing solutes and producing secondary minerals which are more stable under these new conditions.

Mineralogical transformations. The "stability series of mineral weathering" proposed by *Goldich*

[1938] summarizes the sequence of relative stability of primary minerals in soils. For mafic rocks the series is olivine < augite < hornblende < biotite and for felsic rocks the series is calcic plagioclase < alkali plagioclase < K feldspar < muscovite < quartz. When a granite gneiss weathers, for example, the essential minerals of the fresh rock (oligoclase, orthoclase, microcline, quartz, biotite, and hornblende) are altered at different rates: plagioclase and hornblende are the least stable primary minerals, biotite, microcline, and orthoclase are moderately stable, and quartz and zircon are the most stable; the residual clays are composed chiefly of kaolinite [*Goldich*, 1938].

An example of a weathering profile developed on granite is shown in Figure 2. In comparison to the composition of fresh rock, oligoclase and biotite have completely disappeared from the upper layers of the soil profile, and microcline and quartz have declined significantly. In contrast, kaolinite becomes increasingly important toward the top of the profile. The thickness of such a weathering profile and the extent of alteration depend on factors such as temperature, rate of water movement, pH, oxidation potential, the reactive surface area of the reacting particles, and the specific nature of the mineral being altered [*Jackson et al.*, 1948; *Loughnan*, 1969; *Carroll*, 1970].

Chemical transformations. The mineralogical changes which take place during weathering result in the losses of alkali and alkaline earth metal cations and silica and the accumulation of Al and Fe oxides and

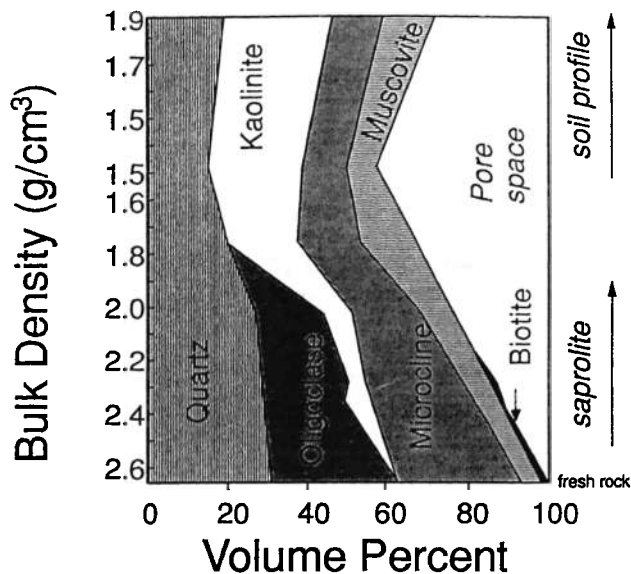


Figure 2. Soil profile and underlying saprolite derived from the weathering of Stone Mountain granite, Georgia [from Grant, 1963]. The friable, white saprolite is dominated by kaolinite, quartz, muscovite, and microcline; plagioclase and biotite have disappeared. When the base of the soil B horizon is encountered, the original rock texture is replaced by a soil texture, with an increase in bulk density and the appearance of iron staining. (Reprinted with permission.)

hydroxides [Polynov, 1937; Bear, 1964]. Goldich [1938], for example, noticed that the rate of loss of cations relative to Al from the Morton gneiss decreased in the order $\text{Na} > \text{Ca} > \text{Mg} > \text{K} > \text{Si}$. In fresh, young soils the sum of the concentrations of Na, K, Mg, and Ca are high in relation to that of Al or Fe, whereas highly weathered tropical soils consist essentially of Al_2O_3 and Fe_2O_3 (Figure 3). The degree of loss of alkali and alkaline earth cations relative to Al or Fe may be used to calculate a quantitative index of weathering intensity [Jackson and Sherman, 1953; Ruxton, 1968; Parker, 1970; Nesbitt and Young, 1982; Harnois, 1988]. Of particular interest today is the rate at which the mineralogical and chemical transformations take place.

Weathering rates. Rates of mineral dissolution in weathering profiles may be calculated from the chemical composition of natural waters [Johnson et al., 1968; Katz et al., 1985; Stauffer and Wittchen, 1991], from the mineralogical and chemical composition of soil profiles [April et al., 1986; Kirkwood and Nesbitt, 1991], or from experimental studies of the rate of dissolution of whole soils [Brown and Lund, 1991]. The book by Sverdrup [1990] provides an excellent introduction to the kinetics of mineral dissolution in soils and summarizes most of the recent literature. Rates of mineral dissolution in the laboratory are usually calculated from the measured concentrations of dissolved constituents in the output solutions of continuously stirred, flow-through reactors [Rimstidt and Dove, 1986]. Mineral dissolution rates measured in the field may be 10–1000 times slower than the corre-

sponding rates measured in the lab [e.g., Paces, 1973, 1983; Velbel, 1985, 1986, 1989]. Are field and laboratory mineral weathering rates comparable [Brantley, 1992; Casey et al., 1993]?

First, the reacting surface area (i.e., the surface area actually in contact with the weathering solution) in natural soils may be much less than the total mineral surface area available for reaction [Drever and Swoboda-Colberg, 1989; Swoboda-Colberg and Drever, 1992]. In stirred reactors, for example, the entire mineral surface area is available for reaction. In a soil the reactive surface area is probably a very small percentage of the total surface area, depending on the soil texture, pore size distribution, and rate of water movement [Swoboda-Colberg and Drever, 1993; Velbel, 1993]. Second, in soils of the temperate zone, average annual temperatures are low enough to account for differences in rates of dissolution of up to 5 times [Velbel, 1990]. Third, batch techniques which include stirring or shaking may give artificially high weathering rates, probably due to mechanical abrasion [van Grinsven and van Riemsdijk, 1992]. Finally, lab experiments typically omit the wetting and drying cycles characteristic of soil profiles [Inskeep et al., 1993].

In addition to physical differences between leaching conditions in the lab and the field, there are usually

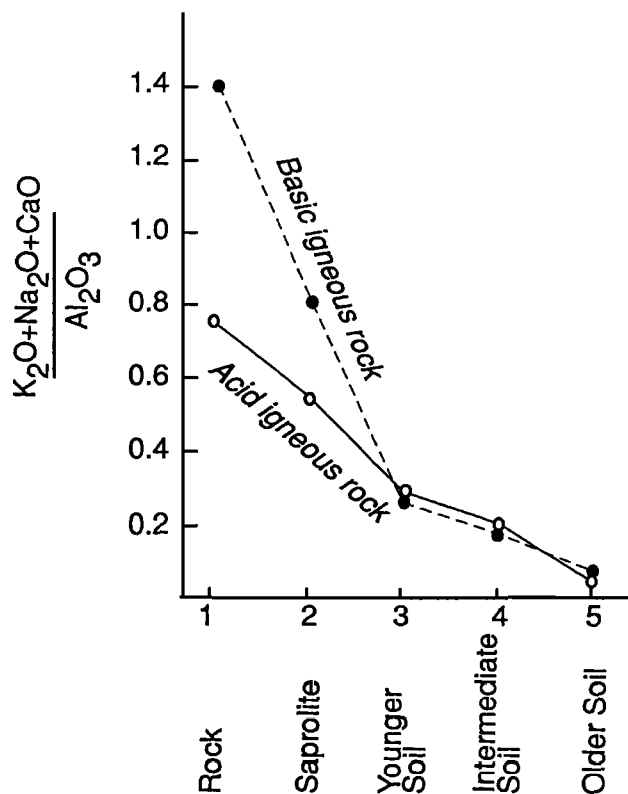


Figure 3. The depletion of alkali and alkaline earth metals relative to Al (or Fe, or Si) increases with increasing weathering intensity. Ratios such as these have been used in a variety of ways to produce chemical indices of weathering intensity. (After Jenny [1941].)

significant chemical differences between the two environments. For example, the compositions of the leaching solutions used in lab studies are simple, often consisting only of HCl. Natural soil solution compositions are much more complex. Consider the distribution of cationic charge in forest soil solutions, for example. Even at pH 4, H^+ may account for less than 20% of the total cationic charge (Figure 4). The presence of other cations, especially Al^{3+} and its hydrolysis products, may significantly reduce dissolution rates [Chou and Wollast, 1984; Casey et al., 1988; Drever and Swoboda-Colberg, 1989; Swoboda-Colberg and Drever, 1992]. Also, the anionic charge in forest soil solutions may be completely dominated by organic ligands which may accelerate or retard rates of dissolution, depending on their size and charge [Stumm et al., 1987]. However, the possible effects of dissolved cations and organic anions on rates and mechanisms of mineral dissolution are not well known.

In section 2 of the paper an introduction is provided to some chemical factors affecting the rates and mechanisms of silicate mineral dissolution, including the effect of dissolved salts and complex-forming organic ligands. Until recently, such studies and their interpretation were based primarily upon chemical analyses of the leaching solutions before and after reacting with a solid phase, with inferences then made about surface reactions. Today, however, we are able to study dissolution and precipitation processes directly as they take place at the solid-solution interface [Hochella and

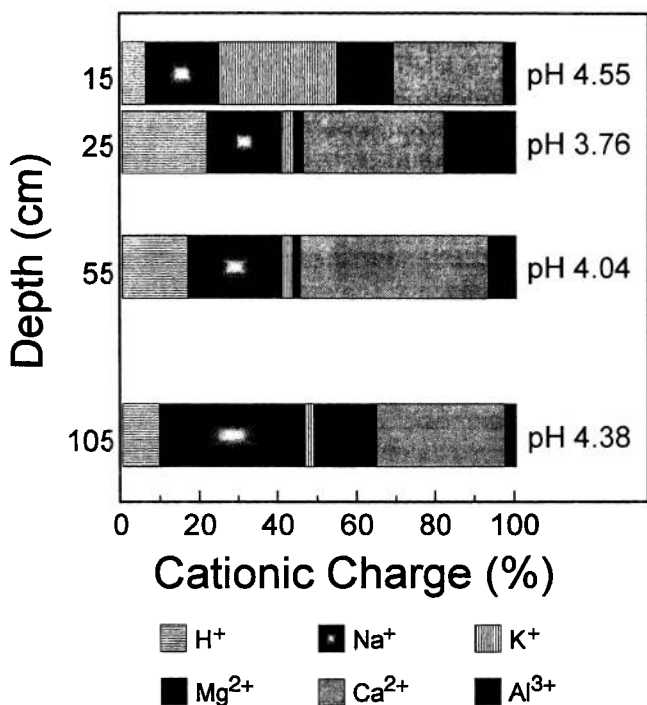


Figure 4. Cationic charge balance in a Cryptopodzolic forest soil solution at Copera in Canton Ticino, Switzerland. Even at pH 3.8, H^+ accounts for only 20% of the total cationic charge.

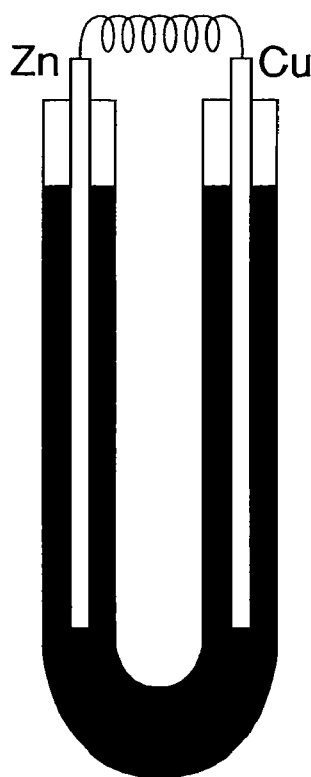


Figure 5. Brongniart's [1841] apparatus for the electrolysis of dissolving K feldspar. Finely ground feldspar was placed in the tube, with a strip of copper in one arm and a strip of zinc in the other. The metal strips were connected by a wire. After 15 days the liquid on the zinc side was still opaque whereas that on the copper side had settled and was quite clear. The experiment was continued for 2 years. By this time the zinc electrode was heavily coated with a residue of leached feldspar. The copper electrode remained clean and the copper arm contained a strong solution of alkaline potassium carbonate. (From Cushman and Hubbard [1907].)

White, 1990]. SIMS is a powerful analytical technique for studying this region. In section 3 the principles of the SIMS method are described, and a comparison is made with other methods of surface analysis. In section 4, examples are given of successful SIMS applications to selected problems in chemical weathering.

2. LABORATORY STUDIES OF MINERAL DISSOLUTION

The traditional approach to quantifying mineral dissolution rates and identifying reaction mechanisms is based upon the chemical analyses of aqueous solutions before and after reaction with a solid phase. Brongniart [1841] showed that during electrolysis potassium feldspar dissolves incongruently in water, with K^+ becoming separated from the negatively charged, residual colloid (Figure 5). This process was first quantified by Daubrée [1879] when he found that K feldspar

dissolving in distilled water released to solution 10 times as much K as either Al or Si.

2.1. The "Amorphous Precipitate Hypothesis"

The first systematic studies of rates of feldspar dissolution in closed systems were presented in a series of papers by Cushman [Cushman, 1905a, b, 1907; Cushman and Hubbard, 1907, 1908]. These studies included a range of feldspar compositions and showed that the rate of dissolution was highly dependent upon their composition and particle size (reactive surface area). In closed systems the dissolution rates were relatively rapid initially, but soon the minerals were found to stop dissolving altogether. This led to the suggestion that the rate of dissolution of feldspar in water was controlled by protective coatings formed by amorphous solids on the surface of the mineral; these coatings formed by precipitation from saturated solutions in closed systems and were seen under the microscope [Cushman, 1905a]. Under the condition of the experiments the removal of insoluble decomposition products was controlling the rates of dissolution of the feldspars. If the reacted feldspar with its protective surface layer was dried and reground, the rate of dissolution was again relatively fast initially because of the regeneration of reactive surfaces.

The formation of such precipitates on dissolving feldspars leaching in closed systems containing saturated solutions eventually became known as the "amorphous precipitation hypothesis" (see the review by Mogk [1990]). In closed systems the formation of protective coatings was believed to control the rate of feldspar dissolution. In a series of similar experiments using closed systems, Busenberg and Clemency [1976] and Busenberg [1978] reported the mineralogical composition of such precipitated phases for a range of feldspar compositions.

2.2. The "Leached Layer Hypothesis"

The first systematic studies of feldspar dissolution in open systems were published by Correns and co-workers [Correns and von Engelhardt, 1938a, b; von Engelhardt, 1939; Correns, 1940; Correns, 1962a, b]. Using flow-through reactors, they found that the relative proportion of Al and Si which is released from dissolving alkali feldspar depended upon the pH of the reacting solution. At pH 3, for example, K feldspar lost more than 4 times as much Al as Si. In contrast, at pH 6.6 the mineral lost slightly more Si than Al [von Engelhardt, 1939].

On the basis of the chemical composition and molar volume of the unreacted mineral and the chemical composition of the output solutions, Correns and von Engelhardt [1938b] concluded that cation- and Al-depleted, residual, amorphous leached layers were forming on the surface of the dissolving feldspar. They suggested that the ratio of Al to Si in the residual surface layer depended upon the solution pH, with

increasingly siliceous layers favored in more acidic solutions. Assuming that dissolution was uniform over the surface of the mineral, leached layer thicknesses of up to 2000 Å were calculated. This theory eventually became known as the "leached layer hypothesis." At the time there were no surface-sensitive analytical instruments for testing this theory. More recent solution chemical studies by Chou and Wollast [1984, 1985], Holdren and Speyer [1985], Wollast and Chou [1985], and Schweda [1989] also predicted cation- and Al-depleted leached layers on the surface of feldspars dissolving in open systems using acidic solutions. Until recently, however, there was no direct evidence to confirm the formation of such layers.

The leached layer hypothesis of Correns did not in any way contradict the amorphous precipitate hypothesis of Cushman: Cushman's studies were performed in closed systems in which the primary minerals dissolved, the products of dissolution were allowed to accumulate, and secondary phases precipitated. The studies by Correns were performed in open systems in which aqueous reaction products were continually removed from the reaction vessel, making it impossible for secondary phases to precipitate.

Studies of naturally weathered feldspars using the scanning electron microscope (SEM) showed clearly that feldspar dissolution is nonuniform, resulting in deep, extensively developed etch pits [Wilson, 1975; Berner and Holdren, 1977, 1979]. In order to calculate the thicknesses of his proposed cation- and Al-depleted leached layers, however, Correns had assumed that the feldspars dissolved uniformly to produce a leached layer laterally constant in thickness around the surface of each grain [Berner et al., 1985]. Thus the discovery of etch pits on the surface of naturally weathered feldspars appeared to constrain the "leached layer hypothesis" as proposed by Correns to explain the experimental studies of feldspar dissolution. Furthermore, studies using X ray photoelectron spectroscopy (XPS) and Auger spectroscopy failed to detect any significant (greater than 100 Å) leached layers either on naturally or experimentally weathered feldspars [Petrovic et al., 1976; Berner and Holdren, 1977, 1979; Holdren and Berner, 1979; Fleer, 1982; Fung and Sanipelli, 1982; Hochella et al., 1988]. Mainly on the basis of the lack of direct evidence of significant leached layers on the surface of dissolving aluminosilicates, the leached layer hypothesis was largely discredited.

2.3. Effect of Dissolved Salts

Beyer [1871] found that salts of NH_4 and Na increased the release of K from alkali feldspar by a factor of about 3, in comparison to distilled water. Cushman and Hubbard [1907] and André [1913] reported similar results. Andersson and Lindqvist [1956] found that the dissolution rate of microcline in 0.1 M salt solutions at pH 6 decreased in the order $\text{LiCl} >$

water > NaCl > KCl > CsCl, with the rates of dissolution in a given salt solution decreasing with increasing salt concentration. The results of the experiments were interpreted in terms of the selective adsorption of cations on the dissolving mineral surface. *Nash and Marshall* [1956a, b] performed similar experimental studies.

More recently, *Sjöberg* [1989] examined the effects of salt solutions on the rate of dissolution of labradorite over a wide pH range at temperatures up to 70°C. In HCl solutions containing no significant concentrations of cations other than H⁺, Al was released preferentially over Si, consistent with the formation of residual leached layers. Although no direct analyses of the reacted surfaces were made, the calculated thicknesses of the leached layers predicted to have formed were 100 Å at pH 4, 1000 Å at pH 3, and 4000 Å at pH 2. Adding KCl (0.1, 0.01, or 0.001 M) significantly reduced the dissolution rates.

2.4. Effect of Complex-Forming Organic Acids

The first observations of siliceous layers on the surfaces of silicates dissolving in solutions containing organic acids were published by *Monier* [1877]. He leached 500 cm³ of sodium silicate in a 1-L solution containing 75 g of oxalic acid and described the growth of siliceous layers which achieved a thickness of 7–8 mm after 48 hours. These and other pioneering studies were summarized in an exhaustive review of early work published by *Julien* [1879]. With respect to acidic, organic-rich forest soils such as podzols, soil scientists have long been in favor of an important role for organic acids in mineral weathering and soil profile development [*McKeague et al.*, 1986; *Robert and Berthelin*, 1986; *Tan*, 1986]. This theory is indirectly supported by studies which have shown that a large proportion of the dissolved Al in forest soil solutions is organically bound [*Driscoll et al.*, 1985; *Litaor*, 1987; *Manley et al.*, 1987] and can help explain the high concentrations of total dissolved Al (up to 5 mg/L) in such solutions [*Antweiler and Drever*, 1983]. However, a number of unanswered questions remain. First, do organic acids promote or inhibit the rates of mineral dissolution? It has been suggested that simple, low-molecular weight organic acids tend to promote mineral dissolution while complex, large-molecular weight humic materials inhibit this process (see below), but there have been few systematic studies. Since very few data have been published regarding the concentrations of individual organic acids in forest soil solutions, it is difficult to design realistic experiments. Second, the relative importance of organic acids as proton donors versus their role as ligands or reductants is unclear [*Manley and Evans*, 1986; *McCull and Pohlman*, 1986; *Pohlman and McCull*, 1986, 1988].

Individual, low-molecular weight organic acids in forest soil solutions are thought to be present at concentrations of the order of 10⁻⁵ to 10⁻⁴ M [*Vedy and*

Bruckert, 1982], but there have been few measurements. In a forest soil solution, *Hue et al.* [1986] measured a total of 480 μmol/L of organic acids, including succinic, malic, lactic, malonic, citric, and oxalic (282, 117, 52, 20, 5, and 4 μmol/L, respectively). In experimental lab studies of mineral dissolution, however, ligand concentrations as high as 0.1 M have been used [*Schalscha et al.*, 1967]. *Chin and Mills* [1991] showed that millimolar concentrations of oxalic, malonic, and salicylic acids promoted the rate of kaolinite dissolution in comparison to solutions at the same pH without organic ligands. *Welch and Ullman* [1992, 1993] also used millimolar concentrations and reported similar results for plagioclase feldspar dissolution. However, even millimolar concentrations may be 10–100 times higher than the organic acid concentrations present in soil solutions and other natural waters.

The effect of simple organic acids versus more complex organic ligands on the rates and mechanisms of silicate dissolution has not been extensively investigated. In contrast, the effect of organic ligands on the rates of dissolution of oxide and hydroxide minerals is now reasonably well documented [*Furrer and Stumm*, 1986; *Stumm et al.*, 1985; *Schindler and Stumm*, 1987; *Stumm and Furrer*, 1987]. The mechanistic interpretation of aluminosilicate dissolution is more complicated than that of oxides and hydroxides, but, as a first approximation, the concepts developed for oxide and hydroxide surfaces may be extended and applied to the kinetics and mechanisms of weathering reactions of silicates [*Stumm et al.*, 1987; *Stumm and Wollast*, 1990]. The rate constants for the dissolution of Al₂O₃, for example, in the presence of aliphatic organic acids decrease in the order oxalic > malonic > succinic, which form five-, six-, and seven-member chelate rings, respectively [*Stumm et al.*, 1985; *Furrer and Stumm*, 1986]. For aromatic ligands the rate constant for salicylic acid, which forms a six-member ring, was 4 times that of phthalate, which forms a seven-member ring. These ligands form surface complexes by ligand exchange with surface hydroxyl groups, bringing negative charge into the coordination sphere of the surface Al species. This polarizes the critical Al-oxygen bonds, thus facilitating the detachment of Al from the surface. The surface-binding step (adsorption) is fast, followed by a slow detachment step in which the complexed metal ion is transferred to the solution. Five-member chelate rings are the most detachable, followed by six- and seven-member rings. For comparison, using millimolar concentrations of organic acids, the rate of dissolution of kaolinite decreases in the order oxalate > malonate > salicylate > phthalate [*Chin and Mills*, 1991]; this is the same order as given above for Al₂O₃.

Unlike the low-molecular weight organic acids, higher-molecular weight degradation products of biota such as humic and fulvic acids are expected to become

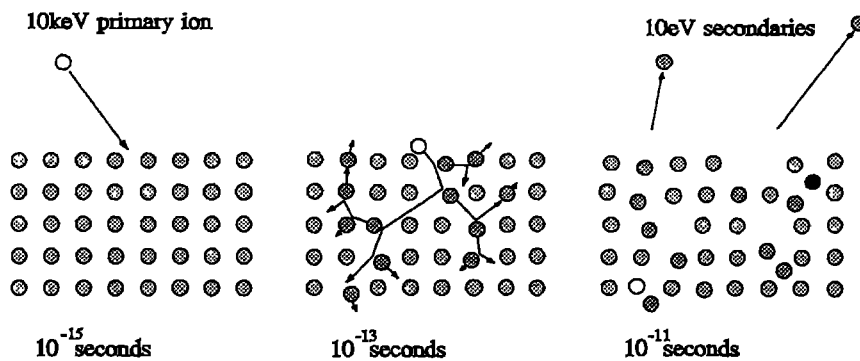


Figure 6. The progress of the collision cascade in a solid surface, resulting in secondary ion emission.

strongly adsorbed upon silicate surfaces and inhibit mineral dissolution [Stumm *et al.*, 1987]. Experimental studies of Fe oxide dissolution with aqueous extracts of chestnut (*Castanea sativa*) leaf litter have shown that this chemically complex, organic-rich "tea" forms protective coatings on the mineral surface and inhibits the release of Fe [Blaser, 1974; Blaser *et al.*, 1981]. At pH 4.5, pyrocatechol violet is effectively adsorbed by albite and oligoclase and decreases their rates of dissolution [Schenk *et al.*, 1989]. Experimental studies of kaolinite weathering have shown that humic acid decreases dissolution rates in comparison to solutions at the same pH without humic acid [Chin and Mills, 1991].

The effects of salts and organic ligands on the chemical composition of dissolving glass and mineral surfaces may be studied directly using SIMS.

3. SURFACE ANALYSES USING SIMS

31. Introduction

To analyze the surface of a mineral and study processes such as leaching occurring at such surfaces, it is necessary to utilize methods which can directly examine a zone a few atomic layers in depth. In addition to surface sensitivity, such methods should have reasonable absolute sensitivity for a wide range of elements and allow the analysis of composition as a function of depth normal to the mineral surface. Secondary ion mass spectrometry (SIMS), in its simplest form, is based on the erosion or "sputtering" of a surface by a primary ion beam and the subsequent collection and analysis of the secondary ions produced. SIMS fulfils most of the above criteria and is thus an extremely powerful tool in weathering/surface exchange studies. The acronym SIMS embraces a family of related techniques and instrument configurations, of which only some are relevant to this type of work. The attributes of these methods and their limitations in geochemical analysis are discussed below. A detailed review of SIMS in general can be found in the work by Benninghoven *et al.* [1987].

3.2. The SIMS Method and Selection of Instrumentation

When an incident ion beam of energy between 5 and 30 kV impacts on the surface of a solid, a "collision

cascade" is initiated, in which the incident energy is dissipated through a number of collision partners in the solid [Williams, 1979]. During the course of this "cascade" the primary ion is typically implanted into the surface, and secondary particles are dislodged and may subsequently escape the surface (Figure 6). A small proportion, perhaps only 1%, of this "sputtering yield" is ionized and can be extracted directly into a mass spectrometer for analysis. Thus in the simplest form of SIMS the user observes a mass spectrum of secondary ions ejected from the sample surface. These ions reflect the composition of the surface, although it is important to note they are not directly proportional to relative element abundances at the surface. Ion yields suffer from a significant chemical matrix effect. Although the efficiency of secondary ion production is low, detection limits still extend to around 10 ppb for favorable elements, particularly the alkali and alkaline earth metals (Figure 7).

Because the generation of secondary ions is the limiting analytical process in SIMS, any species which can be ionized (positive or negative) can, in theory, be analyzed. Thus most of the periodic table can be ac-

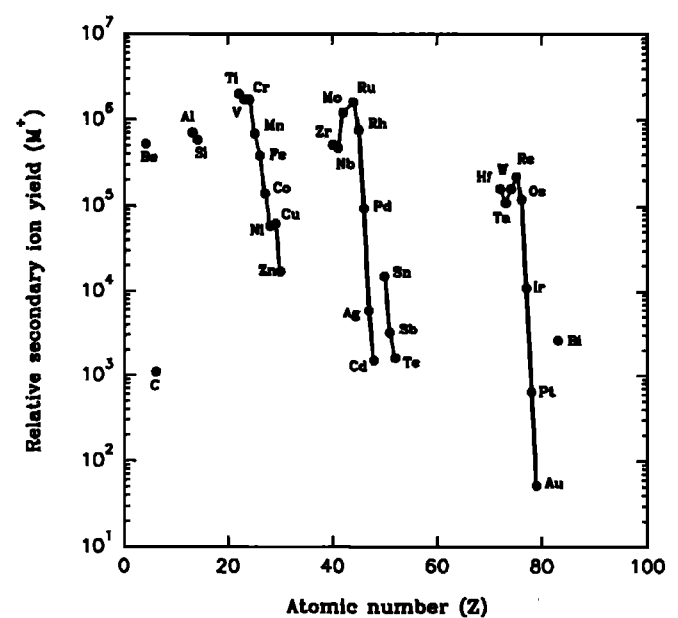


Figure 7. Ion yields from oxygen bombardment of elemental samples. (From the data of Storms *et al.* [1977].)

cessed, including hydrogen [e.g., *Yurimoto et al.*, 1989a]. The raw spectrum will, however, contain any readily ionizable species, which includes molecular ions, most importantly in mineral analysis, oxides. Thus in geochemical applications, some form of spectral filtering is usually applied to extract the elemental ion signature [*Reed*, 1980].

The experimental conditions used for geochemical analysis generally involve "dynamic" conditions [*Benninghoven et al.*, 1987], where high primary ion current densities rapidly erode the sample surface. Thus the total ion yield is high, and mass resolution of the analyzing spectrometer is generally important in resolving isobaric interferences to identify the target species. High-transmission magnetic spectrometers, and predominantly the Cameca IMS3f through 5f instruments, currently dominate this type of study. Although magnetic spectrometers lack the transmission attributes of the time of flight (TOF) analyzers typically used in "static" SIMS, the large extraction fields used offer considerable flexibility, both in achieving reasonable transmission efficiency and particularly in energy filtering to remove molecular ions from the spectrum.

In the Cameca instruments the spatial distribution of secondary ions is maintained through the spectrometer; thus the instrument is a real-time ion microscope, and a mass-resolved image of a large area can be viewed simultaneously. This gives significant transmission advantages over an instrument which collects signal while rastering the primary beam across the surface (ion microprobe), although the Cameca can also be used in this way. Because the microscope spatial resolution is dictated by the ion optical resolution of the extraction optics and secondary ion column, which is generally inferior to that of the primary column, ion microprobes offer an advantage in ultimate resolution [*Betz and Rudenauer*, 1991]. This can be useful in imaging but is only rarely useful in analysis because of the sacrifice in sensitivity.

The most significant advantages of SIMS over, for example, X ray methods are as follows: (1) The very large signal-to-noise advantages of mass spectrometric detection give a very large usable dynamic range, typically better than 8 orders of magnitude, between the most and least abundant elements which can be observed. (2) The very limited escape depth of secondary ions, typically several atomic layers, makes SIMS extremely surface sensitive. (3) SIMS is a natural depth-profiling method, in that the analyzed zone progressively moves into the sample, as the surface is removed by sputtering. Erosion rates vary from fractions of a monolayer to more than a nanometer per second, depending on primary ion species and current density. (4) Mass spectrometric analysis allows isotopes to be resolved. Thus tracer studies such as leaching in deuterated solutions can be used to great effect.

The most significant limitations include the following: (1) There are difficulties involved in converting ion abundances in the secondary ion spectrum into element abundances at the surface. The process of ionization at these relatively low energies is matrix sensitive and modeled only with considerable difficulty. (2) Mineral surfaces are usually insulating; thus the use of charged particle beams in sputtering and extraction means charging must be controlled, and this is sometimes difficult. Negatively charged oxygen is the most convenient primary beam for mineral analysis; positive cesium is the most difficult. (3) The geometry of ion incidence at the mineral surface means shadowing effects from surface roughness can severely limit the accuracy of the depth profile. (4) SIMS is an ultrahigh vacuum method, so samples must be examined *ex situ*. Thus sample handling and preparation are especially critical.

It is worth considering the impact of some of these factors in more detail by considering how the SIMS process works.

The generation of secondary ions. The process of generating a secondary ion can be separated into several steps. The sputtering process is relatively well understood. On the basis of the *Sigmund* [1969, 1987] model the transfer of energy between the incident ion and its collision partners can be reasonably well modeled, and the total sputtering yield is obtained from calculation. Accuracy is good for samples where preferred orientation and channeling effects do not interfere, such as most metal surfaces, but is limited for crystalline solids and thus many surfaces of geochemical interest. Typically the "collision cascade" is complete in 10^{-13} s and yields sputtered particles with an energy distribution peaking strongly below 10 eV and extending many hundreds of eV above this energy. However, predicting which of these sputtered species will be ions is difficult.

Secondary ion yields from similar matrices follow an inverse exponential relationship to either the ionization potential (positive ions) or electron affinity (negative ions). However, a strong dependence on chemical state or, rather, the position of the Fermi level, is also observed. This partly explains why the use of an electronegative species, such as oxygen, as the primary ion enhances positive ion yields by up to several orders of magnitude, while electropositive cesium enhances negative ion yields [*Wittmaack*, 1981; *Yu*, 1986a]. Figure 7 shows the relative ion yields of positive ions, mostly from elemental samples, under oxygen ion bombardment. In enhancing ion yields, the source of oxygen is not important. Thus oxygen leaks have been used, and yields are enhanced from oxide matrices.

Numerous models have been developed to predict ion yields. It should be noted that none of these models is universal to all sample types. The model of most relevance to this review is the bond-breaking model

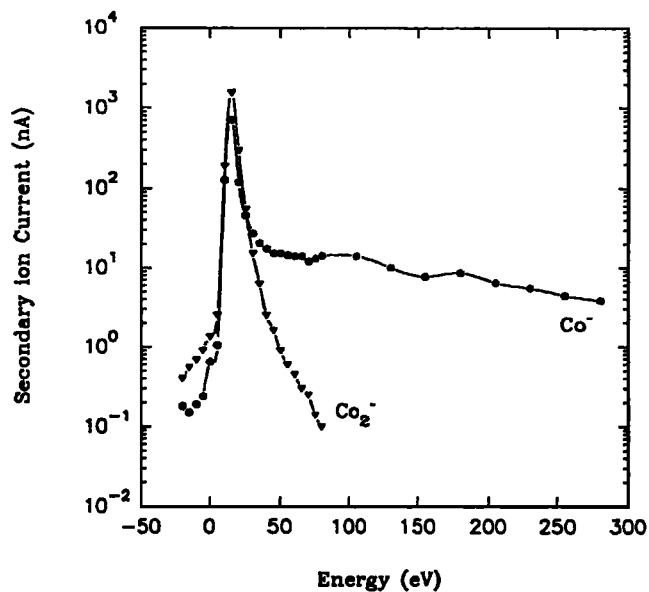


Figure 8. The energy distribution of Co^- and Co_2^- from a metal specimen, bombarded with a Cs^+ primary beam.

proposed by Slodzian [1975] to explain the large secondary ion yields from ionic solids. This is the model which also most comfortably applies to oxides [Williams, 1979]. The ion ejection process is seen as a single bond cleavage which in the case of cation emission results in a vacancy site's trapping a free electron. If this electron is trapped at the vacancy longer than the timescale of the sputtering event (10^{-13} s), then the cation will escape the surface. The model is not easily formulated into a usable relationship, because of the difficulty in describing the properties of the vacancy (electron affinity and amplitude of the wave function). However, where usable approximations have been applied, reasonable correlation with experimentally observed positive ion yields has been found [Yu, 1986b].

The problem of quantifying ion yields can, in general, be avoided when depth profiling because the matrix is often not substantially modified with depth, and thus relative ion yields do not vary as the depth profile proceeds. The usual procedure is to take the ratio of the element of interest to a matrix element, for example Si or Al, which is either not anticipated to vary or varies predictably in the regime being examined. This procedure also removes the effects of artifacts, such as surface roughening, which alter total secondary ion yields.

If quantitation is essential, the only universal, but often impractical, approach is still to have standards available which match the matrix of the sample to be analyzed. In whole rock analysis, matrix dilution has been very successfully used to mitigate matrix effects

on ion yields [Nesbitt *et al.*, 1986]; however, the same approach is not available in depth profiling.

The specimen isolation method. Although the ion yield problem may not seriously interfere with depth profiling, the discrimination of molecular ions from elemental ions certainly does. A major advantage of the sector instrument is that mass resolution can be used to discriminate between many common isobars. Also, when using a large extraction field, the secondary ion energy spectrum can be used to select energy windows where the elemental ion spectrum dominates over the molecular ion spectra. This is best explained by reference to Figure 8 where the narrow energy spectrum of Co_2^- is effectively removed by analyzing ions with emission energies above 100 eV.

This approach is limited by the degree of energy filtering which is needed to eliminate the molecular ion spectra. Hydrides and the oxides of heavier elements are difficult to remove this way. One technique which avoids this problem is an extreme form of energy filtering known as the specimen isolation method [Metson *et al.*, 1983; Lau *et al.*, 1985]. Although more widely used for trace element analysis, this method has been used with considerable success in depth profiling feldspars [Nesbitt and Muir, 1988; Muir *et al.*, 1989, 1990; Muir and Nesbitt, 1991, 1992; Nesbitt *et al.*, 1991; Shotyky and Nesbitt, 1992]. Extreme energy filtering is achieved by allowing the sample surface to charge, thus creating a large in situ energy filter or threshold, controlled only by the dimension of a conductive aperture placed above the surface (Figure 9). The method is a straightforward way to achieve both control of charging and extreme energy filtering on insulating surfaces and is thus well suited to geochemical analysis.

3.3. Depth Profiling

SIMS, in dynamic mode, is a natural depth-profiling method, because the primary ion beam progressively

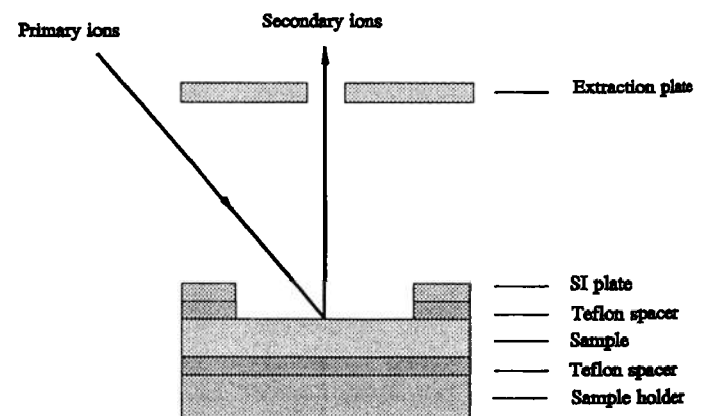


Figure 9. The sample support geometry used to exploit the specimen isolation (SI) method. Note the isolation of the sample from the secondary ion extraction voltage applied to the SI plate.

erodes the sample surface. Thus relative ion signals as a function of time represent a depth profile of element concentrations. If the primary beam is raster scanned across the sample surface, then a symmetrical crater is formed; the erosion front is flat and ideally moves perpendicular to the surface. There are, however, a number of factors which complicate this picture and limit the accuracy of such an element profile.

Limits are imposed by three principal factors: crater edge effects, surface roughness, and ion beam mixing and selective sputtering.

Crater edge effects. If the signal from the edges of the sputtered crater contributes to the profile, then ion intensities are simultaneously being collected from a range of depths, rather than the crater bottom. This is most readily eliminated by either raster gating the secondary ion beam in a microprobe-type instrument, or by constraining secondary ion optics in a microscope-type instrument, so then only signal from the central zone of the sputtered crater is collected.

Surface roughness. In typical instrument geometries the primary beam impacts the surface at an angle between 30° and 45° to the surface normal. Angles can increase dramatically in high-extraction field instruments, when low primary beam energies are used [Meuris *et al.*, 1989]. Thus surface roughness will act to shadow the surface and thus, at least initially, cause substantial loss of definition in the observed profile. Published profiles on mineral surfaces are rarely as dramatic as those from, for example, semiconductor surfaces, for both this reason and the natural inhomogeneities in processes occurring at mineral surfaces.

Ion beam mixing and selective sputtering. The dynamics of the sputtering process are complex. Initially, primary ions are implanted into the surface and thus alter its composition. Also some surface species may be selectively sputtered due to the nature of their bonding. Both effects are transitory, and despite the continued erosion of the surface a steady state condition is rapidly reached, usually within seconds. The collision cascade will, however, continue to mix the composition in the zone ahead of the sputtering front. This mixing ultimately limits the resolution of sharp interfaces and the useful total depth of a profile. Owing to the nature of interfaces in most natural systems, this is rarely a limitation in depth profiling minerals.

3.4. Comparison With Other Methods of Surface Analysis

The use of SIMS in these applications must be weighed against other possible methods of surface analysis. Both X ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) have been used with considerable success in the surface analysis of minerals. The application of these methods to the surface analysis of geologic materials has been reviewed in the book by Perry [1990], and Mogk [1990] reviewed the application of AES to chemical weather-

ing. AES is rather sample restricted in that samples are required to be at least partially conductive [Hochella, 1988], and XPS has been more widely used. Both methods rely for their surface sensitivity on the limited escape depth of low-energy (10–2000 eV) electrons and are thus similarly sensitive to the outer 5–20 atomic layers. They lack the absolute surface sensitivity of SIMS and require the sputtering of the surface as a separate step, in order to create a depth profile. The reliance on an external (usually inert gas) ion gun typically limits sputtering rates to an order of magnitude lower than SIMS using a Cs⁺ primary beam. This restricts the accessible depth in an XPS/AES profile to fractions of a micrometer.

A more significant limitation is the relatively poor sensitivity of these methods, particularly for light elements. Although considerably better than X ray methods, sensitivity for elements below boron is poor and, importantly, hydrogen is inaccessible. At best, these methods are capable of detecting elements at the 0.1 at. % level, far inferior to SIMS. On the other hand, the cross sections for photoelectron and Auger electron emission are well known, and thus both methods, but especially XPS, are immediately quantitative. Electron yields are not matrix sensitive, and thus accurate major element profiles can be obtained.

Other ion beam techniques, based on the interaction of energetic (MeV) ion beams with surfaces, have been applied with some success to mineral surface leaching problems [Schott and Petit, 1987; Petit *et al.*, 1990b]. Although particle-induced X ray emission (PIXE) has insufficient depth resolution (>1 μm) to be useful in this respect, Rutherford backscattering (RBS), elastic recoil detection analysis (ERDA), and especially nuclear reaction analysis (NRA) all have application in this area. NRA has been used with great effect in hydrogen profiling of glasses and other materials where the modified zone of interest is up to a micrometer in depth, and the depth resolution (at best 5–10 nm) can be usefully applied [Della Mea *et al.*, 1983; Schreiner *et al.*, 1988; Petit *et al.*, 1987, 1989a, b, 1990a, b]. Casey and coworkers have contributed significantly to our understanding of feldspar dissolution using RBS and NRA to study the formation of leached layers on the surface of dissolving labradorite [Casey *et al.*, 1988, 1989a, b]. Despite success with hydrogen, boron, fluorine, sodium, and some other elements, however, NRA is extremely element selective. There are a limited number of suitable interactions, and because depth resolution is energy sensitive, they do not generally have sufficient depth resolution for many mineral weathering problems. Also, lateral resolution is currently rarely better than 100 μm for the energetic ion beam methods. Microfocused beams of a few micrometers are being further developed, but the problem is technically challenging with MeV particles.

TABLE 2. Comparison of Surface Analysis Methods Applied to Geologic Materials

	SIMS	RBS	XPS	AES
Elements analyzed	H-U	Z > Li*	Z > Li	Z > Li
Spatial resolution	<30 nm	5 μm	100 μm	50 nm
Depth resolution	<1 nm	30–80 nm†	1 nm	1 nm
Best sensitivity	0.01 ppm	100 ppm	0.1%	0.1%
Quantitative	difficult	yes	yes	yes
Insulating samples	yes	yes	yes	difficult
Chemical information	some	no	yes	yes

*The ability to detect and resolve elements is a sensitive function of the detector resolution and the particular element/substrate combination.

†Depth resolution is again very sensitive to detector resolution and particle straggling in the particular substrate (thus it is itself a function of depth).

A broad comparison of the attributes of SIMS, AES, XPS, and RBS is shown in Table 2.

4. APPLICATION OF SIMS TO CHEMICAL WEATHERING

4.1. Dissolution of Glasses

Lab studies. Dissolving glasses have been successfully depth profiled using SIMS by a number of authors [e.g., Gossink *et al.*, 1979; Smets and Lommen, 1982; Lacharme and Lehuède, 1985; Richter *et al.*, 1985; Zoitos *et al.*, 1989]. Gossink *et al.* [1979], for example, used SIMS to depth profile a glass (20 Na₂O · 10 CaO · 70 SiO₂ mol %) leached in water at 75°C for 15, 30, and 40 min. Using a 100-nA O⁻ primary beam and a Ta diaphragm to reduce surface charging, a plot of measured crater depth versus sputter time showed an excellent linear correlation, giving an average sputter rate of approximately 0.5 Å/s. The sample which was reacted for 30 min showed that Na was significantly depleted relative to Si for more than 2000 s; this corresponds to a leached layer approximately 1000 Å thick. Calcium was also depleted in relation to Si, but only to a depth of 500 Å, revealing a preferential leaching of Na.

Titanite (CaTiSiO₅) is being considered as the ceramic component of a glass-ceramic host for immobilizing radioactive wastes. To confirm the expected thermodynamic stability of this mineral in groundwater environments, glass ceramics were leached for up to 1 year in synthetic saline groundwater including 15,500 mg/L Ca, 5047 mg/L Na, and 33,410 mg/L Cl at pH 6–8 [Hayward *et al.*, 1984]. SIMS analyses of the glass-ceramic leaching in deionized water showed depletions of Ca at depths up to 500 nm and Na, Cs, and Sr to depths greater than 900 nm; Si, Ti, Ce, La, and U were enriched at the surface. These results suggested that the glass phase dissolved preferentially, with the subsequent precipitation of Si, Ti, Ce, La, and U. In contrast, the synthetic groundwater effectively suppressed leaching of the titanite; in addition to the

surface enrichments noted above, the SIMS depth profiles revealed significant enrichments of Mg and Si. Observations using SEM/energy-dispersive X ray indicated that a hydrated Mg silicate had precipitated on the reacted surface [Hayward *et al.*, 1984]. Both of these results were consistent with the calculated saturation state which indicated the solution was supersaturated with respect to sepiolite, a chain lattice clay mineral.

Schreiner [1989] performed leaching experiments with two glass compositions: 15 K₂O · 25 CaO · 60 SiO₂ (wt %) and 16 K₂O · 15 CaO · 39 SiO₂ · 15 PbO · 10 P₂O₅ · 3 MgO · 2 Al₂O₃ (wt %); the latter is a dark green glass similar in composition to the glass used in medieval stained glass windows. The glasses were leached in HCl and H₂SO₄ ranging from 0.1 M to 0.1 mM at room temperature for up to 5 hours. The glass samples were gold coated to reduce surface charging and probed with a 100-nA O⁻ primary beam. Each acid produced an altered layer severely depleted in K and Ca but enriched in H and Si; however, the depth of alteration in 0.1-N H₂SO₄ was approximately one half that produced by 0.1-N HCl (Figure 10). Using high mass resolution ($M/\Delta M$ from 2600 to 3100), Schreiner [1989] was able to clearly distinguish ³²S from ³²O₂ and depth profile both ³²S and ³⁵Cl in the dark green glass: The glass leached in HCl showed a significant enrichment of Cl, while the glass leached in H₂SO₄ was enriched in S (Figure 10). The difference in leached layer thickness for a given glass composition in the two acids suggests that the anions play an important role in glass dissolution kinetics.

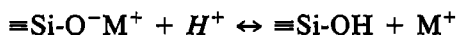
Field studies. A number of reports have been published describing the surfaces of medieval glasses weathered in the ambient air for 600–700 years [Schreiner *et al.*, 1984, 1988; Schreiner, 1988, 1989]. These glasses were produced north of the Alps between the years 1100 and 1500 and are characteristically low in SiO₂ (40–50 wt %) and high in K₂O (10–20 wt %), with 10–15% CaO. The dark green stained glasses produced during the same period contain, in addition to the above constituents, 5–10% P₂O₅ and 10–30% PbO. Whereas the potash-lime glass shows a

low chemical durability, the dark green versions are much more stable [Schreiner *et al.*, 1984].

Using an O^- primary beam, Au-coated naturally weathered glasses were depth profiled for $^1H^+$, $^{23}Na^+$, $^{27}Al^+$, $^{29}Si^+$, $^{41}K^+$, $^{42}Ca^+$, $^{65}Cu^+$, $^{138}Ba^+$, and $^{208}Pb^+$. To convert the plot of secondary ion intensities as a function of sputter time to concentration depth profiles, the "relative sensitivity factor" method was used in conjunction with measured sputtering rates [Schreiner *et al.*, 1984]. The sensitivity factor ($S_{X/M}$) relates the measured ion intensity (I_M^+) to the atomic concentration (c_M) as follows:

$$S_{X/M} = [(I_X/c_X)f_X]/[(I_M/c_M)f_M]$$

where I is the secondary ion signal, c the atomic concentration, and f the isotopic abundance of the analytical (X) or reference element (M); in this case, Si was selected as the reference element. The relative sensitivity factor method has been discussed elsewhere [Metson, 1990]. The concentration-depth profiles revealed a surface layer apparently enriched in H, Si, and Al (the "gel zone") and depleted in K and Ca. Schreiner *et al.* [1984] assumed that the dominant process was the following ion exchange reaction:



and further that the atomic concentration of Si remained constant during dissolution. The relative enrichment of Si at the surface was interpreted in terms of an increased sputtering rate of Si in this zone. The concentration-depth profiles were then corrected for this and are shown in Figure 11a. The leached layer is

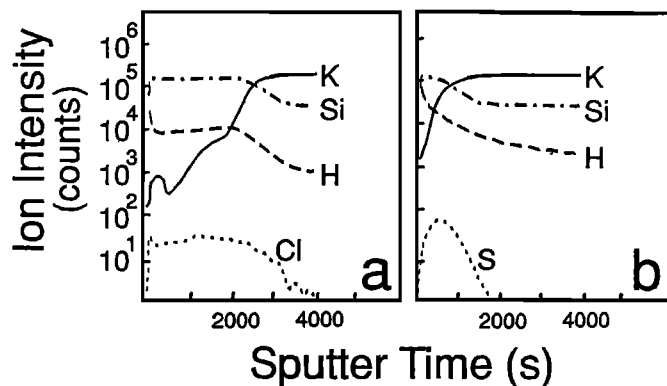


Figure 10. (a) Raw SIMS depth profile of 1H , ^{41}K , ^{29}Si , and ^{35}Cl of glass containing 15 wt % K_2O , 25% CaO , and 60% SiO_2 leached in 0.1 N HCl for 1 hour. An altered layer has developed which is depleted in K but enriched in H, Si, and Cl, as well as Ca (not shown). (b) Raw SIMS depth profile of 1H , ^{41}K , ^{29}Si , and ^{32}S in the same glass composition, but leached in 0.1 N H_2SO_4 for 1 hour. The altered layer which has developed is similarly depleted in K and enriched in H and Si, as well as Ca (not shown), but the depth of alteration is approximately one half that produced by HCl. Notice the enrichment of S. (From Schreiner [1989]. Reprinted by permission of the American Ceramic Society.)

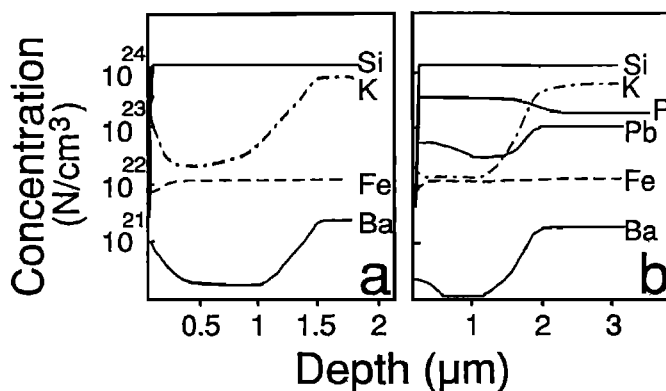


Figure 11. (a) Concentration-depth profiles of K, Fe, and Ba, relative to Si, in medieval glass 19 naturally weathered since the fifteenth century. An altered layer has developed which is strongly depleted in K and Ba, as well as Na and Ca (not shown), and slightly depleted in Mg, Al, and Mn (not shown) in relation to Si. Iron is neither enriched nor depleted. (b) Concentration-depth profiles of K, P, Fe, Ba, and Pb, relative to Si, in dark green medieval glass 22 naturally weathered since the fourteenth century. An altered layer has developed which is strongly depleted in K and Ba, as well as Ca (not shown), and slightly depleted in Pb, as well as Mg, Al, and Mn (not shown), in relation to Si. Again, Fe in the leached layer is unchanged in comparison to the bulk composition. Notice the enrichment of P in the leached layer. (From Schreiner [1988]. Reprinted with permission.)

approximately 1.5 μm thick and significantly depleted in K, Ca, and Pb. The outermost layer, however, revealed an enrichment of many elements, including Pb, which may help to explain the durability of this glass. This outermost layer was also clearly enriched in Cl and S in relation to the bulk glass.

The constant Si assumption was confirmed in subsequent studies of these glasses [Schreiner, 1988; Schreiner *et al.*, 1988]. Shorter analysis times and subsequent crater depth measurements with a profilometer showed that the increased intensities of Si near the surface were caused partly by a higher erosion rate of that layer by the primary ion beam. Using high mass resolution, Schreiner [1988] showed that the intensity of $^{31}P^+$ was more than 10 times that of $^{30}Si^1H^+$, allowing P to be depth profiled quantitatively (Figure 11b). The P depth profiles showed that the leached layer formed on the dark green, phosphorus-containing glass was significantly enriched in P [Schreiner, 1988]. The H depth profiles obtained by depth profiling with SIMS [Schreiner *et al.*, 1984] were confirmed using NRA [Schreiner, 1988; Schreiner *et al.*, 1988].

A radwaste glass consisting of 85 wt % nepheline syenite and 15% CaO was analyzed using SIMS after leaching in groundwater for 28 years [Tait *et al.*, 1986]. The chemical composition of the fresh glass was 51.2% SiO_2 , 20.4% Al_2O_3 , 15.0% CaO , 8.5% Na_2O , and 4.3% K_2O . SIMS analyses of the leached glass revealed the following: Al, Ca, and Na were depleted to depths of

approximately 20, 35, and 90 nm, respectively, and Si enriched to 60 nm. Iron and Mg were slightly enriched to depths of 45 nm, possibly because of accumulation from groundwater. Uranium was found to be slightly enriched and Th highly enriched to depths of about 100 nm; the Th profile was interpreted in terms of a residual enrichment caused by the preferential release of the major glass constituents Al, Ca, and Na [Tait *et al.*, 1986].

4.2. Dissolution of Silicates

Lab studies. SIMS depth profiles of a titanite which had been leached at pH 4 for 28 days at 90°C showed that Ca and Fe were strongly depleted in relation to Si and Ti [Bancroft *et al.*, 1987]. On the same mineral leaching at pH 8 in solutions containing 400 mg/L Ca and saturated with respect to dissolved Si, no leached layers were observed; the lack of significant dissolution in these experiments was confirmed by inductively coupled plasma analyses of the leaching solutions. In long-term leaching experiments, SIMS depth profiles showed significant surface enrichments of Ca, Si, and Al, suggesting the regrowth of a phase approaching titanite in composition. SIMS depth profiles of rutile (TiO₂) leaching in solutions containing titanite showed that Ca, Si, Al, La, and U were actually enriched by up to 2 orders of magnitude in comparison to bulk values; these profiles confirmed that under appropriate conditions, not only does titanite not dissolve, it may actually grow. The titanites were also leached in D₂O, and D⁺ penetration followed using SIMS. The depth profiles showed that Ca depletion was restricted to the first 300 Å, whereas D penetrated at least 10 times as deep [Bancroft *et al.*, 1987].

In experimental studies of diopside dissolution in deionized water at 100°C and pH 5.5, Schott and Petit [1987] used both SIMS and NRA to follow the reaction. The SIMS depth profiles showed that Ca and Mg were depleted in relation to Fe and Si, and H enriched, from the surface of the mineral over distances of up to 2000 Å. The profiles were interpreted as having documented the formation of a hydrated silicate depleted in Mg and Ca, but enriched in Fe owing to the precipitation of ferric oxide on the surface.

Potassium feldspar leached at pH 1 from 25° to 200°C was analyzed using SIMS and a variety of other surface techniques [Goossens *et al.*, 1989]. The SIMS depth profiles revealed an amorphous surface layer up to 75 nm thick, depleted in Na, Al, and K (plus Rb, Cs, Sr, Ba), and enriched in H. The thickness of this residual layer was found to increase with increasing reaction time and increasing temperature. SEM and transmission electron microscopy images supported the view that the leached layer was a residual product of dissolution and not an amorphous precipitate.

Dissolving plagioclase feldspars: Muir *et al.* [1989] showed that the surface of labradorite feldspar leached

for 60 days in HCl at pH 3.5 was significantly depleted in Al and Ca in relation to Si, for approximately 600 s. Given the measured sputter rates of 1–2 Å/s, the results indicated a cation- and Al-depleted leached layer approximately 600–1200 Å thick. In contrast, leaching the feldspar in distilled water at pH 5.7 produced only very thin leached layers: Al was depleted for 60–120 Å, and Ca for 100–200 Å. Using XPS, Muir *et al.* [1989] provided independent confirmation that the surface of dissolving labradorite was also depleted in Na.

Cation- and Al-depleted leached layers on the surface of plagioclase feldspar dissolving at room temperature have since been reported in several studies (see Casey and Bunker [1991] for a review). The steps involved in the formation of these residual layers are thought to be [Casey *et al.*, 1989a, b] (1) penetration of water molecules (hydration), (2) protonation of cation-oxygen bonds near the surface of the mineral (the depth of penetration depends upon pH, reaction time, and temperature), (3) replacement of alkali and alkaline earth cations near the mineral surface by hydronium ions, (4) hydronium ion attack of Al in bridging Si-O-Al sites, thereby depolymerizing the surface, (5) diffusion of alkali, alkaline earth cations, and Al through the reacting surface layer, (6) partial repolymerization of remaining silanol groups in the silica-rich surface to produce Si-O-Si or Si-O-Al bonds, and (7) hydrolysis of the Si-O-Si bonds in the remaining siliceous surface layer. This last step is thought to control the overall rate of feldspar dissolution in acidic chloride solutions [Chou and Wollast, 1984, 1985; Wollast and Chou, 1985; Brady and Walther, 1989; Casey *et al.*, 1989a, b; Blum and Lasaga, 1991].

Effect of plagioclase composition: Albite, oligoclase, labradorite, and bytownite were leached in HCl at pH 3.5 for 90 days and depth profiled using the SIMS [Muir *et al.*, 1990]. In each case, significant leached layers were found in which the cations and Al are depleted in relation to Al over distances as great as 1600 Å. The thicknesses of the leached layers increased with increasing Al and decreasing Si content (i.e., increasing mole percent anorthite) as shown in Figure 12. The SIMS findings are consistent with kinetic studies which have shown that the reactivities of plagioclase feldspars in acidic solutions increase with increasing Al content [Blum and Lasaga, 1988; Brady and Walther, 1989].

The thickness of leached layers may vary significantly with small differences in plagioclase composition [Shotyk and Nesbitt, 1992]. For example, compare the leached layers formed on an An₅₄ labradorite versus an An₆₀ labradorite composition, both leached in HCl at pH 4.0 (Figure 13). The leached layer formed on the more calcic labradorite composition is about 5 times thicker than that formed on the more sodic composition. Once again, these results are consistent with recent kinetic studies which have shown that the rates of dissolution of the calcic plagioclases are very

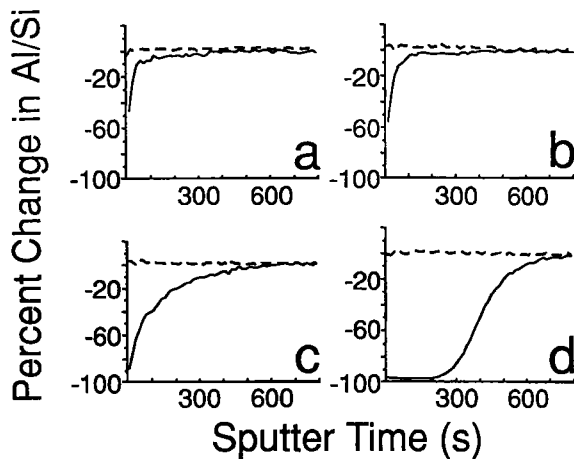


Figure 12. Percentage change in Al/Si of four plagioclase feldspar compositions leached for 90 days in HCl at pH 3.5: (a) albite, (b) oligoclase, (c) labradorite, (d) bytownite. (After Muir *et al.* [1990].)

sensitive to small differences in chemical composition. For example, Casey *et al.* [1991] found that the rates of dissolution of labradorite (An_{60}) and bytownite (An_{76}) were 14 and $212 \times 10^{-15} \text{ mol Si cm}^{-2} \text{ s}^{-1}$, respectively.

Effect of dissolved salts: The effect of dissolved salts (Na, K, Ca, Al, and Si) on the formation of leached layers on the surface of labradorite feldspar has been evaluated in a series of simple experiments [Nesbitt *et al.*, 1991]. The experimental conditions selected for study are shown in Table 3. Leached layers up to 1500 Å thick developed on labradorite (An_{54}) dissolving in 10^{-4} M HCl at pH 4 (Figure 14). In solutions at the same pH containing 1 mg/L Na, K, and Ca, the leached layers formed after the same period of dissolution were about one half as thick (about 700 Å) as those formed in HCl alone. In solutions at pH 4 containing these cations and also 0.01 mg/L Al, a leached layer formed which was indistinguishable from the second case (about 700 Å). In other words, adding 0.01 mg/L Al had no significant effect on leached layer formation at pH 4 in comparison to the combined effect of 1 mg/L Na, K, and Ca. In solutions containing these cations plus 1 mg/L Al, no significant leached layer formed (Figure 14). In the solution at pH 4 containing 1 mg/L Na, K, Ca, and Al, therefore, the labradorite dissolved congruently.

In the experiment consisting only of 10^{-4} M HCl, there were no significant concentrations of cations other than H^+ . The hydronium ion, therefore, accounted for 100% of the total cationic charge of the solution (Table 3). In the next experiment (HCl plus Na, K, Ca), the addition of other cations reduced the contribution of H^+ to total cationic charge to 45% (Table 3). In the experiment containing HCl, Na, K, Ca, plus 0.01 mg/L Al, the addition of Al did not significantly reduce the contribution of H^+ to the total cationic charge in comparison to the solution containing Na, K, and Ca. In the last two experiments (HCl

plus Na, K, Ca, and 1 mg/L Al, with either 1 or 0.1 mg/L Si), the contribution of H^+ to the total cationic charge was reduced to approximately 30% (Table 3). As the relative importance of H^+ in the bulk solution decreased, so too did the thickness of the residual surface layer.

The SIMS depth profiles support kinetic studies which have demonstrated the inhibiting effect of dissolved salts on feldspar dissolution rates [Sjöberg, 1989]. The rate of dissolution of oxides and silicates is proportional to the surface concentration of H^+ [Blum and Lasaga, 1991; Casey *et al.*, 1992]. The presence of cations other than H^+ in the bulk solution results in additional adsorption equilibria which compete with H^+ for surface sites [Stumm and Wollast, 1990]. Adding Si to the solutions (Table 3) had no significant effect on leached layer formation (Figure 14) because aqueous silica does not compete with H^+ and the other cations for surface sites.

Effect of complex-forming ligands: SIMS analyses showed that labradorite (An_{54} and An_{60}) leached at pH 4 for 72 days dissolved incongruently both in 10^{-4} M oxalic acid and in 10^{-4} M HF, yielding altered layers

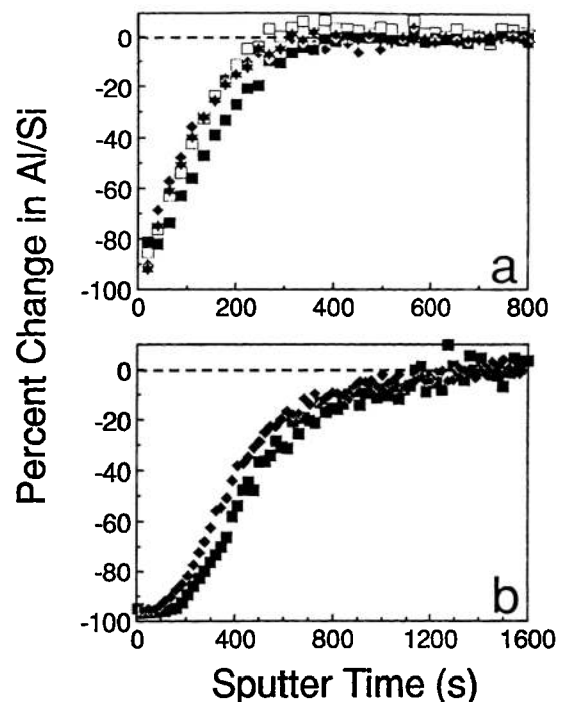


Figure 13. (a) Percent change in Al/Si of labradorite (An_{54}) leached for 72 days in HCl. Four spots on the surface of the sample were depth profiled. Given that the sputtering rate was approximately 2 Å/s , an Al-depleted leached layer approximately 800 Å thick has formed on the surface of the dissolving feldspar. (b) Percent change in Al/Si of labradorite (An_{60}) leached for 72 days in HCl at pH 4. Two spots on the mineral surface were depth profiled. Here, Al is depleted in relation to Si for 1500 s, corresponding to a leached layer approximately 3000 Å thick. From Shotyk and Nesbitt [1992]. (Reprinted with permission.)

TABLE 3. Dissolved Solids Concentrations and Distribution of Cationic Charge in Labradorite (An_{54}) Leaching Experiments in HCl at pH 4 [Nesbitt et al., 1991]

Species	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
	Concentration, mg/L	Percent of Cationic Charge	Concentration, mg/L	Percent of Cationic Charge	Concentration, mg/L	Percent of Cationic Charge	Concentration, mg/L	Percent of Cationic Charge
H ⁺	...	45.7	...	45.4	...	30.3	...	30.3
Na ⁺	1.0	19.9	1.0	19.8	1.0	13.2	1.0	13.2
K ⁺	1.0	11.7	1.0	11.6	1.0	7.8	1.0	7.7
Ca ²⁺	1.0	22.8	1.0	22.7	1.0	15.1	1.0	15.1
Al _T	...	0.0	0.01	0.5	1.0	33.6	1.0	33.6
Si _T	...	0.0	1.0	0.0	1.0	0.0	0.1	0.0

strongly depleted in Al and Ca and residually enriched in Si. The thickest leached layers were produced by HF (up to 1700 Å on An_{54} and up to 5000 Å on An_{60}). Because the H⁺ concentration was the same in each solution (10^{-4} M), it was possible to clearly separate the relative importance of proton-promoted dissolution (in HCl) and ligand-promoted dissolution (in oxalic acid and in HF) for a given feldspar composition. To do this, the SIMS

depth profiles obtained from An_{60} labradorite leached in oxalic acid and in HF were normalized to those produced in response to HCl. This comparison clearly shows that the ligands oxalate and fluoride significantly increased the formation of leached layers in comparison to the effect of H⁺ alone (Figure 15).

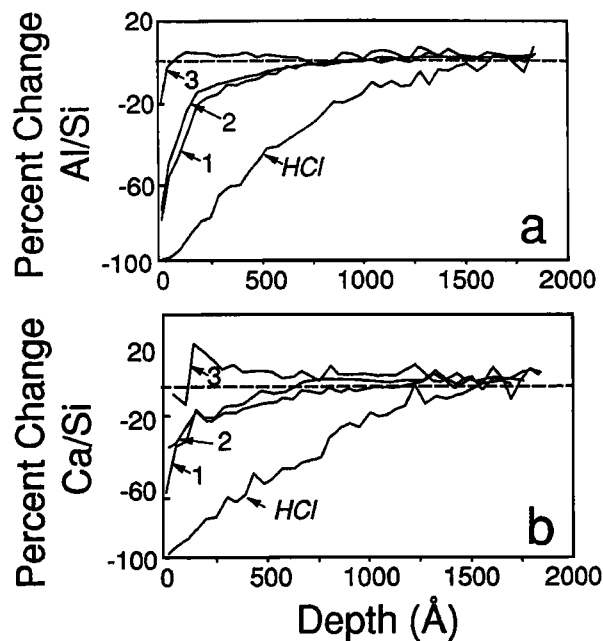


Figure 14. Percentage change in (a) Al/Si and (b) Ca/Si of labradorite (An_{54}) leached in HCl at pH 4 with varying concentrations of dissolved salts. The composition of each solution is shown in Table 3. The thickness of the leached layer formed in the solution containing Na, K, and Ca (experiment 1) is about one half that formed in HCl, even though the pH is the same in each case. The addition of 1 mg/L Si and 0.01 mg/L Al to the solution containing the cations has no effect (experiment 2), in comparison to the cations alone. In solutions containing the cations plus 1 mg/L Al, no significant leached layer is found (experiment 3). With 1 mg/L Al plus each of the cations, increasing Si from 0.1 to 1 mg/L had no effect on leached layer thickness. (After Nesbitt et al. [1991].)

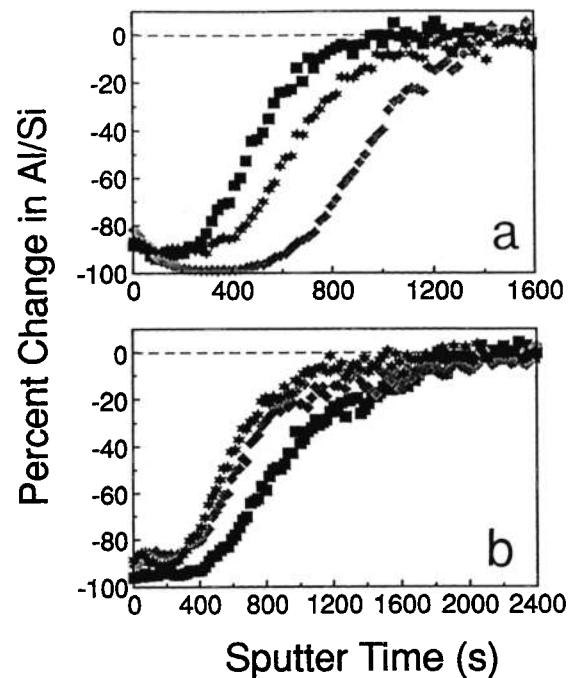


Figure 15. (a) Percent change in Al/Si of labradorite (An_{60}) leached in oxalic acid, normalized to labradorite leached in HCl. The pH and acid concentrations were the same in each solution, allowing the effects of proton-promoted and ligand-promoted dissolution to be clearly separated. The leached layer shown here has formed in response to the oxalate ligand. The differences between the three depth profiles probably reflect chemical zonation in the mineral. (b) Percent change in Al/Si of labradorite (An_{60}) leached in HF, normalized to labradorite leached in HCl. Again, the pH and acid concentrations were the same in each solution, allowing the effects of proton-promoted and ligand-promoted dissolution to be separated. The extent of leaching shown here can be attributed to the fluoride ligand. (From Shotyk and Nesbitt [1992]. Reprinted with permission.)

The three spots which were depth profiled show approximately the same depth of leaching, but clearly differ in respect to the extent of surface attack (Figure 15). These differences in extent of leaching within a sample are attributed to zoning, which is commonly observed within feldspar crystals [Barth, 1969]. The less extensive dissolution probably corresponds to more sodic zones within the crystal, and the more extensively dissolved areas to more calcic zones. *Inskip et al.* [1991] have observed similar variation in leached layer thicknesses on the surface of labradorite leached in acidic solutions. They reported leached layers up to 700 Å in the sodic zones of labradorite, compared to 1400 Å in the leached layers of the calcic zones.

In contrast to the two labradorite compositions, anorthite leached in HCl showed much thinner leached layers, even though it is a more reactive composition. Also, no significant leached layers were observed on anorthite leached in oxalic acid and in HF (Figure 16). Significantly higher concentrations of Si and Al were found in the oxalic acid and HF leaching solutions in comparison to anorthite in HCl, indicating a more extensive dissolution of the solid phase. However, in each case the molar ratio of Si to Al in the solutions reflected the molar proportion of Si to Al in the fresh solid. In other words, in each of these experiments, dissolution of the anorthite was essentially congruent [Shotyk and Nesbitt, 1992].

These findings may help to explain why *Mast and Drever* [1987] found that 1-mM oxalic acid had no effect on the overall rate of dissolution of oligoclase feldspar (An_{13}) while *Amrhein and Suarez* [1988] reported an accelerated rate of anorthite (An_{93}) dissolution in the presence of similar concentrations of oxalic acid. The effect of complex-forming organic ligands on the overall rate of plagioclase feldspar dissolution, as measured by the rate of release of Si, depends strongly upon the molar proportions of Al and Si in the solid. Promotion of rates of feldspar dissolution by organic ligands is favored by a relatively large ratio of Al to Si (e.g., 1:1 as in the case of the anorthite endmember).

Field studies. Samples of naturally weathered oligoclase from a soil profile weathering for 10,000 years have been depth profiled using the SIMS [Nesbitt and Muir, 1988]. Naturally weathered faces of the feldspar were depth profiled and compared with freshly cut surfaces. The freshly cut oligoclase surface revealed no significant difference in Si, Al, and Ca ion intensities with depth through the surface of the mineral. In contrast, the depth profiles of nine naturally weathered plagioclase grains all showed that Si was strongly depleted in relation to Al over a distance of up to 1000 Å (Figure 17). At the same time, however, the SIMS depth profiles clearly showed that Ca in the weathered grains was not depleted in relation to Al [Nesbitt and Muir, 1988; Muir, 1989]. Although the authors concluded that naturally weathered plagioclase feldspars

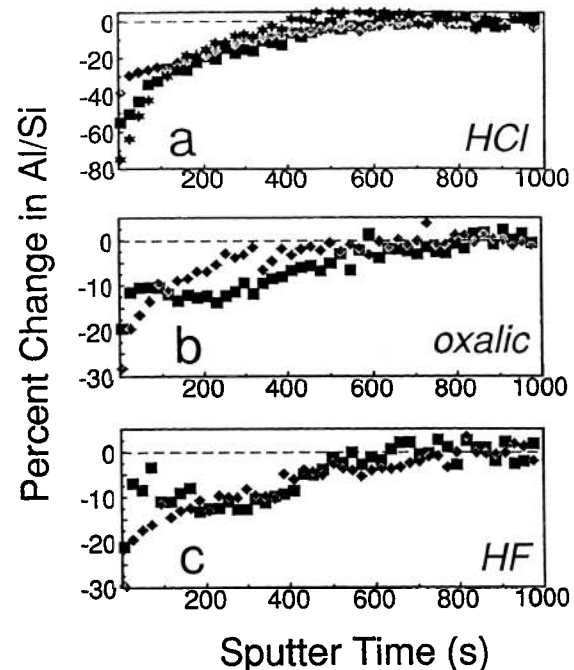


Figure 16. (a) Percent change in Al/Si of anorthite (An_{100}) leached in HCl at pH 4 for 72 days. This leached layer is significantly thinner than that of the An_{60} labradorite composition shown in Figure 12. However, the measured concentrations of Al and Si in the output solutions confirmed that the anorthite was dissolving more rapidly than the labradorite. (b) Percent change in Al/Si of anorthite leached in oxalic acid at the same pH. Although the percent change in Al relative to Si is less than that produced in HCl, the concentrations of Al and Si in the oxalic acid output solutions are significantly higher than in the HCl, confirming that oxalic acid has enhanced the dissolution of anorthite, in comparison to HCl at the same pH. (c) Percent change in Al/Si of anorthite leached in HF. Again, even though the leached layer produced by HF is smaller than the slight layer produced in response to HCl, the concentrations of Al and Si in the HF output solutions are significantly greater than in HCl at the same pH. (From *Shotyk and Nesbitt* [1992]. Reprinted with permission.)

dissolve incongruently, with Si being leached out of the mineral preferentially over Al, they failed to explain how Si could have been removed without also removing Ca.

In contrast to the naturally weathered oligoclase, all of the feldspars leached in acidic solutions in experimental laboratory studies show altered layers in which Al is depleted in relation to Si [Casey et al., 1988, 1989a, b; Goossens et al., 1989; Muir et al., 1989, 1990; Hellmann et al., 1990; Nesbitt et al., 1991; Muir and Nesbitt, 1991, 1992; Shotyk and Nesbitt, 1992]. The main difference between the natural weathering environment and all of the laboratory studies is the pH and composition of the solution in the till which leached the feldspar for thousands of years. Although no pH or solution chemical information is given in the original paper [Nesbitt and Muir, 1988], if the pH of

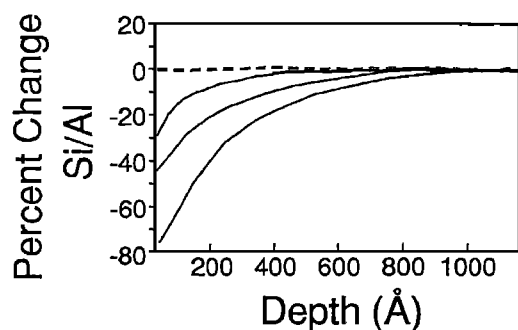


Figure 17. Percent change in the ratio Si/Al versus depth of naturally weathered plagioclase grains. The dashed curve corresponds to a fresh (unweathered) oligoclase and the other curves correspond to three weathered grains. The low ^{28}Si secondary ion intensities in relation to ^{27}Al in the raw SIMS depth profiles were interpreted as evidence of preferential removal of Si in comparison to Al from the surface of the feldspar by natural weathering solutions. The calculated Si/Al ratios emphasize this change. (From Nesbitt and Muir [1988]. Reprinted with permission.)

the soil solution at the base of the profile was sufficiently close to the neutral $p\text{H}$ range, perhaps Si could have been released preferentially over Al as lab experiments have shown [von Engelhardt, 1939; Schweda, 1989]; however, this could not account for the Ca depth profile. A second possibility is that the presence of dissolved cations and Al in the leaching solution, combined with a near-neutral $p\text{H}$, allowed Si to be removed preferentially over Al as feldspars dissolving in salt solutions [Nesbitt *et al.*, 1991]. Again, this probably would not explain the Ca depth profile.

Perhaps the SIMS depth profiles simply indicated an aluminous precipitate covering the feldspar surface. Aluminous coatings have been found on the surface of naturally weathered minerals from soils, including hornblende [Mogk and Locke, 1988] and oligoclase [Inskeep *et al.*, 1993]. Given that the fundamental process of podzolization is the chemical separation of Fe and Al from Si in upper soil layers and the precipitation of amorphous Fe and Al phases further down in the profile, this latter possibility seems the most likely. Unfortunately, there appear to be no other published SIMS studies of naturally weathered minerals from soils for comparison.

5. SUMMARY AND CONCLUSIONS

SIMS is extremely surface sensitive and allows chemical and isotopic analyses of elements ranging from H to U. Using the specimen isolation method to reduce surface charging, SIMS is ideally suited to depth profiling glasses and minerals. With sputtering rates of the order of 1 \AA/s , SIMS depth profiles have been used successfully to illustrate chemical changes that take place at the solid-solution interface during the dissolution of glasses and minerals.

SIMS depth profiles of dissolving glasses and silicates illustrate the complexity of the dissolution process. The behavior of dissolving plagioclase feldspar, for example, is very sensitive to both the composition of the mineral and the leaching solution. Small differences in mineral composition may give rise to large differences in rates of dissolution and thickness of leached layers. The presence of relatively low concentrations of dissolved salts may greatly influence both the rate and the mechanism of dissolution. Simple, complex-forming organic ligands may promote the release of Al in acidic solutions, but this may or may not affect the overall rate of feldspar dissolution, depending on the mole percent anorthite.

Many questions remain concerning rates and mechanisms of mineral weathering in soils and sediments. The effect of organic acids on silicate dissolution, for example, requires systematic study to clearly separate the effects of simple and complex organic acids as ligands versus reducing agents. The combined effect of complex-forming organic ligands and dissolved salts on the formation of leached layers and dissolution rates has not yet been investigated. There is a need for more detailed experimental studies of the rates and mechanisms of dissolution in systems more closely resembling natural weathering solutions, using representative conditions of mineral composition, temperature, $p\text{H}$, and solution composition. Such experiments should include analyses of output leaching solutions, as has been done traditionally, but should also include surface analyses of the dissolving solid using a method such as the SIMS. Given the potential of the SIMS to help us understand processes at the mineral-water interface, there is also a great need to do much more work with reacted surfaces of naturally leached minerals from soils.

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REFERENCES

- Aagaard, P., and H. C. Helgeson, Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, I, Theoretical considerations, *Am. J. Sci.*, 282, 237–285, 1982.

- Amrhein, C., and D. L. Suarez, The use of a surface complexation model to describe the kinetics of ligand-promoted dissolution of anorthite, *Geochim. Cosmochim. Acta*, 52, 2785–2793, 1988.
- Andersson, L.-H., and B. Lindqvist, Some experiments on the interaction between feldspars and salt solutions, *Geol. Foeren. Stockholm Foerh.*, 78, 459–462, 1956.
- André, G., Déplacement de la potasse contenue dans certaines roches feldspathiques par quelques substances employées comme engrais, *C. R. Hebd. Seances Acad. Sci.*, 157, 856–858, 1913.
- Antweiler, R. C., and J. I. Drever, The weathering of a late Tertiary volcanic ash: Importance of organic solutes, *Geochim. Cosmochim. Acta*, 47, 623–629, 1983.
- April, R., R. Newton, and L. Truettner Coles, Chemical weathering in two Adirondack watersheds: Past and present-day rates, *Geol. Soc. Am. Bull.*, 97, 1232–1238, 1986.
- Arehart, G. B., C. S. Eldridge, S. L. Chryssoulis, and S. E. Kesler, Ion microprobe determination of sulfur isotope variations in iron sulfides from the Post/Betze sediment-hosted disseminated gold deposit, Nevada, USA, *Geochim. Cosmochim. Acta*, 57, 1505–1519, 1993.
- Bancroft, G. M., J. B. Metson, R. A. Kresovic, and H. W. Nesbitt, Leaching studies of natural and synthetic titanites using secondary ion mass spectrometry, *Geochim. Cosmochim. Acta*, 51, 911–918, 1987.
- Barth, T. F. W., *Feldspars*, Wiley-Interscience, New York, 1969.
- Bear, F. E., *Chemistry of the Soil*, 2nd ed., Reinhold, New York, 1964.
- Benninghoven, A., F. G. Rudenauer, and H. W. Werner, *Secondary Ion Mass Spectrometry*, John Wiley, New York, 1987.
- Berner, E. K., and R. A. Berner, *The Global Water Cycle: Geochemistry and Environment*, Prentice-Hall, Englewood Cliffs, N. J., 1987.
- Berner, R. A., and G. R. Holdren, Jr., Mechanism of feldspar weathering: Some observational evidence, *Geology*, 5, 369–372, 1977.
- Berner, R. A., and G. R. Holdren, Jr., Mechanism of feldspar weathering, II, Observations of feldspars from soils, *Geochim. Cosmochim. Acta*, 43, 1173–1186, 1979.
- Berner, R. A., G. R. Holdren, Jr., and J. Schott, Surface layers on dissolving silicates: Comments on "Study of the weathering of albite at room temperature and pressure with a fluidized bed reactor" by L. Chou and R. Wollast, *Geochim. Cosmochim. Acta*, 49, 1657–1658, 1985.
- Betz, G., and F. G. Rudenauer, Collision cascade limit to spatial resolution in focused ion beam processes, *Appl. Surf. Sci.*, 51, 103–112, 1991.
- Beyer, A., Ueber die Zersetzung des Feldspathes unter dem Einfluss von Salzlösungen und einigen anderen Agentien, *Landwirtsch. Vers. Stn.*, 14, 314–322, 1871.
- Blaser, P., Mechanismen der Eisenaufnahme und -verlagerung durch wasserlösliche Streusubstanzen in podsoligen Boden, *Mitt. Dtsch. Bodenk. Ges.*, 20, 447–457, 1974.
- Blaser, P., H. Flüher, and T. Sidler, Rückkoppelungsmechanismen beim Stofftransport: Verlagerung von Fe(III) durch wasserlösliche Streusubstanzen, *Mitt. Dtsch. Bodenk. Ges.*, 30, 111–122, 1981.
- Blum, A., and A. Lasaga, Role of surface speciation in the low-temperature dissolution of minerals, *Nature*, 331, 431–433, 1988.
- Blum, A. E., and A. C. Lasaga, The role of surface speciation in the dissolution of albite, *Geochim. Cosmochim. Acta*, 55, 2193–2201, 1991.
- Bottazzi, P., L. Ottolini, and R. Vannucci, Determination of rare earth elements in sixteen silicate reference samples by secondary ion mass spectrometry using conventional energy filtering technique, *Geostand. Newsl.*, 15, 51–57, 1991.
- Bottazzi, P., L. Ottolini, and R. Vannucci, SIMS analyses for rare earth elements in natural minerals and glasses: An investigation of structural matrix effects on ion yields, *Scanning*, 14, 160–168, 1992.
- Brady, P. V., and J. V. Walther, Controls on silicate dissolution rates in neutral and basic pH solutions at 25 C, *Geochim. Cosmochim. Acta*, 53, 2823–2830, 1989.
- Brantley, S. L., Kinetics of dissolution and precipitation—Experimental and field results, in *Water-Rock Interaction*, edited by Y. K. Kharaka and A. S. Maest, pp. 3–6, A. A. Balkema, Rotterdam, Netherlands, 1992.
- Brongniart, A., De la cavité veineuse et de ses poches accessoires: Sur le nautille flambé, *Arch. Mus. Hist. Nat. Paris*, 2, 285–314, 1841.
- Brookins, D. G., *Geochemical Aspects of Radioactive Waste Disposal*, Springer-Verlag, New York, 1984.
- Brown, A. D., and L. J. Lund, Kinetics of weathering in soils from a subalpine watershed, *Soil Sci. Soc. Am. J.*, 55, 1767–1773, 1991.
- Busenberg, E., The products of the interaction of feldspars with aqueous solutions at 25 C, *Geochim. Cosmochim. Acta*, 42, 1679–1686, 1978.
- Busenberg, E., and C. V. Clemency, The dissolution kinetics of feldspars at 25 C and 1 atm CO₂ partial pressure, *Geochim. Cosmochim. Acta*, 40, 41–49, 1976.
- Carroll, D., *Rock Weathering*, Plenum, New York, 1970.
- Casey, W. H., and B. Bunker, The leaching of mineral and glass surfaces during dissolution, in *Mineral-Water Interface Geochemistry*, *Rev. Mineral.*, 23, 397–426, 1991.
- Casey, W. H., H. R. Westrich, and G. W. Arnold, Surface chemistry of labradorite feldspar reacted with aqueous solutions at pH = 2, 3, and 12, *Geochim. Cosmochim. Acta*, 52, 2795–2807, 1988.
- Casey, W. H., H. R. Westrich, G. W. Arnold, and J. F. Banfield, The surface chemistry of dissolving labradorite feldspar, *Geochim. Cosmochim. Acta*, 53, 821–832, 1989a.
- Casey, W. H., H. R. Westrich, T. Massis, J. F. Banfield, and G. W. Arnold, The surface of labradorite feldspar after acid hydrolysis, *Chem. Geol.*, 78, 205–218, 1989b.
- Casey, W. H., H. R. Westrich, and G. R. Holdren, Jr., Dissolution rates of plagioclase at pH = 2 and 3, *Am. Mineral.*, 76, 211–217, 1991.
- Casey, W. H., C. Eggleston, P. A. Johnsson, H. R. Westrich, and M. F. Hochella, Jr., Aqueous surface chemistry and corrosion of minerals, *MRS Bull.*, 17(5), 23–29, 1992.
- Casey, W. H., J. F. Banfield, H. R. Westrich, and L. McLaughlin, What do dissolution experiments tell us about natural weathering?, *Chem. Geol.*, 105, 1–15, 1993.
- Chesworth, W., Weathering systems, in *Weathering, Soils, and Palaeosols*, edited by I. P. Martini and W. Chesworth, pp. 19–40, Elsevier, New York, 1992.
- Chin, P.-K. F., and G. L. Mills, Kinetics and mechanisms of kaolinite dissolution: Effects of organic ligands, *Chem. Geol.*, 90, 307–317, 1991.
- Chou, L., and R. Wollast, Study of the weathering of albite at room temperature and pressure with a fluidized bed reactor, *Geochim. Cosmochim. Acta*, 48, 2205–2217, 1984.
- Chou, L., and R. Wollast, Steady-state kinetics and dissolution mechanism of albite, *Am. J. Sci.*, 285, 963–993, 1985.
- Chryssoulis, S. L., Quantitative trace precious metal analysis of sulfide and sulfarsenide minerals by SIMS, in *Sec-*

- ondary Ion Mass Spectrometry, SIMS 7*, edited by A. Benninghoven, pp. 405–408, John Wiley, New York, 1990.
- Colman, S. M., and D. P. Dethier (Eds.), *Rates of Chemical Weathering of Rocks and Minerals*, Academic, San Diego, Calif., 1986.
- Correns, C. W., Die chemische Verwitterung der Silikate, *Naturwissenschaften*, 28, 369–376, 1940.
- Correns, C. W., The experimental chemical weathering of silicates, *Clay Miner. Bull.*, 26(4), 249–265, 1962a.
- Correns, C. W., Ueber die chemische Verwitterung von Feldspaten, *Nor. Geol. Tidsskr.*, 42, 272–282, 1962b.
- Correns, C. W., and W. von Engelhardt, Neue Untersuchungen über die Verwitterung des Kalifeldspates, *Naturwissenschaften*, 26, 137–138, 1938a.
- Correns, C. W., and W. von Engelhardt, Neue Untersuchungen über die Verwitterung des Kalifeldspates, *Chem. Erde*, 12, 1–22, 1938b.
- Crozaz, G., and E. Zinner, Quantitative ion microprobe analysis for the rare earth elements in minerals, *Scanning Electron Microsc.*, no. II, 369–376, 1986.
- Cushman, A. S., A study of rock decomposition under the action of water, *Circ.* 38, 10 pp., Off. of Public Roads, U.S. Dep. of Agric., Washington, D. C., 1905a.
- Cushman, A. S., The effect of water on rock powders, *Bull.* 92, 24 pp., Bur. of Chem., Washington, D. C., 1905b.
- Cushman, A. S., Rock decomposition and clay formation in the laboratory, *Trans. Am. Ceram. Soc.*, 8, 180–197, 1907.
- Cushman, A. S., and P. Hubbard, The decomposition of feldspars, *Bull.* 28, 29 pp., Off. of Public Roads, U.S. Dep. of Agric., Washington, D. C., 1907.
- Cushman, A. S., and P. Hubbard, The extraction of potash from feldspathic rock, *Am. Chem. Soc. J.*, 30, 779–797, 1908.
- Daubrée, A., *Etudes Synthétiques de Géologie Expérimentale*, Dunod, Paris, 1879.
- Dana, S. L., *A Muck Manual for Farmers*, 4th ed., A. O. Moore, New York, 1858.
- Davy, H., *Elements of Agricultural Chemistry*, 1st American ed., Eastburn, Kirk and Co., New York, and Ward and Lily, Boston, Mass., 1815.
- Della Mea, G., J.-C. Dran, J.-C. Petit, G. Bezzon, and C. Rossi-Alvarez, Use of ion beam techniques for studying the leaching properties of lead-implanted silicates, *Nucl. Instrum. Methods Phys. Res.*, 218, 493–499, 1983.
- Diamond, L. W., D. D. Marshall, J. A. Jackman, and G. B. Skippen, Elemental analysis of individual fluid inclusions in minerals by secondary ion mass spectrometry, *Geochim. Cosmochim. Acta*, 54, 545–555, 1990.
- Drever, J. I. (Ed.), The chemistry of weathering, *NATO ASI Ser., Ser. C*, Mathematical 149D, 1985.
- Drever, J. I., *The Geochemistry of Natural Waters*, 2nd ed., Prentice-Hall, Englewood Cliffs, N. J., 1988.
- Drever, J. I., and N. Swoboda-Colberg, Mineral weathering rates in acid-sensitive catchments: Extrapolation of laboratory experiments to the field, in *Water-Rock Interaction*, edited by D. L. Miles, pp. 211–214, A. A. Balkema, Rotterdam, Netherlands, 1989.
- Driscoll, C. T., N. van Breemen, and J. Mulder, Aluminum chemistry in a forested Spodosol, *Soil Sci. Soc. Am. J.*, 49, 437–443, 1985.
- Fleer, V. N., The dissolution kinetics of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and synthetic strontium feldspar ($\text{SrAl}_2\text{Si}_2\text{O}_8$) in aqueous solutions at temperatures below 100 °C: With applications to the geological disposal of radioactive nuclear wastes, Ph.D. thesis, Penn. State Univ., University Park, 1982.
- Fung, P. C., and G. G. Sanipelli, Surface studies of feldspar dissolution using surface replication combined with electron microscopic and spectroscopic techniques, *Geochim. Cosmochim. Acta*, 46, 503–512, 1982.
- Furrer, G., and W. Stumm, The coordination chemistry of weathering, I, Dissolution kinetics of $\delta\text{-Al}_2\text{O}_3$ and BeO , *Geochim. Cosmochim. Acta*, 50, 1847–1860, 1986.
- Gijbels, R., Determination of lanthanides and of uranium and thorium in geological samples, *Inorg. Chim. Acta*, 140, 215–230, 1987.
- Goldich, S. S., A study in rock-weathering, *J. Geol.*, 46, 17–58, 1938.
- Goossens, D. A., J. G. Philippaerts, R. Gijbels, A. P. Pijpers, S. Van Tendeloo, and E. Althaus, A SIMS, XPS, SEM, TEM, and FTIR study of feldspar surfaces after reacting with acid solutions, in *Water-Rock Interaction*, edited by D. L. Miles, pp. 271–274, A. A. Balkema, Rotterdam, Netherlands, 1989.
- Gossink, G. G., Application of secondary ion mass spectrometry (SIMS) to glass surface problems, *Glass Technol.*, 21, 125–133, 1980.
- Gossink, R. G., H. A. M. de Grefte, and H. W. Werner, SIMS analysis of aqueous corrosion profiles in soda-lime-silica glass, *J. Am. Ceram. Soc.*, 62, 4–9, 1979.
- Grant, W. H., Weathering of Stone Mountain granite, *Clays Clay Miner. Proc. Conf.*, 11, 65–73, 1963.
- Harnois, L., The CIW index: A new chemical index of weathering, *Sediment. Geol.*, 55, 319–322, 1988.
- Havette, A., Mineralogical application of the ion microscope elementary analysis, *Scanning Electron Microsc.*, no. II, 585–594, 1985.
- Hayward, P. J., W. H. Hocking, S. L. Mitchell, and M. A. Stanchell, Leaching studies of sphene-based glass-ceramics, *Nucl. Chem. Waste Manage.*, 5, 27–37, 1984.
- Helgeson, H. C., V. M. Murphy, and P. Aagaard, Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, II, Rate constants, effective surface area and the hydrolysis of feldspar, *Geochim. Cosmochim. Acta*, 48, 2405–2432, 1984.
- Hellmann, R., C. M. Eggleston, M. F. Hochella, Jr., and D. A. Crerar, The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions, *Geochim. Cosmochim. Acta*, 54, 1267–1281, 1990.
- Hervig, R. L., Oxygen isotope analysis using extreme energy filtering, *Chem. Geol.*, 101, 185–186, 1992.
- Hervig, R. L., and P. Williams, SIMS microanalysis of minerals and glasses for hydrogen and deuterium, in *Secondary Ion Mass Spectrometry, SIMS 6*, edited by A. Benninghoven, A. M. Huber, and H. W. Werner, pp. 961–964, John Wiley, New York, 1988.
- Hervig, R. L., P. Williams, R. M. Thomas, S. N. Schauer, and I. M. Steele, Microanalysis for oxygen isotopes in insulators by secondary ion mass spectrometry, *Int. J. Mass Spectrom. Ion Processes*, 120, 45–63, 1992.
- Hochella, M. F., Jr., Auger electron and X-ray photoelectron spectroscopies, in *Spectroscopic Methods in Mineralogy and Geology, Rev. Mineral.*, 18, 573–637, 1988.
- Hochella, M. F., Jr., and A. F. White, (Eds.), Mineral-water interface geochemistry, *Rev. Mineral.*, 23, 1990.
- Hochella, M. F., Jr., H. B. Ponader, A. M. Turner, and D. W. Harris, The complexity of mineral dissolution as viewed by high resolution scanning Auger microscopy: Labradorite under hydrothermal conditions, *Geochim. Cosmochim. Acta*, 52, 385–394, 1988.
- Holdren, G. R., Jr., and R. A. Berner, Mechanism of feldspar weathering, I, Experimental studies, *Geochim. Cosmochim. Acta*, 43, 1161–1171, 1979.
- Holdren, G. R., Jr., and P. M. Speyer, Reaction rate–surface area relationships during the early stages of weathering, I,

- Initial observations, *Geochim. Cosmochim. Acta*, 49, 675–681, 1985.
- Home, F., *The Principles of Agriculture and Vegetation*, 3rd ed., A. Kincaid and J. Bell, Edinburgh, 1762.
- Hue, N. V., G. R. Craddock, and F. Adams, Effect of organic acids on aluminum toxicity in subsoils, *Soil Sci. Soc. Am. J.*, 50, 28–34, 1986.
- Inskeep, W. P., E. A. Nater, P. R. Bloom, D. S. Vandervoort, and M. S. Erich, Characterization of laboratory weathered labradorite surfaces using X-ray photoelectron spectroscopy and transmission electron microscopy, *Geochim. Cosmochim. Acta*, 55, 787–800, 1991.
- Inskeep, W. P., J. L. Clayton, and D. W. Mogk, Naturally weathered plagioclase grains from the Idaho Batholith: Observations using scanning electron microscopy, *Soil Sci. Soc. Am. J.*, 57, 851–860, 1993.
- Jackson, M. L., and G. D. Sherman, Chemical weathering of minerals in soils, *Adv. Agron.*, 5, 221–317, 1953.
- Jackson, M. L., S. A. Tyler, A. L. Willis, G. A. Bourbeau, and R. P. Pennington, Weathering sequence of clay-size minerals in soils and sediments, I, Fundamental generalizations, *J. Phys. Colloid Chem.*, 52, 1237–1260, 1948.
- Jenny, H., *Factors of Soil Formation*, McGraw-Hill, New York, 1941.
- Johnson, N. M., G. E. Lickens, F. H. Bormann, and R. S. Pierce, Rate of chemical weathering of silicate minerals in New Hampshire, *Geochim. Cosmochim. Acta*, 32, 531–545, 1968.
- Johnston, J. F. W., *Lectures on the Applications of Chemistry and Geology to Agriculture*, Wiley and Putnam, New York, 1847.
- Julien, A. A., On the geological action of the humus acids, *Proc. Am. Assoc. Adv. Sci.*, 28, 311–410, 1879.
- Katz, B. G., O. P. Bricker, and M. M. Kennedy, Geochemical mass-balance relationships for selected ions in precipitation and stream water, Catoctin Mountains, Maryland, *Am. J. Sci.*, 285, 931–962, 1985.
- Kirkwood, D. E., and H. W. Nesbitt, Formation and evolution of soils from an acidified watershed: Plastic Lake, Ontario, Canada, *Geochim. Cosmochim. Acta*, 55, 1295–1308, 1991.
- Kittrick, J. A. (Ed.), *Soil Mineral Weathering*, Van Nostrand Reinhold, New York, 1986.
- Lacharme, J.-P., and P. Lehuède, Interpretation of analyses of silicate glasses and minerals obtained by secondary-ion mass spectrometry, *J. Am. Ceram. Soc.*, 68, C134–C135, 1985.
- Lau, W. M., N. S. McIntyre, J. B. Metson, D. Cochrane, and J. D. Brown, Stabilization of charge on electrically insulating surfaces—Experimental and theoretical studies of the specimen isolation method, *SIA Surf. Interface Anal.*, 7, 275–281, 1985.
- Liebig, J., *Chemistry in Its Applications to Agriculture and Physiology*, 3rd English ed., Taylor and Walton, London, 1843.
- Lindsay, N. M., and J. P. F. Sellschop, Routine SIMS microanalysis: Trace gold and platinum in sulfides, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 35, 358–363, 1988.
- Linton, R. W., and J. G. Goldsmith, The role of secondary ion mass spectrometry (SIMS) in biological microanalysis: Technique comparisons and prospects, *Biol. Cell.*, 74, 147–160, 1992.
- Litaor, M. I., Aluminum chemistry: Fractionation, separation, and mineral equilibria of soil interstitial waters of an alpine watershed, Front Range, Colorado, *Geochim. Cosmochim. Acta*, 51, 1285–1295, 1987.
- Lodding, A., H. Odelius, D. E. Clark, and L. O. Werme, Element profiling by secondary ion mass spectrometry of surface layers in glasses, *Mikrochim. Acta Suppl.*, 11, 145–161, 1985.
- Lodding, A. R., P. M. Fischer, H. Odelius, J. G. Noren, L. Sennerby, C. B. Johansson, J. M. Chabala, and R. Levi-Setti, Secondary ion mass spectrometry in the study of biomineralizations and biomaterials, *Anal. Chim. Acta*, 241, 299–314, 1990.
- Lorin, J. C., Oxygen isotope analysis on the Cameca ims-300, *Chem. Geol.*, 101, 193–195, 1992.
- Lorin, J. C., G. Slodzian, R. Dennebouy, and M. Chain-treau, SIMS measurement of oxygen isotope-ratios in meteorites and primitive solar system matter, in *Secondary Ion Mass Spectrometry, SIMS 7*, edited by A. Benninghoven, pp. 377–380, John Wiley, New York, 1990.
- Loughnan, F. C., *Chemical Weathering of the Silicate Minerals*, 154 pp., Elsevier, New York, 1969.
- MacRae, N. D., Quantitative analysis for rare earth elements by SIMS, *Am. Mineral.*, 72, 1263–1268, 1987.
- MacRae, N. D., P. Bottazzi, L. Ottolini, and R. Vannucci, Quantitative REE analysis of silicates by SIMS: Conventional energy filtering vs. specimen isolation mode, *Chem. Geol.*, 103, 45–54, 1993.
- Manley, E. P., and L. J. Evans, Dissolution of feldspars by low-molecular-weight aliphatic and aromatic acids, *Soil Sci.*, 141, 106–112, 1986.
- Manley, E. P., W. Chesworth, and L. J. Evans, The solution chemistry of podzolic soils from the eastern Canadian shield: A thermodynamic interpretation of the mineral phases controlling soluble Al^{3+} and H_4SiO_4 , *J. Soil Sci.*, 38, 39–51, 1987.
- Mast, M. A., and J. I. Drever, The effect of oxalate on the dissolution rates of oligoclase and tremolite, *Geochim. Cosmochim. Acta*, 51, 2559–2568, 1987.
- McColl, J. G., and A. A. Pohlman, Soluble organic acids and their chelating influence on Al and other metal dissolution from forest soils, *Water Air Soil Pollut.*, 31, 917–927, 1986.
- McFarlane, A. W., and N. Shimizu, SIMS measurements of δ sulfur-34 in sulfide minerals from adjacent vein and stratabound ores, *Geochim. Cosmochim. Acta*, 55, 525–541, 1991.
- McKeague, J. A., M. V. Cheshire, F. Andreux, and J. Berthelin, Organo-mineral complexes in relation to pedogenesis, in *Interaction of Soil Minerals with Natural Organics and Microbes*, *SSSA Spec. Publ.*, 17, 549–592, 1986.
- Merrill, G. P., *Rocks, Rock Weathering, and Soils*, Macmillan, New York, 1921.
- Metson, J. B., Secondary ion mass spectrometry, in *Instrumental Surface Analysis of Geologic Materials*, edited by D. L. Perry, pp. 311–352, VCH Publishers, New York, 1990.
- Metson, J. B., G. M. Bancroft, N. S. McIntyre, and W. J. Chauvin, Suppression of molecular ions in the secondary ion mass spectra of minerals, *SIA Surf. Interface Anal.*, 5, 181–185, 1983.
- Metson, J. B., G. M. Bancroft, and H. W. Nesbitt, Analysis of minerals using specimen isolated secondary ion mass spectrometry, *Scanning Electron Microsc.*, no. II, 595–603, 1985.
- Meuris, M., P. De Bisschop, J. F. Leclair, and W. Vander-vorst, Determination of the angle of incidence in a Cameca IMS-4f instrument, *SIA Surf. Interface Anal.*, 14, 739–743, 1989.
- Mogk, D. W., Application of Auger electron spectroscopy to studies of chemical weathering, *Rev. Geophys.*, 28, 337–356, 1990.
- Mogk, D. W., and W. W. Locke, III, Application of Auger electron spectroscopy (AES) to naturally weathered

- hornblende, *Geochim. Cosmochim. Acta*, 52, 2537–2542, 1988.
- Monier, E., Action de l'acide oxalique sur le silicate de soude, quartz hydraté, *C. R Hebd. Seances Acad. Sci.*, 85, 1053–1054, 1877.
- Muir, I. J., Secondary ion mass spectrometry and its application to studies in geochemistry, Ph.D. thesis, Univ. of Western Ont., London, Canada, 1989.
- Muir, I. J., and H. W. Nesbitt, Effects of aqueous cations on the dissolution of labradorite feldspar, *Geochim. Cosmochim. Acta*, 55, 3181–3189, 1991.
- Muir, I. J., and H. W. Nesbitt, Controls on differential leaching of calcium and aluminum from labradorite in dilute electrolyte solutions, *Geochim. Cosmochim. Acta*, 56, 3979–3985, 1992.
- Muir, I. J., G. M. Bancroft, N. D. MacRae, and J. B. Metson, Quantitative analyses of rare-earth elements in minerals by secondary ion mass spectrometry, *Chem. Geol.*, 64, 269–278, 1987.
- Muir, I. J., G. M. Bancroft, and H. W. Nesbitt, Characteristics of altered labradorite surfaces by SIMS and XPS, *Geochim. Cosmochim. Acta*, 53, 1235–1241, 1989.
- Muir, I. J., G. M. Bancroft, W. Shotyk, and H. W. Nesbitt, A SIMS and XPS study of dissolving plagioclase, *Geochim. Cosmochim. Acta*, 54, 2247–2256, 1990.
- Nash, V. E., and C. E. Marshall, The surface reaction of silicate minerals, I, The reactions of feldspar surfaces with acidic solutions, *Res. Bull. Mo. Agric. Exp. Stn.*, 613, 1956a.
- Nash, V. E., and C. E. Marshall, The surface reactions of silicate minerals, II, Reactions of feldspar surfaces with salt solutions, *Res. Bull. Mo. Agric. Exp. Stn.*, 614, 1956b.
- Nesbitt, H. W., and I. J. Muir, SIMS depth profiles of weathered plagioclase, and processes affecting dissolved Al and Si in some acidic soil solutions, *Nature*, 334, 336–338, 1988.
- Nesbitt, H. W., and G. M. Young, Early Proterozoic climates and plate motions inferred from major element chemistry of lutites, *Nature*, 299, 715–717, 1982.
- Nesbitt, H. W., J. B. Metson, and G. M. Bancroft, Quantitative major and trace element whole rock analysis using secondary ion mass spectrometry, *Chem. Geol.*, 55, 139–160, 1986.
- Nesbitt, H. W., N. D. MacRae, and W. Shotyk, Congruent and incongruent dissolution of labradorite in dilute, acidic salt solutions, *J. Geol.*, 99, 429–442, 1991.
- Paces, T., Steady-state kinetics and equilibrium between ground water and granitic rock, *Geochim. Cosmochim. Acta*, 37, 2641–2663, 1973.
- Paces, T., Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments, *Geochim. Cosmochim. Acta*, 47, 1855–1863, 1983.
- Parker, A., An index of weathering for silicate rocks, *Geol. Mag.*, 501–504, 1970.
- Perry, D. L., *Instrumental Surface Analysis of Geologic Materials*, VCH Publishers, New York, 1990.
- Petit, J.-C., G. Della Mea, J.-C. Dran, J.-C. Schott, and R. A. Berner, Mechanism of diopside dissolution from hydrogen depth profiling, *Nature*, 325, 705–707, 1987.
- Petit, J.-C., J.-C. Dran, G. Della Mea, and A. Paccagnella, Dissolution mechanisms of silicate minerals yielded by intercomparison with glasses and radiation damage studies, *Chem. Geol.*, 78, 219–227, 1989a.
- Petit, J.-C., J.-C. Dran, A. Paccagnella, and G. Della Mea, Structural dependence of crystalline silicate hydration during aqueous dissolution, *Earth Planet. Sci. Lett.*, 93, 292–298, 1989b.
- Petit, J.-C., G. Della Mea, J.-C. Dran, M.-C. Magonthier, P. A. Mando, and A. Paccagnella, Hydrated-layer formation during dissolution of complex silicate glasses and minerals, *Geochim. Cosmochim. Acta*, 54, 1941–1955, 1990a.
- Petit, J.-C., J.-C. Dran, and G. Della Mea, Energetic ion beam analysis in the Earth sciences, *Nature*, 344, 621–626, 1990b.
- Petrovic, R., R. A. Berner, and M. B. Goldhaber, Rate control in dissolution of alkali feldspars, I, Study of residual feldspar grains by X-ray photoelectron spectroscopy, *Geochim. Cosmochim. Acta*, 40, 537–548, 1976.
- Pohlman, A. A., and J. G. McColl, Kinetics of metal dissolution from forest soils by soluble organic acids, *J. Environ. Qual.*, 15, 86–92, 1986.
- Pohlman, A. A., and J. G. McColl, Soluble organics from forest litter and their role in metal dissolution, *Soil Sci. Soc. Am. J.*, 52, 265–271, 1988.
- Polynov, B. B., *The Cycle of Weathering*, translated from Russian by A. Muir, Macmillan, New York, 1937.
- Reed, S. J. B., Trace element analysis with the ion probe, *Scanning*, 3, 119–127, 1980.
- Reed, S. J. B., Geological applications of SIMS, in *Secondary Ion Mass Spectrometry, SIMS 4, Springer Ser. Chem. Phys.*, vol. 36, pp. 451–455, Springer-Verlag, New York, 1984.
- Richter, T., G. H. Frischat, G. Borchardt, and S. Scherrer, Short time leaching of a soda-lime glass in H₂O and D₂O, *Phys. Chem. Glasses*, 26, 208–212, 1985.
- Rimstidt, J. D., and P. M. Dove, Mineral/solution reaction rates in a mixed flow reactor: Wollastonite hydrolysis, *Geochim. Cosmochim. Acta*, 50, 2509–2516, 1986.
- Ripoli, C., A. Jauneau, F. Lefebvre, M. Demarty, and M. Thellier, SIMS determination of the distribution of the main mineral cations in the depth of the cuticle and pecto-cellulosic wall of epidermal cells of flax stems: Problems encountered with SIMS depth profiling, *Biol. Cell.*, 74, 135–142, 1992.
- Robert, M., and J. Berthelin, Role of biological and biochemical factors in soil mineral weathering, in *Interactions of Soil Minerals with Natural Organics and Microbes*, *SSSA Spec. Publ.*, 17, 453–495, 1986.
- Ruxton, B. P., Measures of the degree of chemical weathering of rocks, *J. Geol.*, 76, 518–527, 1968.
- Schalscha, E. B., H. Appelt, and A. Schatz, Chelation as a weathering mechanism, I, Effect of complexing agents on the solubilization of iron from minerals and granodiorite, *Geochim. Cosmochim. Acta*, 31, 587–596, 1967.
- Schenk, D., A. Petersen, and G. Matthes, Acceleration and retardation of silicate weathering due to organic substances, in *Water-Rock Interaction*, edited by D. L. Miles, pp. 605–607, A. A. Balkema, Rotterdam, Netherlands, 1989.
- Schindler, P. W., and W. Stumm, The surface chemistry of oxides, hydroxides, and oxide minerals, in *Aquatic Surface Chemistry*, edited by W. Stumm, pp. 83–110, John Wiley, New York, 1987.
- Schott, J., and J.-C. Petit, New evidence for the mechanisms of dissolution of silicate minerals, in *Aquatic Surface Chemistry*, edited by W. Stumm, pp. 292–315, John Wiley, New York, 1987.
- Schreiner, M., Deterioration of stained medieval glass by atmospheric attack, 2, Secondary ion mass spectrometry analysis of naturally weathered glass surfaces, *Glastech. Ber.*, 61, 223–230, 1988.
- Schreiner, M., Secondary ion mass spectrometer analysis of potash-lime-silica glasses leached in hydrochloric and sulfuric acids, *J. Am. Ceram. Soc.*, 72, 1713–1715, 1989.
- Schreiner, M., G. Stinger, and M. Grasserbauer, Quantitative characterization of surface layers on corroded me-

- dieval glass windows with SIMS, *Fresenius Z. Anal. Chem.*, 319, 600–605, 1984.
- Schreiner, M., M. Grasserbauer, and P. March, Quantitative NRA and SIMS depth profiling of hydrogen in naturally weathered medieval glass, *Fresenius Z. Anal. Chem.*, 331, 428–432, 1988.
- Schweda, P., Kinetics of alkali feldspar dissolution at low temperature, in *Water-Rock Interaction*, edited by D. L. Miles, pp. 609–612, A. A. Balkema, Rotterdam, Netherlands, 1989.
- Schweda, P., Kinetics and mechanisms of alkali feldspar dissolution at low temperatures, *Medd. Stockholms Univ. Inst. Geol. Geokem.*, 281, 1990.
- Shimizu, N., and S. R. Hart, Applications of the ion microprobe to geochemistry and cosmochemistry, *Annu. Rev. Earth Planet. Sci.*, 10, 483–526, 1982.
- Shotyk, W., and H. W. Nesbitt, Incongruent and congruent dissolution of plagioclase feldspar: Effect of feldspar composition and ligand complexation, *Geoderma*, 55, 55–78, 1992.
- Sigmund, P., Theory of sputter, I, Sputtering yield of amorphous and polycrystalline targets, *Phys. Rev.*, 184, 383–416, 1969.
- Sigmund, P., Mechanisms and theory of physical sputtering by particle impact, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 17, 1, 1987.
- Sjöberg, L., Kinetics and non-stoichiometry of labradorite dissolution, in *Water-Rock Interaction*, edited by D. L. Miles, pp. 639–642, A. A. Balkema, Rotterdam, Netherlands, 1989.
- Slodzian, G., Some problems encountered in secondary ion emission applied to elementary analysis, *Surf. Sci.*, 48, 161–186, 1975.
- Smets, B. M. J., and T. P. A. Lommen, The leaching of sodium aluminosilicate glasses studied by secondary ion mass spectrometry, *Phys. Chem. Glasses*, 23, 83–87, 1982.
- Stauffer, R. E., and B. D. Wittchen, Effects of silicate weathering on water chemistry in forested upland, felsic terrane of the USA, *Geochim. Cosmochim. Acta*, 55, 3253–3271, 1991.
- Storms, H. A., K. F. Brown, and J. D. Stein, Evaluation of a cesium positive ion source for secondary ion mass spectrometry, *Anal. Chem.*, 49, 2023–2030, 1977.
- Streit, L. A., R. L. Hervig, and P. Williams, Quantitative SIMS microanalysis of trace elements in geological samples using in situ ion-implanted standards, in *Microbeam Analysis*, edited by A. D. Romig and W. F. Chambers, pp. 91–94, San Francisco Press, San Francisco, Calif., 1986.
- Stumm, W., and G. Furrer, The dissolution of oxides and aluminum silicates; examples of surface-coordination-controlled kinetics, in *Aquatic Surface Chemistry*, edited by W. Stumm, pp. 197–219, John Wiley, New York, 1987.
- Stumm, W., and J. J. Morgan, *Aquatic Chemistry*, 2nd ed., John Wiley, New York, 1981.
- Stumm, W., and R. Wollast, Coordination chemistry of weathering: Kinetics of surface-controlled dissolution of oxide minerals, *Rev. Geophys.*, 28, 53–69, 1990.
- Stumm, W., G. Furrer, E. Wieland, and B. Zinder, The effect of complex-forming ligands on the dissolution of oxides and aluminosilicates, in *The Chemistry of Weathering*, edited by J. I. Drever, pp. 55–74, D. Reidel, Norwell, Mass., 1985.
- Stumm, W., B. Wehrli, and E. Wieland, Surface complexation and its impact on geochemical kinetics, *Croat. Chem. Acta*, 60, 429–456, 1987.
- Sverdrup, H. U., *The Kinetics of Base Cation Release due to Chemical Weathering*, 246 pp., Lund University Press, Lund, Sweden, 1990.
- Swart, P. K., Calibration of the ion microprobe for the quantitative determination of strontium, iron, manganese, and magnesium in carbonate minerals, *Anal. Chem.*, 62, 722–728, 1990.
- Swoboda-Colberg, N. G., and J. I. Drever, Mineral dissolution rates: A comparison of laboratory and field studies, in *Water-Rock Interaction*, edited by Y. K. Kharaka and A. S. Maest, pp. 115–118, A. A. Balkema, Rotterdam, Netherlands, 1992.
- Swoboda-Colberg, N. G., and J. I. Drever, Mineral dissolution rates in plot-scale field and laboratory experiments, *Chem. Geol.*, 105, 51–69, 1993.
- Tait, J. C., W. H. Hocking, J. S. Betteridge, and G. Bart, Field burial results and SIMS analysis of the Chalk River glass blocks, *Adv. Ceram.*, 20, 559–565, 1986.
- Tan, K. H., Degradation of soil minerals by organic acids, in *Interactions of Soil Minerals With Natural Organics and Microbes*, *SSSA Spec. Publ.*, 17, 1–27, 1986.
- Thaer, A. D., *The Principles of Practical Agriculture*, translated by W. Shaw and C. W. Johnson, C. M. Saxton, Barker, and Co., New York, 1860.
- Tole, M. P., A. C. Lasaga, C. Pantano, and W. B. White, The kinetics of dissolution of nepheline (NaAlSi₃O₈), *Geochim. Cosmochim. Acta*, 50, 379–392, 1986.
- Vandentop, G. J., M. A. Karolewski, and R. G. Cavell, Secondary ion mass spectra of metal sulfides, *Int. J. Mass Spectrom. Ion Processes*, 89, 319–342, 1989.
- van Grinsven, J. J. M., and W. H. van Riemsdijk, Evaluation of batch and column techniques to measure weathering rates in soils, *Geoderma*, 52, 41–57, 1992.
- Vannucci, R., R. Tribuzio, G. B. Piccardo, L. Ottolini, and P. Bottazzi, SIMS analysis of REE in pyroxenes and amphiboles from the Proterozoic Ikaaulak intrusive complex (SE Greenland): Implications for LREE enrichment processes during postorogenic plutonism, *Chem. Geol.*, 92, 115–133, 1991.
- Vedy, J. C., and S. Bruckert, Soil solution: Composition and pedogenic significance, in *Constituents and Properties of Soils*, by M. Bonneau and B. Souchier, edited and translated by V. C. Farmer, pp. 184–213, Academic, San Diego, Calif., 1982.
- Velbel, M. A., Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge, *Am. J. Sci.*, 285, 904–930, 1985.
- Velbel, M. A., Influence of surface area, surface characteristics, and solution composition on feldspar weathering rates, in *Geochemical Processes at Mineral Surfaces*, *ACS Symp. Ser.*, 323, 615–634, 1986.
- Velbel, M. A., Weathering of hornblende to ferruginous products by a dissolution-precipitation mechanism: Petrography and stoichiometry, *Clays Clay Miner.*, 37, 515–524, 1989.
- Velbel, M. A., Influence of temperature and mineral surface characteristics on feldspar weathering rates in natural and artificial systems: A first approximation, *Water Resour. Res.*, 26, 3049–3053, 1990.
- Velbel, M. A., Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: Implications for hydrologic control differences in absolute rates, *Chem. Geol.*, 105, 89–99, 1993.
- Vickerman, J. C., Secondary ion mass spectrometry, *Chem. Br.*, 23, 969–974, 1987.
- von Engelhardt, W., Versuche über die Verwitterung des Feldspates, *Fortschr. Mineral. Kristallogr. Petrogr.*, 23, 120–123, 1939.
- Welch, S. A., and W. J. Ullman, Dissolution of feldspars in oxalic acid solutions, in *Water-Rock Interaction*, edited

- by Y. K. Kharaka and A. S. Maest, pp. 127–130, A. A. Balkema, Rotterdam, Netherlands, 1992.
- Welch, S. A., and W. J. Ullman, The effect of organic acids on plagioclase dissolution rates and stoichiometry, *Geochim. Cosmochim. Acta*, *57*, 2725–2736, 1993.
- Williams, P., The sputtering process and sputtered ion emission, *Surf. Sci.*, *90*, 588–634, 1979.
- Williams, P., Secondary ion mass spectrometry, *Annu. Rev. Mater. Sci.*, *15*, 517–548, 1985.
- Wilson, M. J., Chemical weathering of some primary rock-forming minerals, *Soil Sci.*, *119*, 349–355, 1975.
- Wittmaack, K., Oxygen concentration dependence of secondary ion yield enhancement, *Surf. Sci.*, *112*, 168–180, 1981.
- Wollast, R., and L. Chou, Kinetic study of the dissolution of albite with a continuous flow-through fluidized bed reactor, in *The Chemistry of Weathering*, edited by J. I. Drever, pp. 75–96, D. Reidel, Norwell, Mass., 1985.
- Yu, M. L., Chemical enhancement effects in SIMS analysis, *Nucl. Instrum. Methods Phys. Res., Sect. B*, *15*, 151–158, 1986a.
- Yu, M. L., Bond breaking and the ionization of sputtered atoms, *Phys. Rev. Lett.*, *57*, 1476–1479, 1986b.
- Yurimoto, H., M. Kurosawa, and S. Sueno, Hydrogen analysis in quartz crystals and quartz glasses by secondary ion mass spectrometry, *Geochim. Cosmochim. Acta*, *53*, 751–755, 1989a.
- Yurimoto, H., A. Yamashita, N. Nishida, and S. Sueno, Quantitative SIMS analysis of GSJ rock reference sample, *Geochem. J.*, *23*, 215–236, 1989b.
- Yurimoto, H., I. Sakaguchi, N. Nishida, and S. Sueno, Determination of nickel in GSJ standard rock samples using secondary ion mass spectrometry, *Geostand. Newsl.*, *15*, 155–159, 1991.
- Zoitos, B. K., D. E. Clark, A. R. Lodding, and G. G. Wicks, Correlation of laboratory and Stripa field leaching studies, in *Scientific Basis for Nuclear Waste Management XII*, edited by W. Lutze and R. C. Ewing, pp. 145–151, Materials Research Society, Pittsburgh, Pa., 1989.

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