

Weathering, secondary mineral genesis, and soil formation caused by lichens and mosses growing on granitic gneiss in a boreal forest environment



Togwell A. Jackson

Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario L7R 4A6, Canada

ARTICLE INFO

Article history:

Received 22 September 2014
 Received in revised form 5 February 2015
 Accepted 8 March 2015
 Available online 7 April 2015

Keywords:

Weathering
 Biogenic minerals
 Clay minerals
 Soil formation
 Lichens
 Mosses

ABSTRACT

Lichens and mosses growing on granitic gneiss in a boreal forest environment caused intense chemical weathering of the rock, producing exclusively biogenic secondary minerals and soils and accumulating solubilised rock-forming elements (Si and metals), but weathering in the absence of these organisms was relatively ineffective. Apart from primary biotite, the only phyllosilicates in the rock were sericite and chlorite formed by hydrothermal metamorphism or abiotic weathering, or both, but the biogenic soils contained expandable clay minerals and, in several cases, kaolinite and calcite, together with illite and chlorite. Lichens were especially effective in altering feldspars to clay, but mosses generally produced a greater abundance of expandable clay minerals, and kaolinite was produced *only* by certain species of moss – specifically the ones whose rock-derived element concentrations and Mg/Ca ratios were highest. Rock-derived element concentrations were usually highest in mosses, and element enrichment increased with the charge/radius ratio of the cation of the element, suggesting carrier-mediated transport across cell membranes. Furthermore, lichens and mosses produced different assemblages of expandable clay minerals, and most mosses (but none of the lichens) produced authigenic amphiboles and pyroxenes. Biological weathering is attributable to solubilisation of rock-forming elements by chelating agents and H_2CO_3 , bioaccumulation of the elements, and nucleation of secondary silicates by chelate complexes functioning as templates for epitaxial growth of specific crystal structures. The different weathering and soil-forming processes of lichens and mosses suggest a mutualistic strategy for maximising the release of inorganic nutrients from rocks and retaining them in bioavailable forms in the soil.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Chemical weathering is of key importance to life on Earth. Above all, the process releases essential inorganic nutrients, notably phosphate and various metals (K, Ca, Mg, Fe, Cu, Zn, etc.), from rock and soil minerals, solubilising them and making them available for uptake and utilisation by organisms. Another major ecological function of weathering is the production of colloidal secondary minerals (clay minerals and oxides or oxyhydroxides) which, together with humic and non-humic organic matter, form soils and fine-grained sediments, thereby providing organisms not only with habitats but also with supplies of bioavailable nutrients reversibly bound to ligands and other sorption sites of the colloidal minerals and humic matter. Moreover, the weathering action of carbonic acid (H_2CO_3) formed by the reaction of CO_2 with water, plays a pivotal role in the regulation of the Earth's climates by withdrawing CO_2 from the atmosphere, thereby counteracting the heat-trapping effect of atmospheric CO_2 (Schwartzman and Volk, 1989; Berner, 1995; Schwartzman, 1999; Lovelock, 2009; Lenton et al., 2012).

A large body of empirical evidence has established that the activities of organisms greatly intensify and accelerate chemical weathering and mediate the formation of secondary minerals (Schwartzman, 1999). To begin with, the Biosphere as a whole controls the weathering process to a significant degree by regulating atmospheric CO_2 levels (Schwartzman and Volk, 1989; Berner, 1992, 1993, 1995; Berner et al., 2005; Lenton et al., 2012). Thus, biological withdrawal of CO_2 from the air by photosynthesis, carbonate deposition, and the formation of refractory organic substances (notably humic matter), which accumulate as carbon sinks in soils and sediments (Jackson, 1975), is balanced by the emission of respiratory CO_2 ; moreover, the CO_2 emitted by volcanoes is probably for the most part of a product of the thermal decomposition of biogenic sedimentary organic matter by igneous and metamorphic processes. Hence the “abiotic” weathering action of carbonic acid is, in fact, largely, if not wholly, a consequence of biological activities. However, this universal background process is enormously augmented by much more intense weathering processes mediated by various organisms that inhabit rock surfaces and soils.

Laboratory experiments have demonstrated that bacteria and fungi inhabiting weathered rock surfaces and soils release phosphate and metal cations by solubilising apatite and silicate minerals (Sperber,

E-mail address: t.a.jackson@ec.gc.ca.

1958; Webley et al., 1963; Duff et al., 1963; Henderson and Duff, 1963; Voigt, 1965; Boyle et al., 1967; Frankel, 1977; Naga et al., 1977; Berthelin, 1983; Robert and Berthelin, 1986; Welch et al., 1999). Similarly, there is evidence that bacteria in groundwater, lake sediments, and mine tailings decompose silicate minerals (Hiebert and Bennett, 1992; Bennett et al., 2001; Bhatti et al., 2011; Jackson et al., 2011) and that bacteria may preferentially colonise particular minerals whose solubilised constituents supply their inorganic nutrient requirements (Bennett et al., 2001; Jones and Bennett, 2014). Among soil microbes, the rhizosphere bacteria associated with the roots of trees and other plants are especially efficient weathering agents, and there are grounds for believing that their relationship with the host plants is mutually beneficial, the plants providing the bacteria with organic nutrients exuded by their roots, whilst the bacteria decompose soil minerals, releasing inorganic nutrients required by the plants (Gerretsen, 1948; Jackson and Voigt, 1971; Ochs et al., 1993; Drever, 1994; Calvaruso et al., 2006; Taylor et al., 2009; Arocena et al., 2012; Parmar and Sindhu, 2013). This raises the possibility that bacteria associated with the pioneer lichens and mosses which inhabit rock surfaces perform comparable functions.

Be that as it may, lichens colonising rock surfaces have been found to enhance enormously the chemical weathering of the rocks on which they grow, and they mediate the formation of distinctive biogenic secondary minerals. Thus, a comprehensive investigation of the chemical weathering and secondary mineral-forming activities of the lichen *Stereocaulon vulcani* growing on basaltic lava flows of known age in wet and dry climatic zones on the Island of Hawaii showed that in regions of high rainfall the lichen [1] accelerated the rate of weathering by orders of magnitude relative to the abiotic weathering of bare rock surfaces, producing conspicuous, relatively thick reddish weathering crusts, and [2] produced copious quantities of an exclusively biogenic form of ferric oxide along with other residual oxides (but no clay minerals, owing to the intensity of the biochemical leaching of silica and metal cations), whereas the ferric oxide produced by abiotic weathering consisted solely of trace quantities of the common mineral hematite which, together with trace quantities of clay minerals, formed an incipient weathering rind that was orders of magnitude thinner than the biogenic weathering crust – so thin, in fact, that it was barely detectable, even under a microscope (Jackson, 1968, 1993; Jackson and Keller, 1970a,b). Detailed analysis employing various techniques established that the biogenic ferric oxide was a mineral previously unknown to science, and its unique crystal structure was attributed to epitaxial growth nucleated by Fe(III) chelate complexes produced by the lichen. This ferric oxide polymorph was subsequently rediscovered elsewhere by others and officially recognised as a new mineral named “ferrihydrite” (Schwertmann and Fischer, 1973; Schwertmann et al., 1986), but the credit for the original discovery of the mineral in nature, the first detailed, systematic investigation of its properties, and appreciation of its biogeochemical significance belongs to T.A. Jackson, as documented elsewhere (Jackson, 1968, 1993; Jackson and Keller, 1970a,b). Subsequent reports by other workers independently confirmed the observation that lichens accelerate chemical weathering and produce biogenic secondary minerals, including ferrihydrite, and corroborated the theory that the weathering action of lichens involves biogenic chelating agents (Jones et al., 1980; Wilson and Jones, 1983; Adamo and Violante, 1991, 2000; Adamo et al., 1993, 1997; Johnston and Vestal, 1993; Hen and Gong, 1995; Chen and Blume, 1999, 2002; Chen et al., 2000; Aghamiri and Schwartzman, 2002; Matthews and Owen, 2008; Zambell et al., 2012). Berner (1992) and Cochran and Berner (1992) put forward the unfounded opinion that the reddish material associated with the Hawaiian lichens consisted of wind-blown dust, but Jackson (1993) proved conclusively that this material was, instead, a weathering crust formed in situ by the lichen, as maintained originally by Jackson (1968) and Jackson and Keller (1970a,b).

Although much attention has been devoted to the weathering of rocks by lichens, hardly any research seems to have been done on the possible weathering action of mosses. However, one study, at least,

produced experimental evidence for enhancement of weathering by a species of moss (Crouch, 2010), and late Ordovician glaciation has been ascribed to a drop in atmospheric CO₂ levels owing to acceleration of chemical weathering due to the evolution of non-vascular plants such as bryophytes (Lenton et al., 2012).

The weathering action of lichens, mosses, fungi, and bacteria is attributable to biological production of weak organic acids as well as carbonic acid. Many of these organic acids solubilise divalent and polyvalent metal cations of minerals by chelation as well as by acid attack. The chelating agents implicated in biologically enhanced weathering include “lichen acids” (an assortment of unique compounds produced by lichens) along with humic and fulvic acids and various common low molecular weight biochemical compounds such as oxalic acid and citric acid; and experimental studies have demonstrated that the effectiveness of these chelators as weathering agents far exceeds that of carbonic acid (Mandl et al., 1953; Schatz et al., 1954; Wright and Schnitzer, 1963; Jackson, 1968, 1975, 1993; Jackson and Keller, 1970a,b; Ong et al., 1970; Huang and Keller, 1970, 1971, 1972; Huang and Kiang, 1972; Schnitzer and Khan, 1972; Jones et al., 1980; Wilson and Jones, 1983; Adamo and Violante, 1991, 2000; Adamo et al., 1993, 1997; Johnston and Vestal, 1993; Chen et al., 2000; Chen and Blume, 2002). Moreover, the theory that biogenic chelate complexes of Fe(III) nucleated the ferrihydrite produced by the lichens that promote the chemical weathering of Hawaiian lava flows (Jackson, 1968, 1993; Jackson and Keller, 1970a,b) has been independently confirmed (Schwertmann et al., 1986). Similarly, experiments have shown that chelate complexes (including fulvic acid complexes) of Al³⁺ may nucleate the formation of kaolinite (Linares and Huertas, 1971; Hem and Lind, 1974).

The purpose of the present study was [1] to investigate and compare the weathering, secondary mineral-synthesising, and soil-forming activities of different species of lichens and mosses which comprised a pioneer community colonising a granitic gneiss outcrop in a boreal forest environment, [2] to compare the effects of weathering and secondary mineral formation in the presence and absence of these organisms, and [3] to assess the ecological implications of the interactions between the organisms and the rock.

2. Field area, materials, and methods

The sampling site was located in the Experimental Lakes Area (ELA) operated by the Canadian government just east of Kenora, Northwestern Ontario, Canada. The ELA is situated on the Canadian Shield within the longitude and latitude ranges 93°30′–94°00′ W and 49°30′–49°45′ N, respectively, at an altitude of 360–380 m above sea level, and it is characterised by cool, humid temperate climatic conditions, boreal forest vegetation, the common occurrence of soils classed as brunisols, an abundance of lakes, Pleistocene till and glacial outwash deposits, and Precambrian bedrock which comprises part of a “pink granodiorite” batholith of Algoman (late Archean) age (Brunskill and Schindler, 1971).

The samples were collected at or near the top of a low, gently sloping outcrop of gneiss located in a clearing surrounded by spruce forest. The gneiss was characterised by pink, predominantly felsic bands alternating with black bands enriched in mafic minerals. Whether it was an outcrop of local bedrock or the exposed top of a large glacial erratic partially buried in finer-grained glacial drift is uncertain, but for the purposes of this paper it makes no difference. The rock had been colonised by different varieties of lichens and mosses underlain by layers of dark brown or black humus-rich soil up to a few centimetres thick. The soil deposits underlying several of the mosses (but none of the lichens) contained abundant sand-sized particles which presumably consisted of quartz and feldspar grains released from the rock by the weathering action of the organisms. In addition, a few scattered clumps of grass and other small vascular plants were growing among the lichens and mosses. The soils occurred solely in association with lichens, mosses, and plants, implying that they owed their existence to biological factors (i.e.,

biochemically mediated weathering and secondary mineral formation, production of organic matter, and protection from erosion). Although the areas of rock that supported lichens and mosses were, as a rule, so thickly overgrown by these organisms that the nature of the rock immediately underlying individual species could not be distinguished, it was noted that certain species of moss (afterwards identified as *Hedwigia ciliata* and *Grimmia* sp.) preferentially colonised the pink bands of the gneiss (growing mainly along fractures and in depressions) and tended to avoid the black bands. In addition to the rock surfaces that were carpeted by lichens and mosses, there were areas of bare rock, affording an opportunity to compare effects of weathering in the presence and absence of the organisms. The reason for the patchy distribution of the lichens and mosses is uncertain, but a possible explanation (apart from random dispersal of spores) is that the organisms succeeded in becoming established only on areas of the rock surface where water-trapping fractures and depressions happened to occur, as observed in the case of *H. ciliata* and *Grimmia* sp. Samples of lichen, moss, soil, and bare rock were collected in plastic Whirl-Pak bags on 21 June, 1976. The lichen, moss, and soil specimens were temporarily stored at 4 °C and then oven-dried at 35–40 °C and stored at room temperature.

The lichens and mosses were identified by lichen and bryophyte taxonomists, respectively. In addition, portions of the biological samples were analysed for Si, Al, Fe, Ca, Mg, Na, and K using the methods of Horwitz (1980, section 3.007). The specimens were separated as thoroughly as possible from the underlying soil, and moss rhizoids embedded in soil were cut off with a razor blade and discarded, whereupon the specimens were ground up and digested with nitric acid. Perchloric acid was then added, and the mixtures were heated until the perchloric acid started fuming. At this stage, Si was in the form of dehydrated silica precipitate, and all other elements were in solution. Each digest was filtered using a #40 ashless filter paper, and the filter pad together with the silica retained on it was ignited at 1000 °C, after which the silica was weighed and the Si concentration was calculated. Each filtrate was made up to a final volume of 50 mL and analysed for Al, Fe, Ca, Mg, Na, and K using a Jarrell Ash model 1140 inductively coupled plasma atomic emission spectrometry (ICP–AES) unit.

The soil samples and two representative specimens of the bare rock were analysed semi-quantitatively for bulk mineral and clay mineral content by X-ray diffraction techniques (Last, 2002), and thin sections of the rock samples were examined under a petrographic microscope. The X-ray diffraction analyses were performed with a Philips PW1710 Automated Powder Diffraction System employing Ni-filtered monochromatised CuK α radiation generated at 40 kW and 40 milliamps. Prior to X-ray diffraction analysis the soil samples were pretreated with 30% H₂O₂ to remove organic matter and dispersed ultrasonically in distilled water, and the rock samples were pulverised with an agate mortar and pestle.

For bulk mineral analysis by X-ray diffraction, randomly oriented specimens of sample material were mounted on standard petrographic slides (Klug and Alexander, 1974) and irradiated in one direction over the range 3°–70° 2 θ , generally at a scanning speed of 2.4° 2 θ per minute, with a 1° beam slit, 0.01 cm detector slit, 1 second measurement constant, and 0.01 step size, and a count range setting of 200 counts per second. Mineral identification was based on d-spacing values using standard indices of the ASTM X-ray Powder Diffractions File (Chen, 1977), and the abundance of a given mineral was estimated by comparing the intensity of the strongest peak of the mineral in the sample to the intensity of the corresponding peak of the pure mineral (i.e., by application of an “intensity factor”) (Schultz, 1964). The mineral percentages were summed and normalised to 100%. The limit of detection of individual minerals in the samples was ~5% (Last, W.M., personal communication), and replicate analyses indicated that the precision of the method was approximately \pm 8% (Last, 1980). Note that the procedure was designed to derive independent estimates of the relative abundances of the individual minerals expressed as percentages: Variations in the percentage of one mineral do not significantly affect the percentages of others (Hower et al., 1976;

Callender, 1968). The positions of the major peaks used for identification of minerals in the bulk mineralogical analyses (expressed as degrees 2 θ) were as follows: quartz, 26.7; potassium feldspar, 27.4–27.5; plagioclase feldspar, 27.8–27.9; amphiboles, 10.4; pyroxenes, 29.8; total clay minerals, 19.9–20.1; calcite, 29.4–29.8; and dolomite, 30.9.

Before being analysed for clay minerals, the soil samples and pulverised rock samples were subjected to size fractionation using wet sieve and centrifugation techniques (Tanner and Jackson, 1947; Folk, 1968). X-ray diffraction analyses were then performed on the clay-sized fraction, which, in accordance with the geological definition of clay, consisted of all mineral particles that fell in the <3.9 μ m size grade (Wentworth, 1922; Grim, 1968). For convenience, the <3.9 μ m fraction will simply be designated as the “clay” fraction and will be regarded as synonymous with the clay-sized phyllosilicate fraction (i.e., clay minerals and fine-grained mica). Moreover, we may safely assume that pulverisation of the majority of primary minerals in the rock specimens (i.e., feldspars and quartz, which comprised ~80–100% of the rock) produced no artificial clay-sized material, as experience has shown that grinding by hand does not (and, indeed, cannot) result in the production of clay-sized particles from coarser mineral grains of this nature (Last, W.M., personal communication). The hypothetical possibility that coarse biotite crystals, which comprised a small, variable proportion (0–20%) of the primary rock-forming minerals, were to some extent reduced to clay-sized particles by pulverisation cannot be ruled out, but the available evidence implies that no detectable systematic error occurred on that account (see Section 3.2).

For clay mineral analyses, the diffractometer settings were the same as those used for bulk analysis except that the scanning speed was 0.6° 2 θ per minute. Oriented clay mineral mounts were prepared by mixing the clay-sized material with water, spreading an aliquot of the slurry on a petrographic slide using the membrane filter-peel technique of Drever (1973), and allowing the slurry to dry. Two slides of each sample were prepared in this manner. One slide was exposed to ethylene glycol for at least 48 hours at constant relative humidity (Muller, 1967), and the other was heated to 550 °C for 1 hour (Carroll, 1970). Both preparations were then irradiated in one direction over the range 3°–15° 2 θ , and the heated preparation was also irradiated over the range 24°–27° 2 θ . The X-ray diffraction patterns were used to identify the principal clay minerals and to estimate the relative abundances of the major clay mineral groups represented — i.e., illite, chlorite, kaolinite, and “expandable clay,” a category which includes smectite, vermiculite, swelling chlorite, and various mixed-layer species. Illite was defined by a peak at 10 Å (8.8° 2 θ) which was not affected by glycolation or heating. Other mica-ceous minerals, such as muscovite, sericite (a fine-grained variety of muscovite), and biotite, are characterised by similar diagnostic properties, but the 10 Å peak of illite, which is less well crystallised, is commonly broader and tends to tail off toward higher d-spacings (Keller, 1964; Grim, 1968). Collectively, clay-sized phyllosilicate minerals characterised by 10 Å spacing will be referred to as “mica” or “mica-ceous minerals,” and the more specific term “illite” will be applied only if the 10 Å peak is broad and tails off toward higher d-spacings. Kaolinite and chlorite in glycolated preparations were identified by their combined, overlapping peaks at 7 Å (12.4° 2 θ), and the two minerals were differentiated by means of the relative differences in the height of the 7 Å peak after glycolation and heating (Biscaye, 1965; Thorez, 1975). The presence or absence of chlorite was also confirmed by the occurrence of 14 Å (6.3° 2 θ) and 3.5 Å (25.2° 2 θ) peaks. Expandable clay was identified on the basis of evidence for expansion of its lattice. After glycolation, expandable clay yields a peak at approximately 17 Å (5.19° 2 θ), and its exact position depends on the composition of the clay. Heating at >300 °C, however, causes this peak to shift to 10 Å (Carroll, 1970). In addition, the effects of glycolation and heating can be used to identify mixed-layer expandable clay minerals (Thorez, 1975). Relative abundances of major clay minerals were calculated using methods similar to those of Biscaye (1965), and mixed-layer components were characterised by the techniques of Thorez (1975).

Table 1
Description of rock samples from bare (lichen- and moss-free) areas of the gneiss outcrop.

Sample	Description of hand specimens	Description based on microscopic examination of thin sections
Rock-1	Pink granitic gneiss with minor amounts of evenly distributed black mafic mineral grains characterised by lineation (i.e., elongation in the same direction).	Major minerals were potassium feldspar (mainly microcline with “gridiron” texture) and plagioclase feldspar displaying albite twinning, with subordinate quartz and minor amounts of biotite (comprising ~5% of the bulk mineral content). Much of the plagioclase, but very little of the potassium feldspar, showed extensive sericitisation. Edges of biotite crystals showed alteration (a light-coloured zone extending from the outside inward or ragged ends breaking up into minute whiskers, suggesting chloritisation). No primary mafic minerals other than biotite were detected.
Rock-2	Granitic gneiss with a coarse quartz band, a coarse pink band rich in feldspar (comparable to pegmatite), and a black band enriched in mafic mineral grains. The pink and black bands were sharply differentiated from each other.	The pink band consisted almost entirely of potassium feldspar and plagioclase feldspar, with subordinate quartz. Plagioclase was preferentially sericitised, as in Rock-1. No mafic minerals were seen. The black band contained abundant biotite (comprising ~20% of the bulk mineral content). Some biotite crystals had ragged edges, suggesting slight alteration (possibly chloritisation). No primary mafic minerals other than biotite were detected in the black band.

Chemical analyses of soil samples were carried out in the following manner. Coarse moss and lichen debris was removed, and the soil was oven-dried at ~60 °C and ground with a mortar and pestle, whereupon its organic content was determined by weighing out 1 g and measuring loss on ignition (LOI) at 1040 °C for 30 minutes. The ash remaining after ignition was then mixed with lithium tetraborate, and the mixture was melted in a platinum crucible heated by a Bunsen burner to form a fused glass pellet, which was analysed for the major rock-forming elements (Si, Al, Fe, Ca, Mg, Na, and K) by X-ray fluorescence performed under a vacuum by means of a Philips PW 1480 X-ray spectrometer with a rhodium X-ray tube and PW 1510 sample changer. Included with the samples for the purpose of confirming instrument calibration were standard materials (soils and rocks) supplied by the U.S. National Institute of Standards and Technology (NIST). The bare rock samples were analysed using comparable methods: Portions of the rock specimens were pulverised in a tungsten carbide Shatterbox, homogenised, and then subjected to elemental analysis by fused disk wavelength dispersive X-ray fluorescence.

3. Results and discussion

3.1. Baseline conditions: the mineralogy and chemical composition of the bare rock

The mineral composition and other properties of the bare rock samples as determined by examination of hand specimens and thin sections are summarised in Table 1, and the results of X-ray diffraction analysis and chemical analysis of the rocks are presented in Tables 2 and 3, respectively.

X-ray diffraction analysis and microscopic examination of thin sections of pink and black bands of the rock samples revealed that the major minerals of the rock were coarse-grained potassium feldspar (which consisted primarily, if not entirely, of microcline with “gridiron” cleavage) and somewhat less abundant plagioclase feldspar (which displayed albite twinning), together with subordinate quartz and biotite (Tables 1 and 2). As estimated from the study of thin sections using the visual comparison technique of Terry and Chilingar (1955), biotite accounted for only ~0–5% of the pink bands but ~20% of a representative specimen of a prominent black band (Table 1). Biotite appeared to be the only mafic mineral in the rock: No amphiboles or pyroxenes were detected, either by X-ray diffraction or by microscopic examination. The biotite showed perfect micaceous cleavage and “bird’s eye maple” texture, and it was commonly found to be dichroic when viewed in thin section, changing from pale brown to moderately deep green as the stage of the microscope was rotated with the Nicol prisms uncrossed. On the basis of its bulk mineral composition and foliation (which included lineation displayed by evenly scattered biotite crystals

in predominantly pink bands as well as differentiation into distinct, large-scale pink and black bands), the rock may, with confidence, be classed as granitic gneiss.

Considering the heterogeneity of the outcrop (in particular its large-scale banding) and the fact that the data represent only two hand specimens of the rock, the mineral abundances are to be regarded as rough preliminary estimates. Nevertheless, the mineralogical data are of key importance, as they reveal the identities and, to a first approximation, the abundances of the major and minor primary rock-forming minerals and secondary minerals formed by hydrothermal alteration or weathering processes unrelated to the activities of the lichens and mosses (e.g., abiotic weathering by meteoric water), or both. Thus, the mineralogical data for the bare rock samples establish the baseline conditions for assessment of the effects of biologically enhanced chemical weathering (i.e., a basis for comparison of rock-altering processes in the presence and absence of the lichens and mosses). Note that the two rock samples had similar concentrations of potassium feldspar, plagioclase feldspar, and quartz (Tables 1 and 2) and were similar in chemical composition (Table 3). Spatial variations in the mineral composition of the rock appear to have been due mainly to variations in the abundance of biotite (Table 1) – not surprisingly, as the gneiss was made up of macroscopic biotite-poor felsic bands alternating with biotite-enriched bands. Moreover, only one of the two rock samples contained detectable amounts of clay-sized phyllosilicate minerals (Table 2), probably reflecting the uneven distribution and low concentrations of these phyllosilicates.

The bare rock showed no sign of alteration on a macroscopic scale, but microscopic examination revealed extensive sericitisation of feldspar crystals and indications of presumptive chloritisation of biotite. Sericitisation was mostly confined to plagioclase feldspar; in contrast, potassium feldspar showed very little alteration. Accordingly, many plagioclase crystals were riddled with sericite crystals, which occupied large regions of the host crystals or were concentrated along cleavage lines. Alteration of biotite crystals, however, was limited to the edges of the crystals. Thus, the ends of the biotite crystals commonly had ragged edges broken up into minute whiskers, suggesting alteration to chlorite, and some biotite crystals were surrounded by light-coloured zones indicative of chemical alteration which advanced from the outside inward.

X-ray diffraction analysis of the clay-sized fractions of the two rock samples revealed the presence of small but measurable amounts of mica and chlorite in one of them (Table 2). Judging from the results of thin section examination, we may conclude that [1] the mica consisted of sericite formed by alteration of feldspar, possibly accompanied by illite owing to degradation of the sericite or feldspar, or both, and that [2] the chlorite was formed by alteration of biotite. Additional research, however, would be needed to establish the exact mineral composition

Table 2
Results of X-ray diffraction analysis of bare rock samples.^a

Sample	Mineral abundance in bulk sample (%)							Mineral abundance in clay fraction ^b (%)			
	Potassium feldspar	Plagioclase feldspar	Quartz	Amphiboles	Pyroxenes	Calcite	Clay ^b	Mica ^c	Chlorite ^d	Expandable clay	Kaolinite
Rock-1	43.3	31.7	14.6	0	0	0	10.2	37.5	62.4	0	0
Rock-2	54.0	32.4	13.4	0	0	0	0	0	0	0	0

^a For additional information, see descriptions of hand specimens and thin sections in Table 1.

^b <3.9 μm fraction.

^c Evidence obtained by examination of thin sections supports the inference that the “mica” consisted predominantly, if not wholly, of sericite (fine-grained muscovite) formed by hydrothermal alteration or abiotic weathering of feldspar (see Table 1), although some of this material may have been degraded to illite. The presence of trace quantities of clay-sized primary biotite particles produced by pulverisation of the rock is also a possibility, although the distribution of points in Fig. 1 suggests that this is unlikely (see explanation in Section 3.2 of the text).

^d Evidence obtained by examination of thin sections suggests that the chlorite was formed by hydrothermal alteration or abiotic weathering of biotite (see Table 1).

of the mica and to test the hypothetical possibility that the mica included fine particles of unaltered biotite formed by pulverisation of the rock. The formation of sericite (possibly accompanied by illite) by degradation of feldspar and the formation of chlorite by degradation of biotite could be attributed to abiotic weathering or hydrothermal alteration at a late stage of igneous and metamorphic activity, or both (Millot, 1970). The fact that sericitisation preferentially affected the plagioclase feldspar suggests that this process was caused by meteoric water slowly infiltrating the rock during the initial stage of abiotic weathering (Millot, 1970).

Despite the ambiguity surrounding the process responsible for the abiotic alteration of the feldspars and biotite, one fundamentally important conclusion may be drawn: The process had relatively weak effects, as the end products consisted solely of fine-grained mica and chlorite. More intense alteration would have yielded end products such as expandable clay minerals and kaolinite (Keller, 1964). As revealed in the next section, biological alteration of the rock was much more intense and effective.

3.2. Weathering, secondary mineral genesis, and soil formation caused by lichens and mosses

The taxonomic classification of the lichens and mosses is recorded in Table 4, the results of the chemical analyses of the organisms are shown in Table 5, and the mineralogical and chemical data for the associated soils are presented in Tables 6 and 7, respectively.

The soils underlying the lichens and mosses contained assemblages of secondary minerals whose abundances and composition clearly indicated that alteration of the rock by the organisms was far more intense and effective than alteration in the absence of those organisms. As the production of the secondary minerals and the soils which contained them occurred only in the presence of the lichens and mosses, these processes are attributable solely to biochemical activities of the lichens and mosses and associated microorganisms. Thus, the clay-sized fraction of the bare rock comprised a very minor proportion of the rock-forming minerals ($\leq 10\%$) and consisted solely of chlorite and mica (Table 2), whereas the clay-sized fraction of the soil associated with the lichens and mosses comprised a much larger proportion of the mineral fraction of the soil (~30–80%) and contained various kinds of expandable clay and, in several cases, kaolinite, which was usually accompanied by calcite, in addition to mica and chlorite (Table 6). The expandable clay minerals and, in particular, the kaolinite, prove that weathering due to the activities of the lichens and mosses colonising

the rock had much stronger effects than the weathering of bare rock surfaces, and the presence of calcite implies that the weathering action of mosses and associated microorganisms was at least partially due to carbonic acid (H_2CO_3) formed by the reaction of respiratory CO_2 with water.

Another noteworthy feature of the clay in the biogenic soil is that the 10 Å X-ray diffraction peak of the mica was invariably rather broad and tailed off toward higher d-values, demonstrating that the mica consisted primarily, if not entirely, of illite, which was probably formed by degradation of the sericite and feldspars in the rock. The mineral composition of the expandable clay, moreover, varied with the nature of the organisms and therefore showed marked variation over short distances (Table 6). The minerals in this category included smectite, swelling chlorite, and an assortment of mixed layer minerals (illite–smectite, chlorite–smectite, chlorite–swelling chlorite, chlorite–vermiculite, illite–vermiculite, etc.) suggesting degradation of mica and chlorite inherited from the rock. It is also worth mentioning that the soils contained major amounts of organic matter (LOI ≈ 18 –60%) (Table 7) which, judging from its brown or black colour (see above), consisted mainly of humic substances.

The abundance of the clay in the biogenic soils and the heterogeneity of its mineral composition – i.e., the patchy distribution of kaolinite and calcite and specific varieties of expanding clay (Table 6) – constitute strong evidence that the clay minerals and calcite were formed in situ as a result of biologically mediated chemical weathering. These considerations rule out the hypothetical possibility that the minerals were transported to the sampling site as wind-blown dust from the mid-continental prairie region, which lies west and south of the field area: If the mineral deposits had been aeolian, one would expect the mineral composition of the clay-sized fraction of the soil to have been virtually uniform, and the clay fraction as a whole to have been orders of magnitude smaller. Trace quantities of allochthonous airborne montmorillonite (smectite) have been found in snow collected in the ELA (Brunskill et al., 1971), but the evidence presented here strongly supports the conclusion that the secondary minerals in the soils underlying the lichens and mosses were autochthonous and were formed by interactions of the organisms with the rock. However, the weathering and secondary mineral-forming activities of lichens and mosses were found to differ greatly from each other, both qualitatively and quantitatively, and different species and genera of moss differed widely among themselves in that regard.

The mineral fraction of soil associated with lichens invariably had a higher proportion of clay and generally had a lower proportion of

Table 3
Chemical composition of bare rock samples.

Sample	Total element concentration ($\text{mmol} \cdot \text{g}^{-1}$) ^a						
	Si	Al	Fe	Mg	Ca	Na	K
Rock-1	12.0 ± 0.0	2.75 ± 0.00	0.29 ± 0.00	0.13 ± 0.00	0.263 ± 0.003	1.2 ± 0.0	0.976 ± 0.001
Rock-2	12.0 ± 0.1	2.97 ± 0.01	0.25 ± 0.00	0.17 ± 0.00	0.353 ± 0.000	1.5 ± 0.0	0.742 ± 0.001

^a Mean of duplicate values ± standard error.

Table 4
The taxonomic classification of the lichens and mosses.

Type of organism	Sample	Classification
Lichen	L1a	<i>Stereocaulon paschale</i> (L.) Hoffm.
Lichen	L1b	<i>Cladonia mitis</i> (Sandst.) Hustich [dominant species] + <i>Cladonia uncialis</i> + <i>Cladonia phyllophora</i> Ehrh. ex Hoffm.
Lichen	L2	[Unidentified fruticose lichens]
Lichen	L3a	<i>Cladina rangiferina</i> (L.) Nyl.
Lichen	L3b	<i>Cladonia uncialis</i> (L.) Weber ex Wigg [dominant species] + <i>Cladina mitis</i> (Sandst.) Hustich + <i>Cladina rangiferina</i>
Lichen	L4	[Unidentified fruticose lichens]
Moss	M1	<i>Pohlia nutans</i>
Moss	M2	<i>Polytrichum commune</i>
Moss	M3	<i>Polytrichum juniperinum</i>
Moss	M4	<i>Hedwigia ciliata</i> + <i>Grimmia</i> sp.
Moss	M5	<i>Polytrichum</i> sp. (possibly <i>Polytrichum juniperinum</i>)
Moss	M6	<i>Grimmia</i> sp. (possibly <i>Grimmia pilifera</i>)
Moss	M7	<i>Pleurozium schreberi</i>

feldspar (i.e., potassium feldspar + plagioclase feldspar), than the mineral fraction of soil associated with mosses (Fig. 1; Table 6). Similarly, it was noted in the field that the soils associated with several species of moss (*Hedwigia ciliata*, *Grimmia* sp., *Polytrichum juniperinum*, and *Polytrichum* sp.) contained ample quantities of coarse sand-sized mineral particles, which undoubtedly consisted of residual feldspar and quartz grains remaining after disintegration of the underlying rock, whereas sandy material was not detected in any of the soils formed by lichens. Evidently these mosses caused physical disintegration as well as chemical decomposition of the gneiss, but they were less effective than lichens in altering the feldspars to clay.

Furthermore, the mineral fractions of the soils associated with lichens showed a highly significant inverse correlation between total clay and total feldspar concentrations (Fig. 1). In contrast, the soils associated with mosses gave only an extremely weak, statistically insignificant inverse correlation that was almost obscured by scatter (Fig. 1); yet the fact that they show the same general tendency as the soils associated with lichens indicates that the trend is real. Significantly, both of the observed trends, if extrapolated to lower clay and higher feldspar concentrations, converge at or very near a point representing the bare rock (Fig. 1), as would be expected since the rock was the parent material from which the soil minerals were derived. This implies that there was no detectable overestimate of the proportion of clay-sized material in the rock owing to production of artificial clay-sized biotite particles during pulverisation of the rock samples. Otherwise, the position of the point representing the rock would be anomalously high with respect to the trends representing the soil samples. Also note that soils formed by mosses generally had lower concentrations of organic matter

than soils formed by lichens (Table 7), probably owing to their relatively high concentrations of sand-sized mineral grains.

The relationships illustrated in Fig. 1 lead to two major inferences: [1] the lichens and mosses (probably with the aid of associated microorganisms) mediated the alteration of the feldspars in the rock to clay minerals, and [2] the lichens caused more rapid and effective chemical weathering of the feldspars than did the mosses (although the mosses were more effective agents of physical weathering) and therefore produced larger amounts of clay (irrespective of the mineral composition of the clay). In certain other ways, however, the mosses were much more effective chemical weathering and secondary mineral-forming agents than the lichens, as revealed by examination of the identities and abundances of specific kinds of secondary minerals in the mineral assemblages of the biogenic soils.

Now, therefore, let us consider the abundances of particular kinds of clay minerals in the soils produced by the lichens and mosses. For the purpose of judging the effects of biologically mediated weathering, it is useful to compare the combined abundances of expandable clay and kaolinite, which owe their existence solely to biological weathering, relative to the combined abundances of mica and chlorite, which were partly, if not wholly, inherited from the rock, though probably in a somewhat degraded state owing to effects of biological weathering (e.g., alteration of sericite to illite). Thus, it is reasonable to assume that the proportion of expandable clay + kaolinite relative to chlorite + illite in the clay-sized fraction increased with the intensity of the biological weathering process. The presence of kaolinite signifies the most intense weathering of all, as particularly strong leaching of Si and metal cations tends to degrade expandable clay and other silicates, such as feldspars and mica, to kaolinite (Keller, 1964, 1970).

Despite the evidence that lichens were more effective than mosses in altering feldspars to clay minerals (Fig. 1), the clay fraction of soil formed by mosses usually had higher proportions of expandable clay + kaolinite relative to mica + chlorite than the clay-sized fraction of soil formed by lichens (Fig. 2a–d), indicating that in this respect, at least, chemical weathering mediated by mosses was generally more intense, and therefore produced more severely degraded end products, than weathering mediated by lichens. The proportion of expandable clay alone tended to be higher in soils formed by mosses than in soils formed by lichens, although there was some overlap (Table 6); kaolinite, however, was found only in soils formed by certain species of moss (*Pohlia nutans* and *Grimmia* sp., either alone or associated with *Hedwigia ciliata*) (Fig. 2c; Tables 4 and 6), implying that the weathering action of those particular species was especially strong: None of the soils formed by other species of moss or by any of the lichen species contained detectable kaolinite. Evidently *P. nutans* was the most effective biological weathering agent of all, as the clay fraction of the soil associated with it had the highest proportion of kaolinite.

Table 5
The chemical composition of the lichens and mosses.

Sample ^a	Total element concentration (mmol · g ⁻¹) ^{b,c}						
	Si	Al	Fe	Mg	Ca	Na	K
L1a	0.18	0.0164	0.00709	0.00790	0.0150	0.0020	0.0340
L1b	0.13	0.0146	0.00684	0.00786	0.00961	0.00087	0.0274
L2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L3a	0.15	0.0155	0.00706	0.0104	0.0155	0.00722	0.0244
L3b	0.093	0.0123	0.00569	0.00950	0.0125	0.0015	0.0327
M1	5.77	0.574	0.222	0.0749	0.0362	0.00570	0.0683
M2	0.160	0.133	0.00623	0.0308	0.0454	0.0027	0.130
M3	0.655 ± 0.050	0.0426 ± 0.0011	0.0152 ± 0.0003	0.0533 ± 0.0134	0.108 ± 0.036	0.0017 ± 0.0002	0.0956 ± 0.00435
M4	4.20	0.342	0.134	0.0596	0.0379	0.0026	0.0813
M5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M6	3.95	0.213	0.105	0.0506	0.0424	0.0027	0.0803
M7	1.26 ± 0.47	0.121 ± 0.036	0.0445 ± 0.0135	0.0378 ± 0.0132	0.0953 ± 0.0117	0.0023 ± 0.0001	0.0718 ± 0.0160

^a The identities of the lichen and moss species are shown in Table 4.

^b Each value in the table is either the result of a single analysis or the mean of duplicate values ± the standard error.

^c "n.d." means no data.

Table 6
Results of X-ray diffraction analysis of soils formed by lichens and mosses.^a

Sample ^b	Abundance in mineral fraction of bulk sample (%)							Abundance in clay fraction ^c (%)			
	Potassium feldspar	Plagioclase feldspar	Quartz	Amphiboles	Pyroxenes	Calcite	Clay ^c	Mica ^d	Chlorite	Expandable clay	Kaolinite
L1	6.5	7.5	7.1	0	0	0	78.7	57.1	33.8	9.1 ^e	0
L2	0	23.7	71.9	0	0	0	69.1	60.9 ± 3.8	32.6 ± 3.2	6.6 ± 0.7 ^e	0
L3	6.8	4.9	7.1	0	0	0	81.1	59.1	38.6	2.3 ^e	0
L4	5.3	6.4	6.3	0	0	0	81.8	66.5 ± 3.1	32.3 ± 1.9	1.3 ± 1.3 ^e	0
M1	5.5	31.4	8.9	0	0	1.8	52.2	51.3	15.3	17.9 ^f	15.5
M2	8.2	19.0	12.8	2.0	15.9	0	41.8	47.1	29.4	23.5 ^g	0
M3	10.4 ± 0.4	9.5 ± 0.8	21.2 ± 3.2	0 ± 0	3.6 ± 3.6	1.9 ± 1.9	53.4 ± 3.3	44.3 ± 6.8	37.8 ± 12.3	18.0 ± 5.5 ^h	0
M4	5.3	11.5	19.2	2.3	27.6	4.0	29.8	60.5	26.0	9.3 ^h	4.2
M5	19.9	18.5	8.4	7.1	15.4	0	30.4	58.2	29.1	12.7 ^g	0
M6	9.9	36.6	15.6	4.0	0	0	33.6	82.6	7.0	10.1 ^e	0.3
M7	17.9 ± 6.6	30.9 ± 12.2	17 ± 11	4.2 ± 4.2	0 ± 0	0 ± 0	30.0 ± 9.7	62.2 ± 3.7	31.1 ± 0.7	6.8 ± 3.0 ⁱ	0

^a Each value in the table is either the result of a single analysis or the mean of duplicate values ± the standard error.

^b The sample designations identify the organisms associated with the soil (see Table 4). Sample L1 was associated with lichen specimens L1a and L1b, and sample L3 was associated with lichen specimens L3a and L3b; in these two cases it was not possible to separate the soils associated with the individual lichen specimens.

^c The <3.9 μm fraction of the soil minerals.

^d Illite (or mainly illite).

^e Swelling chlorite; mixed layer illite-smectite, chlorite-smectite, and/or chlorite-swelling chlorite; mixed layer illite-chlorite and/or illite-vermiculite; mixed layer illite-swelling chlorite and/or chlorite-vermiculite.

^f Smectite; swelling chlorite; mixed layer illite-smectite, chlorite-smectite, and/or chlorite-swelling chlorite; mixed layer illite-chlorite and/or illite-vermiculite; mixed layer illite-swelling chlorite and/or chlorite-vermiculite.

^g Mixed layer illite-chlorite and/or illite-vermiculite; mixed layer illite-swelling chlorite and/or chlorite-vermiculite.

^h Mixed-layer illite-swelling chlorite and/or chlorite-vermiculite.

ⁱ Smectite; mixed layer illite-chlorite and/or illite-vermiculite; mixed layer illite-swelling chlorite and/or chlorite-vermiculite.

Patterns of variation in the mineral composition of the expandable clay also revealed systematic differences between the secondary mineral-forming processes of lichens and mosses and different taxonomic groups of mosses (Tables 4 and 6). All species of lichen produced the same combination of expandable clay minerals (i.e., swelling chlorite + certain mixed layer clays). However, only one species of moss (*Grimmia* sp.) produced this particular assortment of expandable clay minerals; all other species of moss produced distinctly different mineral assemblages. The mineral composition of the mixture varied considerably among the different species of mosses, but all soils produced by *Polytrichum* species (a total of three samples) had identical combinations of expandable clay minerals. Moreover, pure smectite (as distinct from smectite layers in mixed layer clay) occurred only in soils formed by certain species of moss (*Pohlia nutans* [the species which produced the largest quantity of kaolinite] and *Pleurozium schreberi*). In summary, the nature of the organism determined the mineral composition of the expandable clay fraction as well as the presence or absence of kaolinite. All species of lichen produced the same characteristic assemblage of expandable clay minerals, and all but one of the moss species produced distinctly different assemblages which varied considerably among themselves; moreover, the genus *Polytrichum* consistently produced a distinctive mineral assemblage of its own, and certain species of moss were the

only organisms that produced a pure smectite phase. These observations strongly confirm the conclusion that biochemical activities of the lichens and mosses and associated microorganisms produced the clay and that particular kinds of organisms generated particular assemblages of clay minerals owing to differences in their biochemical activities.

On the basis of these results and well known, well documented processes of chemical weathering (Keller, 1964, 1970; Millot, 1970), we may reasonably assume that intense leaching of Si and metal cations from the rock as a result of biological activities caused the feldspars, biotite, sericite, and chlorite in the rock to be altered to illite and expandable clay minerals, and wherever the leaching process was particularly intense, the end product of the biological weathering process was kaolinite. Obviously these reactions did not go to completion, as chlorite, illite, and expandable clay were present in all soil samples, including the ones containing kaolinite (Table 6), but this would seem to be the most probable tendency of the biological weathering process. In any case, a striking feature of the biological weathering process was that within the microenvironments in which it occurred (i.e., the rock surfaces directly beneath the lichens and mosses) it reached a level of intensity far exceeding that of the weathering processes which occurred in the absence of these organisms. The importance of such microenvironments in chemical weathering and clay

Table 7
The chemical composition of the soils formed by lichens and mosses.

Sample ^a	Total element concentration (mmol · g ⁻¹) ^b							Loss on ignition (%)
	Si	Al	Fe	Mg	Ca	Na	K	
L1	5.569	1.91	0.257	0.16	0.11	0.32	0.261	61.66
L2	6.121	1.93	0.283	0.22	0.15	0.33	0.19	58.58
L3	6.131	1.83	0.285	0.19	0.077	0.19	0.24	58.82
L4	6.509	1.94	0.297	0.19	0.082	0.22	0.25	56.34
M1	6.227	2.12	0.292	0.19	0.095	0.27	0.24	57.96
M2	9.464	3.62	0.405	0.29	0.277	0.796	0.279	31.55
M3	10.32 ± 0.24	2.86 ± 0.01	0.220 ± 0.002	0.14 ± 0.00	0.142 ± 0.005	0.544 ± 0.026	0.545 ± 0.026	33.99 ± 1.49
M4	11.56	3.50	0.510	0.35	0.344	0.992	0.442	18.68
M5	11.26	3.910	0.482	0.473	0.462	1.14	0.281	21.40
M6	12.41	3.68	0.412	0.36	0.372	1.02	0.450	17.54
M7	7.395 ± 0.228	2.35 ± 0.12	0.320 ± 0.025	0.21 ± 0.01	0.18 ± 0.04	0.38 ± 0.07	0.25 ± 0.02	49.70 ± 1.59

^a The sample designations identify the organisms associated with the soil (see Table 4). Sample L1 was associated with lichen specimens L1a and L1b, and sample L3 was associated with lichen specimens L3a and L3b; in these cases it was not possible to separate the soils associated with the individual lichen specimens.

^b Each value in the table is either the result of a single analysis or the mean of duplicate values ± the standard error.

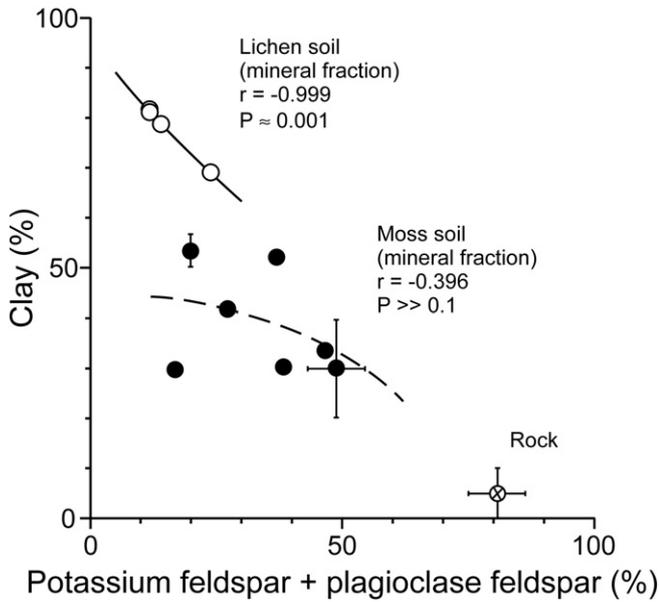


Fig. 1. Relationships between the abundances of clay and feldspars (i.e., potassium feldspar + plagioclase feldspar) in the mineral fraction of soil formed by lichens (○) and mosses (●) and in the bare rock (⊗).

formation has rightly been emphasised by Keller (1970) and has been observed in other instances of highly intensified chemical weathering and secondary mineral production mediated by rock-dwelling organisms, such as the lichens colonising Hawaiian lava flows (Jackson, 1968, 1993; Jackson and Keller, 1970a,b). Similarly, there is evidence that individual bacterial cells in lake sediments may create microenvironments in which alteration and biochemically mediated neof ormation of minerals may occur (Jackson et al., 2011).

Not surprisingly, given the fact that mosses tended to be more effective weathering agents than lichens as implied by the mineral composition of the clay fraction of the biogenic soil, the mosses generally had much higher concentrations of the rock-forming elements Si, Al, Fe, Ca, Mg, K, and Na than the lichens (Fig. 3a–e; Table 5). Clearly the rock-forming elements solubilised by the lichens and mosses were accumulated to a significant extent by the organisms. Evidence for this was provided by the relationship between biogenic kaolinite formation and the bioaccumulation of rock-derived elements. Thus, the mosses that brought about the formation of kaolinite were the ones that were most highly enriched in Si, Al, and Fe released from the rock; and kaolinite concentration in associated soil increased progressively with increasing element concentration in the moss (Fig. 4a–c; Tables 5 and 6). These correlations clearly reflect the fact that intense leaching of Si and metal cations is conducive to kaolinite genesis (Keller, 1964, 1970). Furthermore, portions of the leached elements were undoubtedly retained in exchangeable, bioavailable forms in the biogenic soils

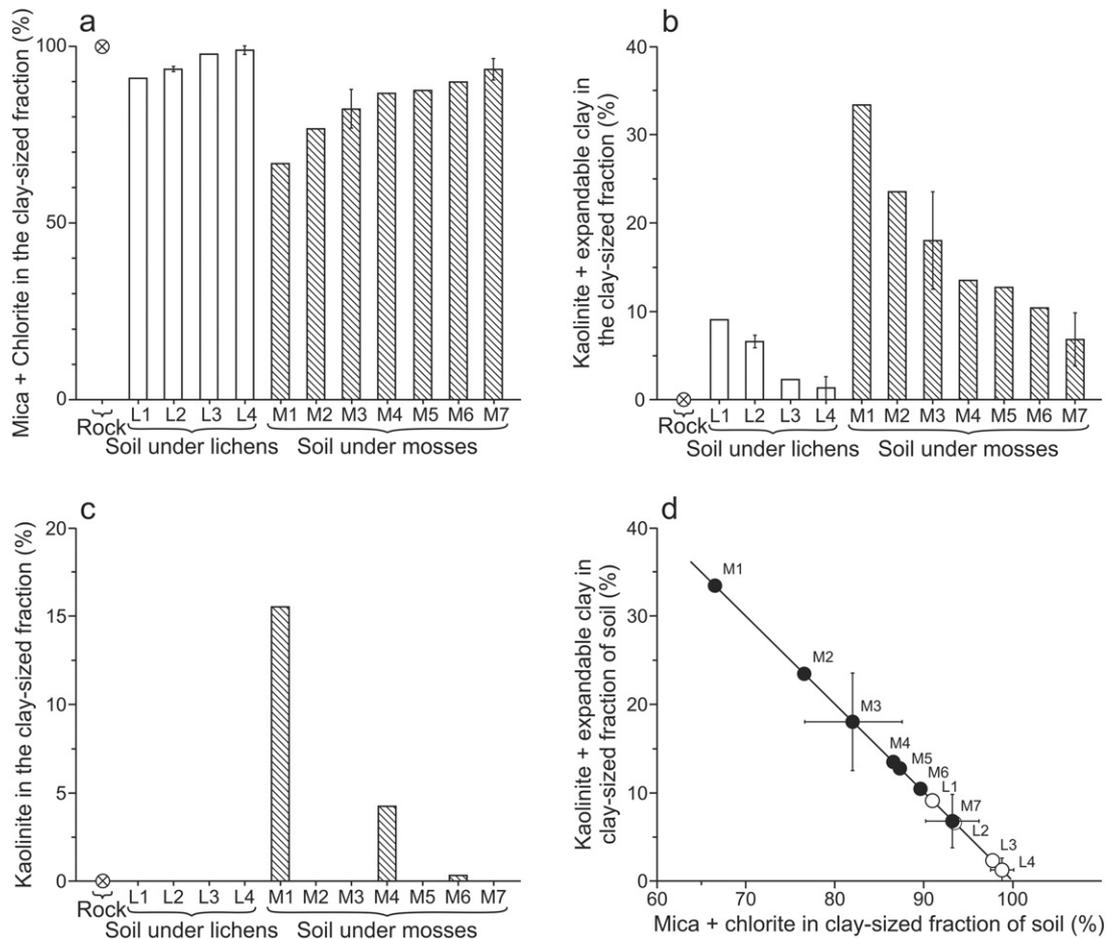


Fig. 2. Concentrations of (a) mica + chlorite, (b) kaolinite + expandable clay, and (c) kaolinite in the clay-sized fractions of the bare rock (⊗) and the soils underlying the lichens (open bars) and mosses (shaded bars), and (d) a plot showing variation in the concentration of kaolinite + expandable clay relative to the concentration of mica + chlorite in the clay-sized fractions of soils associated with lichens (○) and mosses (●). Error bars: mean of duplicates ± standard error. Absence of error bar denotes single value. Note: The purpose of panel d is simply to illustrate the variations in the proportions of different clay minerals (and hence in the relative intensity of chemical weathering) in the soils formed by different species of lichens and mosses. The plot is not intended as statistical proof of the obvious fact that the two variables are inversely related: As the proportions of [kaolinite + expandable clay] and [mica + chlorite] in the clay fraction of each sample add up to a total of 100%, there is, of course, an inherent inverse linear correlation between the two variables.

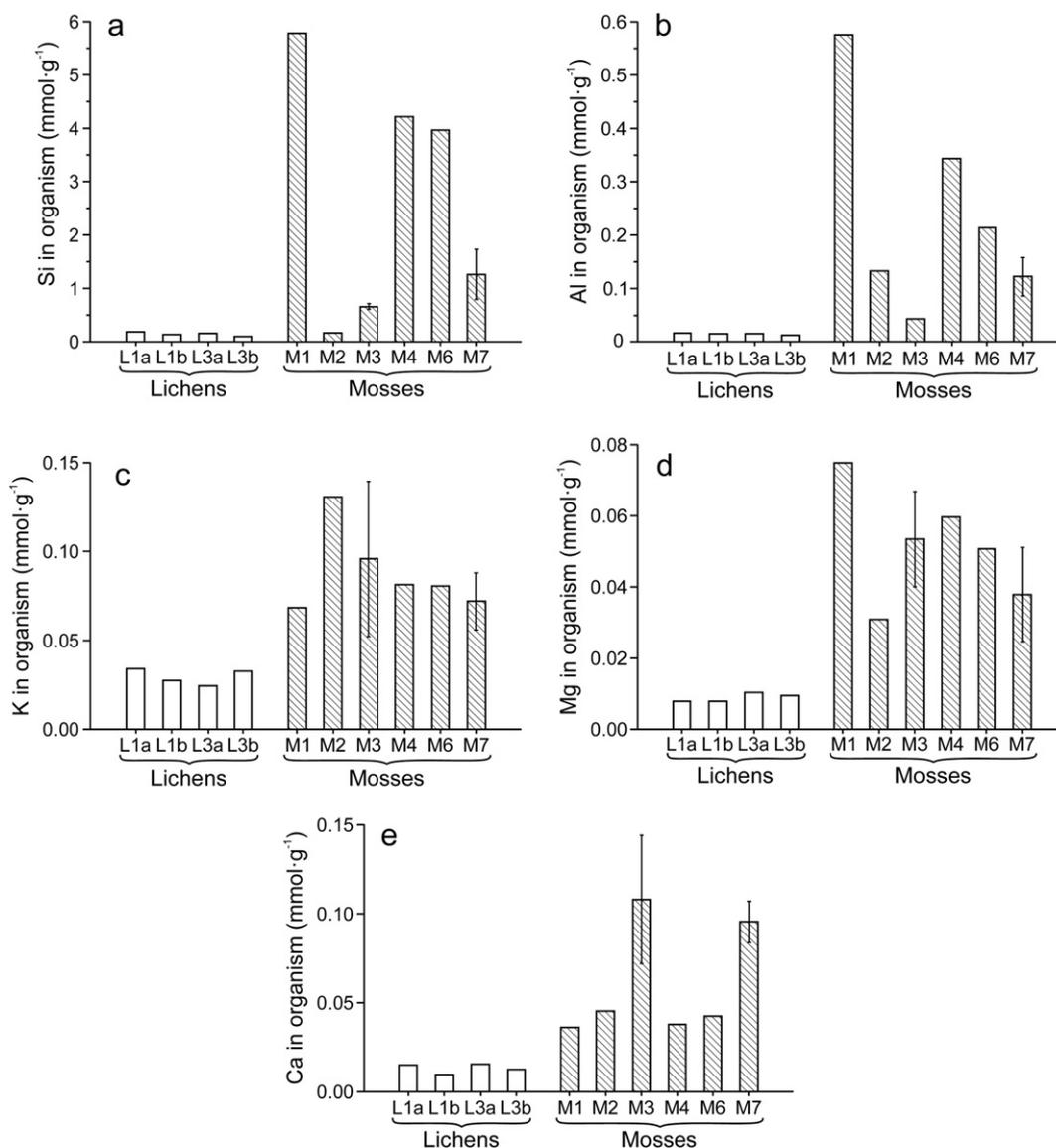


Fig. 3. Concentrations of (a) Si, (b) Al, (c) K, (d) Mg, and (e) Ca in lichens (open bars) and mosses (shaded bars). Error bars: mean of duplicates \pm standard error. Absence of error bar denotes a single value or signifies that the error bar is too small to be shown.

owing to reversible adsorption and surface complexation by clay minerals and humic matter (Jackson, 1995, 1998).

Preferential solubilisation and accumulation of certain rock-forming elements relative to others by lichens and mosses were also involved in the weathering and secondary mineral forming process. Thus, kaolinite formation mediated by mosses increased with the Mg/Ca mole ratio of the moss (Fig. 4d), suggesting that preferential removal of Mg relative to Ca from water in contact with the rock surface helped to promote the formation of kaolinite, and hinting at the possibility that some of the kaolinite was formed by degradation of biotite and chlorite. Similarly, lichens and, to a greater extent, mosses preferentially accumulated Si relative to Al; accordingly, the Si/Al mole ratios of the lichens and mosses were much higher than the Si/Al ratio of the unweathered rock, indicating preferential solubilisation and bioaccumulation of Si relative to Al, and mosses generally had higher Si/Al ratios than lichens (Fig. 5). In contrast, the soils associated with the lichens and mosses had lower Si/Al ratios than the rock (Fig. 5), reflecting depletion in Si relative to Al. Preferential mobilisation and removal of Si relative to Al must have helped to promote the formation of kaolinite, which is poor in Si relative to Al (Keller, 1964, 1970).

The mole concentrations of major rock-forming elements (with the exception of K) in the mosses that mediated kaolinite formation show a highly significant positive correlation with the charge/radius ratio (ionic potential) of the cation of the element (on the reasonable assumption that the coordination number of Si⁴⁺ was 4 [as in the Si–O tetrahedra of clay minerals], that the coordination number of each metal cation was 6 [as in the octahedral layers of clay minerals], and that Fe was in the form of Fe³⁺). This relationship is well illustrated by the data for *P. nutans*, the species of moss which contained the highest mole concentrations of Si and metals and produced the soil containing the greatest abundance of kaolinite (Fig. 6). The other two specimens of moss which produced detectable quantities of kaolinite yielded virtually identical and equally significant results (not shown; see Tables 5 and 6). In contrast, the other kinds of moss and the lichens, none of which produced kaolinite, showed much weaker correlations between the element concentration in the organism and the charge/radius ratio (not shown; see Tables 5 and 6). Enhanced bioaccumulation of rock-forming elements evidently accompanied the exceptionally efficient biochemically promoted solubilisation and leaching of those elements which led to the formation of kaolinite and may well have accelerated this process in accordance with the law of mass action.

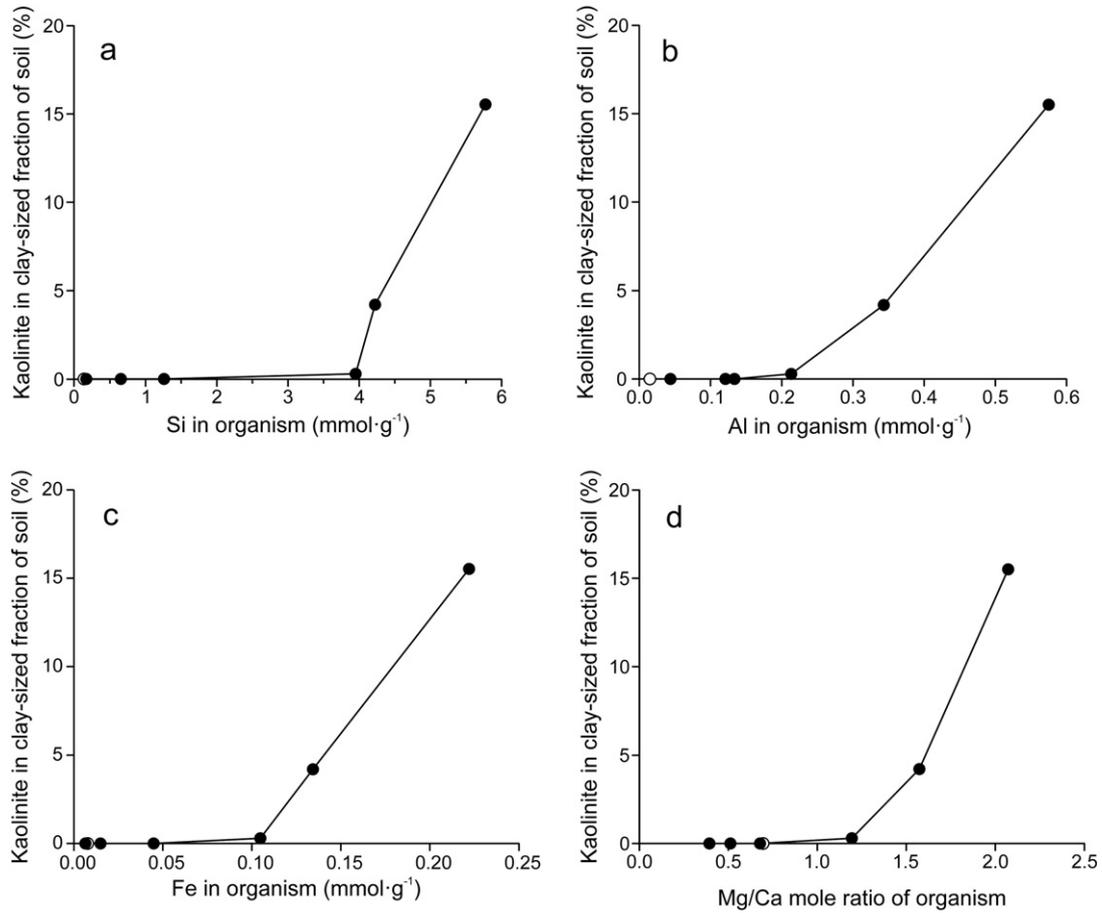


Fig. 4. Plots showing variations in the concentrations of kaolinite in the clay-sized fraction of soil as functions of the concentrations of (a) Si, (b) Al, and (c) Fe in the lichens (○) and mosses (●) that produced the soil and (d) the Mg/Ca mole ratios of the organisms. In each plot the lichens are represented by one point representing the mean value for the four samples, whose individual values were too close together to be shown separately; but the mosses are represented by a single point for each sample, and each point represents a single value.

As the stability and degree of covalence of a bond linking a cation to another chemical species, such as a complexing agent, tends to increase with the charge/radius ratio of the cation (Basolo and Johnson, 1964; Companion, 1964), the relationship between bioaccumulation and the charge/radius ratio implies that the bioaccumulation of Si and metals involved carrier-mediated transport across cell membranes (i.e., the binding of the elements by carrier molecules). However, the concentration of K in the moss was anomalously high relative

to its charge/radius ratio (Fig. 6), implying that bioaccumulation of K was accomplished by a distinctly different and more efficient and selective mechanism which specialised in the active uptake of K⁺ ions. Preferential removal of K⁺ accompanied by a drop in pH

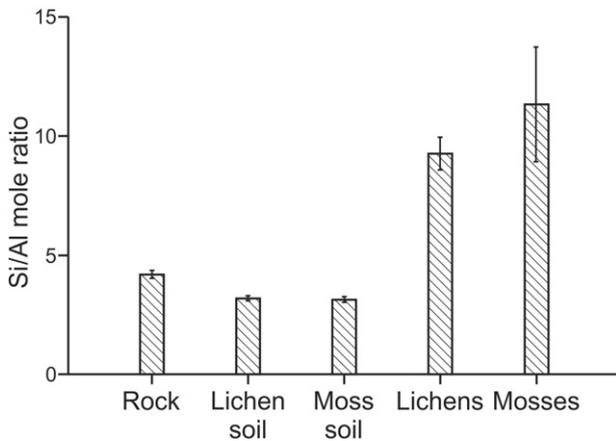


Fig. 5. Bar diagram showing the mean values of the Si/Al mole ratios of the bare rock, the soils associated with lichens and mosses, and the lichens and mosses themselves. Error bars: mean ± standard error. Number of replicates: rock, 2; lichen soil, 4; moss soil, 7; lichens, 4; mosses, 6.

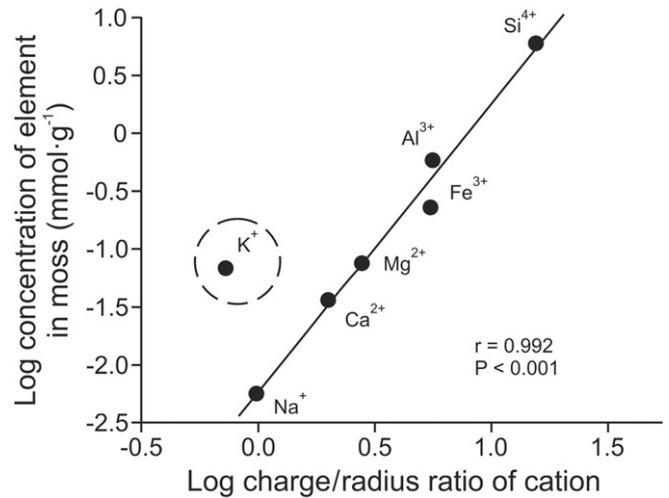


Fig. 6. Relationship between element concentration in the moss species *Pohlia nutans* and the charge/radius ratio of the element cation based on the presumed charge of the cation. The regression line represents all elements except K, whose concentration relative to the charge/radius ratio of its cation was anomalously high. The coordination number of Si⁴⁺ was assumed to be 4, and a coordination number of 6 was assigned to all the other cations. Source of charge/radius ratio values: Lide (2004).

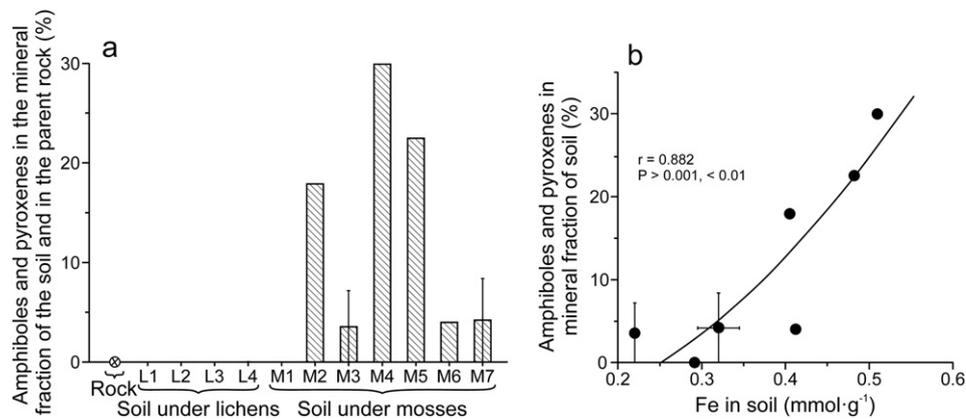


Fig. 7. (a) Concentrations of amphiboles + pyroxenes in the bare rock (⊗) and the mineral fractions of soil associated with lichens (open bars) and mosses (shaded bars); and (b) a plot of the concentration of amphiboles + pyroxenes in the mineral fraction of soil associated with moss against the total Fe concentration in the soil. Error bars: mean of duplicates \pm standard error. Absence of error bar denotes single value except in the case of the rock, which was analysed in duplicate.

owing to biological production of H_2CO_3 and other weak acids, such as humic matter and low molecular weight organic acids, resulting in exceptionally low ambient K^+/H^+ ratios, probably facilitated the biogenesis of kaolinite (Keller, 1970).

A particularly interesting and, indeed, astonishing fact revealed by the research was that the soils associated with all but one of the mosses, but none of the lichens, contained significant quantities of amphiboles or amphiboles + pyroxenes (Fig. 7a; Table 6), although the individual minerals have not been identified. Minerals of this type usually occur in igneous rocks and high-grade metamorphic rocks, but the gneiss on which the organisms were growing was completely devoid of amphiboles and pyroxenes (Tables 1 and 2). These observations lead to the conclusion that the minerals were authigenic and were produced solely by certain biochemical activities of mosses or associated microorganisms, or both. Moreover, the abundance of the combined amphibole and pyroxene components of the mineral fraction of the soil increased with the Fe concentration in the soil (Fig. 7b; Tables 6 and 7), implying that Fe, as might be expected, was one of the principal constituent elements of the minerals. The only species of moss that was not associated with detectable quantities of amphiboles and pyroxenes was *Pohlia nutans*, the species which was most highly enriched in the rock-forming elements Si, Al, Fe, and Mg and whose associated soil had the greatest abundance of kaolinite relative to other clay minerals (Figs. 2c and 3a, b, d; Tables 5 and 6). The absence of authigenic amphiboles and pyroxenes in the immediate vicinity of *P. nutans* suggests that those relatively reactive minerals were unstable in the zone of exceptionally intense chemical weathering created by the activities of this particular species or its microflora.

Surprising though it may seem, authigenic amphiboles and pyroxenes have been found in several ancient sedimentary rock formations (Milton and Eugster, 1959; Enlows and Oles, 1966; Milton et al., 1974; Fortey and Michie, 1978; De Ros et al., 1994), but to the best of the writer's knowledge the present paper is the first to report the discovery of authigenic minerals of this kind in soils and the first to present evidence for biologically mediated formation of such minerals. However, further research will be needed to verify and extend the intriguing but preliminary evidence reported here.

3.3. Mechanisms of chemical weathering and secondary mineral formation by lichens and mosses

As we have seen, all species of lichens and mosses (presumably with the assistance of associated microorganisms) strongly enhanced the chemical weathering of the granitic gneiss on which they were growing and mediated the formation of soils containing various biogenic secondary minerals. However, the weathering and secondary mineral-forming activities of lichens and mosses differed both qualitatively and

quantitatively from each other, and different species and genera of moss differed widely among themselves in that respect. Lichens were invariably more effective than mosses in altering rock-forming silicates (notably the feldspars) to clay minerals but were less effective in degrading the clay to expandable clay minerals and, unlike certain species of moss, were unable to cause sufficiently intense leaching of Si and metals to produce kaolinite. Hence, the clay minerals associated with lichens were illite and chlorite (the major clay minerals) along with minor amounts of expandable clay minerals (the only secondary minerals definitely known to have been produced by lichens), whereas mosses generally produced clay with higher proportions of expandable clay minerals and correspondingly lower proportions of chlorite and illite, and certain species of moss were the *only* organisms that leached Si and metals with sufficient intensity to generate kaolinite. In brief, lichens altered rock-forming silicates to clay at a higher rate, but mosses degraded the rock-forming silicates and the clay itself more intensely. The more intense weathering action of mosses is also demonstrated by the greater tendency of those organisms to accumulate solubilised rock-forming elements (Si and metals), and by the positive correlation of kaolinite abundance in associated soils with the Si, Al, and Fe concentrations and Mg/Ca ratios of the mosses. In addition, lichens consistently produced a distinctive assemblage of expandable clay minerals which differed from the assemblages produced by most species of moss. Moreover, the different species of moss varied greatly among themselves in that respect, and one particular genus of moss consistently produced a characteristic assemblage of its own. Another fundamental difference between the effects of lichens and mosses is that all but one of the moss species formed authigenic amphiboles and pyroxenes, whereas none of the lichens formed any of those minerals. These results imply the existence of major differences in both the intensity and the basic mechanisms of the weathering and secondary mineral-forming processes mediated by the different kinds of rock-dwelling organisms.

The evidence presented here suggests that the mechanisms of weathering and secondary mineral formation by lichens and mosses were as follows:

1. The association of calcite with kaolinite in soil formed by certain species of moss indicates that the weathering action of the mosses and their associated microfloras was at least partly due to H_2CO_3 formed by the reaction of biogenic CO_2 with water. During periods of rainfall this weak but aggressive acid, along with H^+ ions generated by hydrolysis, must have dissolved Ca^{2+} and Na^+ ions from plagioclase feldspars and exchange sites of expandable clay, producing mildly alkaline bicarbonate solutions from which CaCO_3 in the form of calcite precipitated (Keller, 1957). Calcite occurred only in soils containing kaolinite and was detected only in the soils with the highest concentrations of kaolinite (Table 4). Thus, both minerals were indicative of

particularly intense biochemical leaching of alkali and alkaline earth metal cations and silica. Leaching followed by precipitation of calcite and kaolinite as gradually accumulating increments probably took place during repeated episodes of wetting and drying.

2. In accordance with the law of mass action, the bioaccumulation of Si and metals by mosses and, to a generally lesser extent, by lichens increased the rate at which those elements were leached from the rock. The evidence presented here suggests that the formation of kaolinite by mosses resulted from exceptionally intense leaching of Si and metals from silicate minerals owing to particularly efficient uptake of those elements and preferential uptake of K^+ ions accompanied by production of weak biogenic acids (H_2CO_3 , humic matter, and possibly low molecular weight organic acids), leading to a drop in the ambient K^+/H^+ ratio (Keller, 1964, 1970).
3. The complexing of metal cations by chelating agents produced by the lichens and mosses and their associated microfloras probably played a major part in the biochemical weathering process and the formation of distinctive biogenic secondary minerals. In general, decomposition of minerals owing to solubilisation and sequestering of their divalent and polyvalent metal cations by biogenic chelating agents (lichen acids, oxalic acid, humic matter, etc.) is of key importance in chemical weathering (see Introduction). Besides decomposing metal-bearing minerals, chelating agents may nucleate the formation of secondary minerals. Thus, a chelate complex, because of its specific shape and coordination number, may function as a template for the epitaxial growth of a specific crystal structure. The presence of authigenic amphiboles and pyroxenes in soils formed by mosses, and their absence from soils formed by lichens, as well as the distinctly different assemblages of expandable clay minerals produced by lichens and mosses, and by different kinds of moss, constitute presumptive evidence for the involvement of various biogenic chelating agents which performed specific mineral-generating functions. A plausible, though hypothetical, mechanism of amphibole and pyroxene genesis would be [1] release of Si and metals from rock-forming minerals, including the biotite and chlorite as well as feldspars, owing to solubilisation of the minerals by H_2CO_3 and H_2O and by chelating agents which formed Fe, Al, and Ca complexes whose coordination number was 6 (Fig. 6), followed by [2] nucleation of amphibole and pyroxene crystal structures by these complexes. According to this hypothesis, the metal complexes (Fe(III) complexes in particular (Fig. 7b)) bonded dissolved silica anions, thereby nucleating specific metal silicate structures, which then grew incrementally by binding additional metal cations and silica anions through “bridging” mechanisms (Basolo and Johnson, 1964; Jackson et al., 2011). The chelating agents could have been humic substances or non-humic organic acids, or both. A similar mechanism could have played a part in the biological production of the kaolinite. There is independent evidence that chelating agents promote the production of various minerals, including kaolinite (Linares and Huertas, 1971; Hem and Lind, 1974; Jackson et al., 2011) and ferrihydrite (Jackson, 1968, 1993; Jackson and Keller, 1970a,b; Schwertmann et al., 1986). Laboratory experiments have demonstrated crystallisation of kaolinite through the agency of fulvic acid complexes of Al^{3+} with a coordination number of 6 (Linares and Huertas, 1971), and a process of this kind could have caused or facilitated the formation of kaolinite by the mosses or associated microorganisms. A comparable process could account for the formation of different characteristic assemblages of expandable clay minerals by moss and lichen species.
4. The fact that the clay mineral composition of the biogenic soils and the abundances of rock-forming elements in the organisms indicate that weathering mediated by mosses was generally more intense than weathering mediated by lichens probably reflects the tendency of mosses to be metabolically more active than lichens (Sheard, J.W., personal communication). This, in turn, may have caused the soil formed by mosses to support a particularly abundant and active

microflora. Enhancement of chemical weathering and secondary mineral formation in the vicinity of mosses could have been due largely, if not entirely, to microbial (i.e., bacterial and fungal) communities which inhabited the soils associated with the mosses. It is safe to assume that the lichens and mosses supported microbial populations, and their relationships with these microorganisms could well have been mutualistic, the lichens and mosses furnishing the microorganisms with organic nutrients produced by photosynthesis, whilst the microorganisms accelerated the chemical weathering of the rock, thereby releasing inorganic nutrients which benefited the lichens and mosses as well as the microorganisms themselves, as in the case of rhizosphere bacteria associated with the roots of plants (see Introduction).

5. The observation that the soils associated with several species of moss, but none of the soils associated with lichens, contained abundant coarse sand-sized mineral particles indicates that these mosses caused physical as well as chemical weathering of the gneiss. One possible explanation is that rainwater containing dissolved substances released from the rock by the weathering action of the moss diffused into spaces between adjacent crystals (perhaps after expansion and contraction of the crystals by alternate heating and cooling had loosened them slightly), whereupon subsequent drying led to precipitation of relatively bulky hydrated secondary minerals (e.g., Fe and Al oxyhydroxides) which tended to push the feldspar and quartz grains further apart, causing gradual disintegration of the rock. Another possible mechanism is enhanced chemical weathering due to infiltration of the interstitial spaces between the grains by water containing chelating agents and other acids released by the moss, leading to disintegration of the rock along the grain boundaries.
6. The fact that certain species of moss preferentially colonised the pink feldspar- and quartz-rich bands of the gneiss whilst avoiding the black bands enriched in biotite could have contributed to the observed differences between the weathering and secondary mineral-forming processes of lichens and mosses. However, this probably did not have an important effect on the outcome of the biological weathering process, as the mosses, despite their bias in favour of feldspar-rich substrates, altered the feldspars to clay less rapidly and efficiently than the lichens, even though the clay which they did produce was more intensively leached and degraded. Thus, the hypothetical possibility that the relatively low clay content of soil formed by mosses reflects a low proportion of feldspar in the starting material appears to be ruled out.
7. Alternate wetting and drying, with retention of the secondary minerals in the soil (probably owing in large part to binding by humic matter) and partial retention of solubilised elements owing to adsorption and surface complexation by clay and humic matter, probably played a significant part in the biological weathering and secondary mineral-forming process. These processes must have limited the leaching of solubilised elements, thereby preventing the degradation of the primary and secondary minerals from going to completion. Thus, repeated cycles of wetting and drying probably help to explain the occurrence of expandable clay in the soils (Keller, 1964).
8. The fact that the clay associated with mosses was less abundant, and yet was indicative of more intense weathering, than the clay associated with lichens is probably due primarily to more effective solubilisation of rock- and clay-forming elements by the mosses, although stronger retention of clay by soil organic matter produced by lichens could conceivably have been a contributing factor.

3.4. Ecological implications of biological weathering of rock by lichens and mosses

The intimate association of the lichens and mosses in the rock-dwelling community and the characteristic qualitative and quantitative differences in the weathering and secondary mineral-forming activities

of those organisms suggest a mutualistic relationship representing an adaptive strategy for maximising the release of inorganic nutrients from rocks and retaining them in bioavailable forms in the soil. According to this theory, the lichens and mosses, and the different species and genera of mosses, performed complementary functions which, when operating concurrently, caused extraction of inorganic nutrients such as Fe, Ca, Mg, K, Na, P, and trace elements from the rock with maximum efficiency and, at the same time, produced clay minerals and humic substances, one of whose principal ecological functions was to retain a pool of these nutrients in exchangeable, bioavailable forms by binding them reversibly to their ligands and sorption sites. Other ecological advantages of clay and humic matter presumably included retention of water and enhancement of the aeration of the soil owing to the formation of stable aggregates by bridging mechanisms that linked clay minerals, oxides, organic matter, and divalent and polyvalent metal cations (Tisdall and Oades, 1982; Theng, 1986).

Acknowledgements

Drs. D.H. Vitt (Department of Botany, University of Alberta, Edmonton, Alberta, Canada) and J.W. Sheard (Department of Biology, University of Saskatchewan, Saskatoon, Saskatchewan, Canada) kindly identified the mosses and lichens, respectively, and the chemical analyses of these organisms were performed by B. Stanek (Analytical Services, Saskatchewan Research Council, Saskatoon). Dr. W. M. Last (Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada) carried out the mineralogical analyses of the rock and soil samples and provided useful information about the methods of sample preparation and analysis. The chemical analyses of the soil samples were performed by P. Collins (School of Geography and Geology, McMaster University, Hamilton, Ontario, Canada), and the chemical analyses of the rock samples, which had been pulverised beforehand by P. Collins, were conducted by the Analytical Chemistry Section, Mineral Resources Division, Geological Survey of Canada (Ottawa, Ontario, Canada) through the good offices of Dr. R. Garrett. I thank Dr. Garrett for helpful information and opinions relating to the rock samples as well as for his kindness in arranging to have the samples analysed chemically. The research was financed by Environment Canada (Department of the Environment, government of Canada).

References

- Adamo, P., Violante, P., 1991. Weathering of volcanic rocks from Mt. Vesuvius associated with the lichen *Stereocaulon vesuvianum*. *Pedobiologia* 35, 209–217.
- Adamo, P., Violante, P., 2000. Weathering of rocks and neogenesis of minerals associated with lichen activity. *Appl. Clay Sci.* 16, 229–256.
- Adamo, P., Marchettiello, A., Violante, P., 1993. The weathering of mafic rocks by lichens. *Lichenologist* 25, 285–297.
- Adamo, P., Colombo, C., Violante, P., 1997. Iron oxides and hydroxides in the weathering interface between *Stereocaulon vesuvianum* and volcanic rock. *Clay Miner.* 32, 453–461.
- Aghamiri, R., Schwartzman, D.W., 2002. Weathering rates of bedrock by lichens: a mini watershed study. *Chem. Geol.* 188, 249–259.
- Arocena, J.M., Velde, B., Robertson, S.J., 2012. Weathering of biotite in the presence of arbuscular mycorrhizae in selected agricultural crops. *Appl. Clay Sci.* 64, 12–17.
- Basolo, F., Johnson, R., 1964. *Coordination Chemistry*. W.A. Benjamin, New York.
- Bennett, P.C., Rogers, J.R., Choi, W.J., Hiebert, F.K., 2001. Silicates, silicate weathering, and microbial ecology. *Geomicrobiol. J.* 18, 3–19.
- Berner, E.K., Berner, R.A., Moulton, K.L., 2005. Plants and mineral weathering: present and past. In: Drever, J.I. (Ed.), *Surface and Ground Water, Weathering, and Soils*. Treatise on Geochemistry vol. 5. Elsevier, Amsterdam, pp. 169–188.
- Berner, R.A., 1992. Weathering, plants, and the long-term carbon cycle. *Geochim. Cosmochim. Acta* 56, 3225–3231.
- Berner, R.A., 1993. Paleozoic atmospheric CO₂: importance of solar radiation and plant evolution. *Science* 261, 68–70.
- Berner, R.A., 1995. Chemical weathering and its effects on atmospheric CO₂ and climate. *Rev. Mineral.* 31, 565–583.
- Berthelin, J., 1983. Microbial weathering processes. In: Krumbain, W.E. (Ed.), *Microbial Geochemistry*. Blackwell Scientific Publications, Oxford, pp. 223–262.
- Bhatti, T.M., Bigham, J.M., Vuorinen, A., Tuovinen, O.H., 2011. Weathering of biotite in *Acidithiobacillus ferrooxidans* cultures. *Geomicrobiol. J.* 28, 130–134.
- Biscaye, P.E., 1965. Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean. *Geol. Soc. Am. Bull.* 76, 803–832.
- Boyle, J.R., Voigt, G.K., Sawhney, B.L., 1967. Biotite flakes: alteration by chemical and biological treatment. *Science* 155, 1–2.
- Brunskill, G.J., Povoledo, D., Graham, B.W., Stainton, M.P., 1971. Chemistry of surface sediments of sixteen lakes in the Experimental Lakes Area, Northwestern Ontario. *J. Fish. Res. Board Can.* 28, 277–294.
- Brunskill, G.J., Schindler, D.W., 1971. Geography and bathymetry of selected lake basins, Experimental Lakes Area, Northwestern Ontario. *J. Fish. Res. Board Can.* 28, 139–155.
- Callender, E., 1968. *The Postglacial Sedimentology of Devil's Lake, North Dakota*. (Ph.D. thesis). University of North Dakota, Grand Forks.
- Calvaruso, C., Turpault, M.-P., Frey-Klett, P., 2006. Root-associated bacteria contribute to mineral weathering and to mineral nutrition in trees: a budgeting analysis. *Appl. Environ. Microbiol.* 72, 1258–1266.
- Carroll, D., 1970. Clay minerals: a guide to their X-ray identification. Geological Society of America Special Paper 126.
- Chen, J., Blume, H.-P., 1999. Biotic weathering of rocks by lichens in Antarctica. *Chin. J. Polar Sci.* 10, 25–32.
- Chen, J., Blume, H.-P., 2002. Rock-weathering by lichens in Antarctic: patterns and mechanisms. *J. Geogr. Sci.* 12, 387–396.
- Chen, J., Blume, H.-P., Beyer, L., 2000. Weathering of rocks induced by lichen colonization – a review. *Catena* 39, 121–146.
- Chen, P.Y., 1977. Table of key lines in X-ray powder diffractions patterns of minerals in clays and associated rocks. Indiana Geological Survey Occasional Paper 21.
- Cochran, M.F., Berner, R.A., 1992. The quantitative role of plants in weathering. In: Kharaka, Y.K., Maest, A.S. (Eds.), *Water–Rock Interactions (Proceedings of 7th International Symposium on Water–Rock Interaction (Park City, Utah, U.S.A., 13–18 July, 1992))*. Balkema, Rotterdam, pp. 473–476.
- Companion, A.L., 1964. *Chemical Bonding*. McGraw-Hill, New York.
- Crouch, M.J.C., 2010. Quantifying the Biotic Enhancement of Mineral Weathering by Moss. (M. Sc. Thesis). University of East Anglia, Norwich, England.
- De Ros, L.F., Anjos, S.M.C., Morad, S., 1994. Authigenesis of amphibole and its relationship to the diagenetic evolution of lower Cretaceous sandstones of the Potiguar rift basin, northeastern Brazil. *Sediment. Geol.* 88, 253–266.
- Drever, J.I., 1973. The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter-membrane peel technique. *Am. Mineral.* 58, 553–554.
- Drever, J.I., 1994. The effect of land plants on weathering rates of silicate minerals. *Geochim. Cosmochim. Acta* 58, 2325–2332.
- Duff, R.B., Webley, D.M., Scott, R.O., 1963. Solubilization of minerals and related materials by 2-ketogluconic acid-producing bacteria. *Soil Sci.* 95, 105–114.
- Enlows, H.E., Oles, K.F., 1966. Authigenic silicates in marine Spencer Formation at Corvallis, Oregon. *Am. Assoc. Pet. Geol. (AAPG) Bull.* 50, 1918–1926.
- Folk, R.L., 1968. *Petrology of Sedimentary Rocks*. Hemphill, Austin, Texas.
- Fortey, N.J., Michie, U. McL., 1978. Aegirine of possible authigenic origin in middle Devonian sediments in Caithness, Scotland. *Mineral. Mag.* 42, 439–442.
- Frankel, L., 1977. Microorganism induced weathering of biotite and hornblende grains in estuarine sands. *J. Sediment. Res.* 47, 849–854.
- Gerretsen, F.C., 1948. The influence of microorganisms on the phosphate intake by the plant. *Plant Soil* 1, 51–81.
- Grim, R.E., 1968. *Clay Mineralogy*. second ed. McGraw-Hill, New York.
- Hem, J.D., Lind, C.J., 1974. Kaolinite synthesis at 25 °C. *Science* 184, 1171–1173.
- Hen, J., Gong, Z.-T., 1995. Role of lichens in weathering and soil-forming processes in Fildes Peninsula, Antarctic. *Pedosphere* 5, 305–314.
- Henderson, M.E.K., Duff, R.B., 1963. The release of metallic and silicate ions from minerals, rocks, and soils by fungal activity. *J. Soil Sci.* 14, 236–246.
- Hiebert, F.K., Bennett, P.C., 1992. Microbial control of silicate weathering in organic-rich ground water. *Science* 258, 278–281.
- Horwitz, W. (Ed.), 1980. *Official Methods of Analysis of the Association of Analytical Chemists*, thirteenth ed. Association of Official Agricultural Chemists (AOAC), Washington, D.C.
- Hower, J., Eslinger, E.V., Hower, M.E., Perry, E.D., 1976. Mechanism of burial metamorphism of argillaceous sediment, 1. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.* 87, 725–737.
- Huang, W.H., Keller, W.D., 1970. Dissolution of rock-forming silicate minerals in organic acids. *Am. Mineral.* 55, 2076–2094.
- Huang, W.H., Keller, W.D., 1971. Dissolution of clay minerals in dilute organic acids at room temperature. *Am. Mineral.* 56, 1082–1095.
- Huang, W.H., Keller, W.D., 1972. Organic acids as agents of chemical weathering of silicate minerals. *Nat. Phys. Sci.* 239, 149–151.
- Huang, W.H., Kiang, W.C., 1972. Laboratory dissolution of plagioclase feldspars in water and organic acids at room temperature. *Am. Mineral.* 57, 1849–1859.
- Jackson, T.A., 1968. *The Role of Pioneer Lichens in the Chemical Weathering of Recent Volcanic Rocks on the Island of Hawaii*. (Ph.D. dissertation). University of Missouri, Columbia, Missouri, U.S.A.
- Jackson, T.A., 1975. Humic matter in natural waters and sediments. *Soil Sci.* 119, 56–64.
- Jackson, T.A., 1993. Comment on “Weathering, plants, and the long-term carbon cycle” by Robert A. Berner. *Geochim. Cosmochim. Acta* 57, 2141–2144.
- Jackson, T.A., 1995. Effects of clay minerals, oxyhydroxides, and humic matter on microbial communities of soil, sediment, and water. In: Huang, P.M., Berthelin, J., Bollag, J.-M., McGill, W.B., Page, A.L. (Eds.), *Environmental Impact of Soil Component Interactions* vol. II. Lewis Publishers, Boca Raton, pp. 165–200.
- Jackson, T.A., 1998. The biogeochemical and ecological significance of interactions between colloidal minerals and trace elements. In: Parker, A., Rae, J.E. (Eds.), *Environmental Interactions of Clays*. Springer, Berlin, pp. 94–205.

- Jackson, T.A., Keller, W.D., 1970a. A comparative study of the role of lichens and "inorganic" processes in the chemical weathering of recent Hawaiian lava flows. *Am. J. Sci.* 269, 446–466.
- Jackson, T.A., Keller, W.D., 1970b. Evidence for biogenic synthesis of an unusual ferric oxide mineral during alteration of basalt by a tropical lichen. *Nature* 227, 522–523.
- Jackson, T.A., Voigt, G.K., 1971. Biochemical weathering of calcium-bearing minerals by rhizosphere micro-organisms, and its influence on calcium accumulation in trees. *Plant Soil* 35, 655–658.
- Jackson, T.A., West, M.M., Leppard, G.G., 2011. Accumulation and partitioning of heavy metals by bacterial cells and associated colloidal minerals, with alteration, neoformation, and selective adsorption of minerals by bacteria, in metal-polluted lake sediment. *Geomicrobiol J.* 28, 23–55.
- Johnston, C.G., Vestal, J.R., 1993. Biogeochemistry of oxalate in the Antarctic cryptolith lichen-dominated community. *Microb. Ecol.* 25, 305–319.
- Jones, A.A., Bennett, P.C., 2014. Mineral microniches control the diversity of subsurface microbial populations. *Geomicrobiol J.* 31, 246–261.
- Jones, D., Wilson, M.J., Tait, J.M., 1980. Weathering of a basalt by *Pertusaria coralline*. *Lichenologist* 12, 277–289.
- Keller, W.D., 1957. *The Principles of Chemical Weathering*. Lucas Brothers, Columbia, Missouri.
- Keller, W.D., 1964. Processes of origin and alteration the clay minerals. In: Rich, C.I., Kunze, G.W. (Eds.), *Soil Clay Mineralogy*. University of North Carolina Press, Chapel Hill, pp. 1–76.
- Keller, W.D., 1970. Environmental aspects of clay minerals. *J. Sediment. Petrol.* 40, 788–813.
- Klug, H.P., Alexander, L.E., 1974. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. second ed. Wiley, New York.
- Last, W.M., 1980. *Sedimentology and Postglacial History of Lake Manitoba*. (Ph.D. thesis). University of Manitoba, Winnipeg, Manitoba, Canada.
- Last, W.M., 2002. Mineralogical analysis of lake sediments. In: Last, W.M., Smol, J.P. (Eds.), *Tracking Environmental Change Using Lake Sediments. Physical and Geochemical Methods vol. 2*. Springer, Dordrecht, pp. 143–188.
- Lenton, T.M., Crouch, M., Johnson, M., Pires, N., Dolan, L., 2012. First plants cooled the Ordovician. *Nat. Geosci.* 5, 86–89.
- Lide, D.R., 2004. *CRC Handbook of Chemistry and Physics*. eighty-fifth ed. CRC Press, Boca Raton.
- Linares, J., Huertas, F., 1971. Kaolinite: synthesis at room temperature. *Science* 171, 896–897.
- Lovelock, J., 2009. *The Vanishing Face of Gaia*. Penguin Books, London.
- Mandl, I., Grauer, A., Neuberger, C., 1953. Solubilization of insoluble matter in nature. II. The part played by salts of organic and inorganic acids occurring in nature. *Biochim. Biophys. Acta* 10, 540–569.
- Matthews, J.A., Owen, G., 2008. Endolithic lichens, rapid biological weathering and Schmidt Hammer R-values on recently exposed rock surfaces: Storbreen Glacier foreland, Jotunheimen, Norway. *Geogr. Ann. Ser. A Phys. Geogr.* 90, 267–297.
- Millot, G., 1970. *Geology of Clays*. Springer-Verlag, New York (Masson et Cie, Paris; Chapman & Hall, London).
- Milton, C., Eugster, H.P., 1959. Mineral assemblages of the Green River Formation. In: Abelson, P.H. (Ed.), *Researches in Geochemistry*. John Wiley and Sons, New York, pp. 118–150.
- Milton, C., Ingram, B., Breger, I., 1974. Authigenic magnesioarvedsonite from the Green River Formation, Duchesne County, Utah. *Am. Mineral.* 59, 830–836.
- Muller, G., 1967. *Methods in Sedimentary Petrology*. Hafner Press, New York.
- Naga, M.A., Hossny, I., Abdel-Aal, Sh.I., Shahin, R.R., 1977. Biological weathering of silicate minerals. *Egypt. J. Soil Sci.* 17, 237–250.
- Ochs, M., Brunner, I., Stumm, W., Čosović, B., 1993. Effects of root exudates and humic substances on weathering kinetics. *Water Air Soil Pollut.* 68, 213–229.
- Ong, H.L., Swanson, V.E., Bisque, R.E., 1970. Natural organic acids as agents of chemical weathering. United States Geological Survey Professional Paper 700-C, pp. C130–C137.
- Parmar, P., Sindhu, S.S., 2013. Potassium solubilisation by rhizosphere bacteria: influence of nutritional and environmental conditions. *J. Microbiol. Res.* 3, 25–31.
- Robert, M., Berthelin, J., 1986. Role of biological and biochemical factors in soil mineral weathering. In: Huang, P.M., Schnitzer, M. (Eds.), *Interactions of Soil Minerals with Natural Organics and Microbes* (SSSA Special Publication no. 17). Soil Science Society of America, Madison, Wisconsin, USA, pp. 453–495.
- Schatz, A., Cheronis, N.D., Schatz, V., Trelawny, G.S., 1954. Chelation (sequestration) as a biological weathering factor in pedogenesis. *Proc. Pa. Acad. Sci.* 28, 44–51.
- Schnitzer, M., Khan, S.U., 1972. *Humic Substances in the Environment*. Marcel Dekker, New York.
- Schultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. United States Geological Survey Professional Paper 391-C.
- Schwartzman, D., 1999. *Life, Temperature, and the Earth*. Columbia University Press, New York.
- Schwartzman, D.W., Volk, T., 1989. Biotic enhancement of weathering and the habitability of Earth. *Nature* 340, 457–460.
- Schwertmann, U., Fischer, W.R., 1973. Natural "amorphous" ferric hydroxide. *Geoderma* 10, 237–247.
- Schwertmann, U., Kodama, H., Fischer, W.R., 1986. Mutual interactions between organics and iron oxides. In: Huang, P.M., Schnitzer, M. (Eds.), *Interactions of Soil Minerals with Natural Organics and Microbes*. SSSA Special Publication no. 17. Soil Science Society of America, pp. 223–250.
- Sperber, J.L., 1958. Solution of apatite by soil microorganisms producing organic acids. *Aust. J. Agric. Res.* 9, 782–787.
- Tanner, C.B., Jackson, M.L., 1947. Nomographs of sedimentation times for soil particles and gravity or centrifugal acceleration. *Soil Sci. Soc. Am. Proc.* 12, 60–65.
- Taylor, L.L., Leake, J.R., Quirk, J., Hardy, K., Banwart, S.A., Beerling, D.J., 2009. Biological weathering and the long-term carbon cycle: integrating mycorrhizal evolution and function into the current paradigm. *Geobiology* 7, 171–191.
- Terry, R.D., Chilingar, G.V., 1955. Summary of "Concerning some additional aids in studying sedimentary formations", by M.S. Shuetsov. *J. Sediment. Petrol.* 25, 229–234.
- Theng, B.K.G., 1986. Clay-humic interactions and soil aggregate stability. In: Rengasamy, P. (Ed.), *Soil Structure and Aggregate Stability*. Institute for Irrigation and Salinity Research, Tatura, VIC, Australia, pp. 32–73.
- Thorez, J., 1975. *Phyllosilicates and Clay Minerals: A Laboratory Handbook for their X-ray Diffraction Analysis*. Editions G. Leclotte, Dison, Belgium.
- Tisdall, J.M., Oades, J.M., 1982. Organic matter and water-stable aggregates in soils. *J. Soil Sci.* 33, 141–163.
- Voigt, G.K., 1965. Biological mobilization of potassium from primary minerals. *Forest-Soil Relationships in North America* (proceedings of 2nd North American Forest Soils Conference, Oregon State University, Corvallis). Oregon State University Press, Corvallis, pp. 33–46.
- Webley, D.M., Henderson, M.E.K., Taylor, I.F., 1963. The microbiology of rocks and weathered stones. *J. Soil Sci.* 14, 102–112.
- Welch, S.A., Barker, W.W., Banfield, J.F., 1999. Microbial extracellular polysaccharides and plagioclase dissolution. *Geochim. Cosmochim. Acta* 63, 1405–1419.
- Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. *J. Geol.* 30, 377–392.
- Wilson, M.J., Jones, D., 1983. Lichen weathering of minerals: implications for pedogenesis. *Geol. Soc. Lond., Spec. Publ.* 11, 5–12.
- Wright, J.R., Schnitzer, M., 1963. Metallo-organic interactions associated with podsolization. *Soil Sci. Soc. Am. Proc.* 27, 171–176.
- Zambell, C.B., Adams, J.M., Gorrington, M.L., Schwartzman, D.W., 2012. Effect of lichen colonization on chemical weathering of hornblende granite as estimated by aqueous elemental flux. *Chem. Geol.* 291, 166–174.