

## MINERALOGICAL TRANSFORMATION OF BIOWEATHERED GRANITIC BIOTITE, STUDIED BY HRTEM: EVIDENCE FOR A NEW PATHWAY IN LICHEN ACTIVITY

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**Abstract**—The question of whether clay minerals can be biogenically transformed as a result of lichen activity at the lichen-rock interface remains unresolved. We applied several microscopical and analytical techniques—scanning electron microscopy-back-scattered electron (SEM-BSE), energy dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM)—in an attempt to address this issue. Unaffected granitic biotite and bioweathered material from the granitic biotite and *Parmelia conspersa* lichen thalli interface were examined using HRTEM after ultrathin sectioning. The *n*-alkylammonium treatment of ultrathin sections was carried out in order to study the biogenous mineralogical transformation of the biotite. Microsamples proceeding from unaffected biotite zones demonstrated homogenous 10-Å *d*(001)-value biotite phase. HRTEM images of lattice fringes of samples taken from the lichen-biotite contact zone reveal large areas of both unexpanded (10-Å) and randomly and *R* = 3 distributed expanded (from 14- to 30-Å) layers of phyllosilicates identified as interstratified biotite-vermiculite. Results of artificial biotite weathering (replacement of K by Ca ion) also revealed the biotite-vermiculite phase formation, indicating that K release in biotite is one of the mechanisms responsible for interstratified mineral phase formation. Two parallel processes, physical exfoliation of biotite and interlayer ionic exchange of K and subsequent vermiculite formation, are the mechanisms for biotite bioweathering induced by lichens.

**Key Words**—Back-scattered Electrons, Biotite, Bioweathering, Granite, High-Resolution Transmission Electron Microscopy (HRTEM), Lattice-Fringe Images, Lichens, Vermiculite.

### INTRODUCTION

Bioweathering of natural rocks and biodeterioration of monumental stones induced by lithobiontic microorganisms are subjects of numerous studies (Pierivittori et al. 1994). Colonization of rock by lichens is often accompanied by a variety of interactions between biological components and inorganic substrates that are of great interest to both mineralogists and biologists. It has been frequently reported that biophysical weathering of rock is due to penetration of thallus rhizines and by moisture-dependent expansion and contraction of thalli (review in Jones et al. 1987). Saxicolous lichens can also induce biochemical weathering by chelates forming with substrate elements (Purvis et al. 1987, 1990) or by excretion of organic acids (Ascaso et al. 1976; Jones and Wilson 1985) and decomposition of minerals (Wilson and Jones 1983). Recently Wierzechos and Ascaso (1996) demonstrated a strong chemical action of lichens with mineral components of granitic rock leading to distinct chemical changes in biotite, suggesting transformation of this phyllosilicate to vermiculitized biotite. This susceptibility of trioctahedral micas to biogenous weathering has been shown by several authors. Mortland et al. (1956) reported the vermiculitization of trioctahedral mica if interlayer K was used as a nutritional plant source. The transformation of micas into vermiculite by soil fungi has been observed in laboratory experiments by Weed

et al. (1969). Research by Berthelin and Belguy (1979), Leyval et al. (1990), Leyval and Berthelin (1991), Hingsinger and Jaillard (1993) and Hingsinger et al. (1992, 1993) based on pot experiments and field studies (Kodama et al. 1994) also indicate the vermiculitization of micas in the rhizosphere. According to Leyval and Berthelin (1991), the activity of roots and of symbiotic and nonsymbiotic microorganisms and their interaction with mineral phase are certainly influenced by experimental and environmental conditions. Generally, trioctahedral mica transformations have been attributed to release of interlayer K and expansion of the phyllosilicates' interlayer space.

The question of whether clay minerals can be biogenically transformed or synthesized as a result of lichen activity at the lichen-rock interface remains unresolved (Wilson 1995). However, the few X-ray diffraction (XRD) studies performed on lichen colonized rocks (such as Adamo and Violante 1991) have revealed the existence of newly formed clay minerals in the material scraped from the lichen-rock interface zone. Interpretation of results in such studies is beset by problems of possible contamination from extraneous mineral sources as a result of aeolian deposition (Syers and Iskandar 1973; Ascaso and Wierzechos 1994) or even by the possibility that small amounts of altered clay mineral may occur within the fresh parent rock. On the other hand, the XRD technique requires

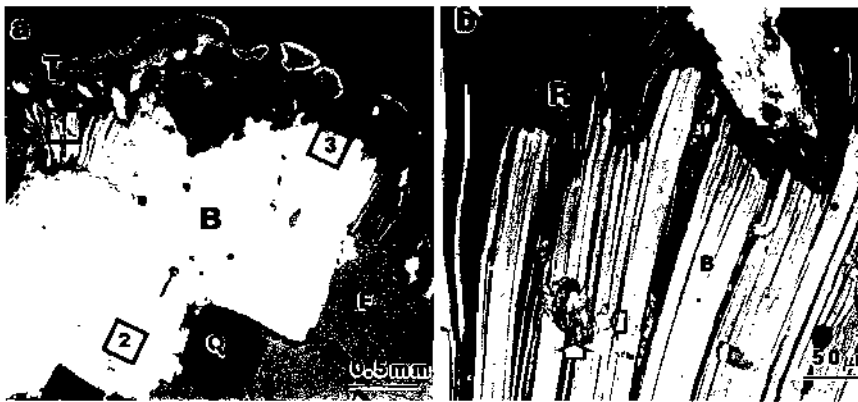


Figure 1. SEM-BSE micrographs of the *Parmelia conspersa* thallus-granitic biotite interface. a) General view of the lichen-granite contact zone. T = thallus; B = biotite; Q = quartz; F = feldspar; 1 = bioweathered biotite area; 2 = unaltered interior biotite area and 3 = surface biotite area. b) Detail of the direct lichen-biotite contact zone (zone 1 shown in Figure 1a). R = rhizine penetrating the biotite (B) sheets and filling the partially dissolved apatite crystals (white arrows).

an appreciable quantity of chemically treated material in order to remove any biological material. This harsh treatment can alter the mineralogical characteristics of the sample (Lakvulich and Wiens 1970; Douglas and Ficssinger 1971) and lead to false results.

The aim of this paper has been to present the evidence for mineralogical transformation induced by lichen activity. With this as a basis, carefully separated mineral samples from the lichen-rock interface zone were examined using HRTEM.

## EXPERIMENTAL

### Samples

Pieces of granitic rock colonized by foliose *Parmelia conspersa* (Ehrh) Ach. were collected near a granitic mine (Bustarviejo de la Sierra, Madrid). The historic record reports that the rock surface from which the samples were taken was uncovered and exposed to climatic and biogeous weathering 15 years ago. Previous mineralogical examination of this material (Ascaso 1985) demonstrated the presence of quartz, orthoclase and plagioclase as major and biotite, zircon and apatite as accessory minerals.

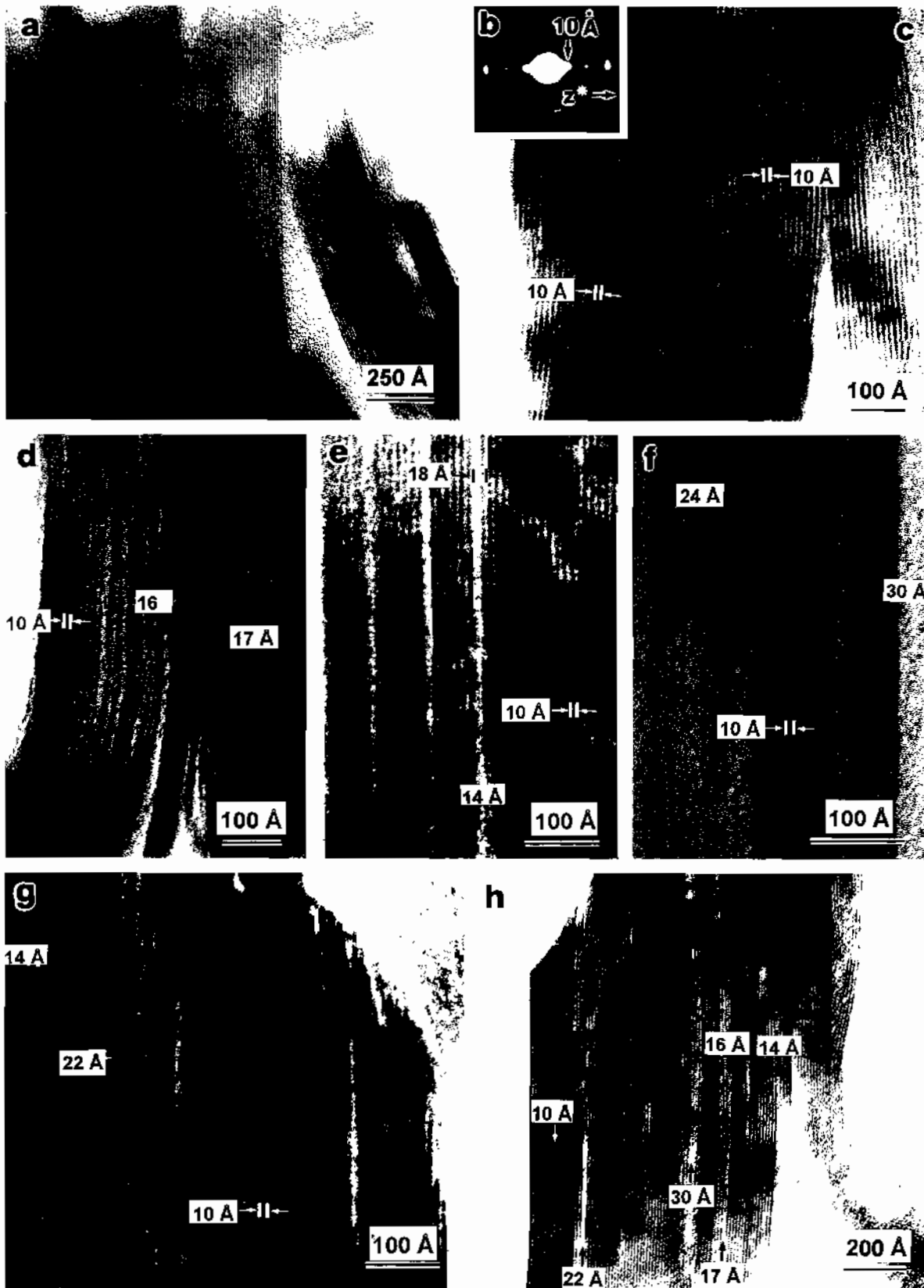
### SEM Examination

Collected samples were processed according to conventional TEM procedure for lichen material (Ascaso et al. 1988). After inclusion in epoxy resin (Araldite), the transversal lichen-rock sections were prepared for SEM operating in BSE emission mode. Details of this preparative procedure are given in Wierzbos and Ascaso (1994). However, for the purpose of this study, some modifications were introduced. The transversal lichen-rock interface was prepared as a fine polished, uncovered thin-section ( $2 \times 2$  cm) adapted also for light microscopy (LM) observation. After coating with evaporated carbon, the thin section was examined using a DSM 960 Zeiss apparatus equipped with BSE

solid-state detector and an EDS system operating under the microscope and analytical conditions reported by Wierzbos and Ascaso (1996). Microanalytical work permitted detection and precise localization of both the K-depleted biotite zones in direct contact with the lichen thallus area (zone 1 on Figure 1a), as well as unaffected biotite particles occurring both within the biotite crystal (area 2 on Figure 1a) and on its surface (area 3 on Figure 1a).

### Isolation of Undisturbed Microsamples and Their Microtomy and Intercalation

In order to study bioinduced clay transformation processes by HRTEM technique, careful isolating and posterior ultrathin sectioning of the biotite microsamples was undertaken from the 3 previously mentioned areas. To do this, we first identified microzones by SEM-BSE-EDS technique. Undisturbed microsamples (about  $50 \times 50 \mu\text{m}$ ) were extracted from thin section under LM observation using the microdrilling method (van Oort et al. 1994). Isolated microsamples were then re-embedded under vacuum. After polymerization, ultrathin sections (50–70 nm thick) were obtained using a diamond knife and mounted on Formvar and carbon film supporting TEM gold grids. Ultrasectioned biotite from the 3 areas was examined by TEM. Other ultrathin sections were treated using *n*-alkylammonium ion (*n* = number of C atoms in the alkyl chains) for examination of expandable layers using HRTEM (Lagaly 1982; Vali and Hesse 1992). Ultrathin sections were treated with 0.5 N heptylammonium chloride (*n* = 7) and 0.02 N octadecylammonium (ODA) chloride (*n* = 18) aqueous solutions at 60 °C for 6 h (Vali and Hesse 1990). To study the alteration process mechanisms by HRTEM, ultrathin sections with no bioweathered biotite microsamples were artificially weathered under laboratory conditions by the Ca cation treatment. For K release, grids with biotite ultra-



thin sections proceeding from area (2) were treated with a 0.1 M CaCl<sub>2</sub> solution at 60 °C for 12 h. For details, see Vali and Hesse (1992). After exchange of interlayer K, ultrathin sections were treated with ODA (Vali and Hesse 1992).

#### HRTEM Study

Both untreated and *n*-alkylammonium-treated ultrathin sections were examined at 120-kV accelerating potential with a Zeiss EM 910 transmission electron microscope mounted with a W filament and operating in high-resolution mode with a structure resolution limit of 2 Å (3.7 Å point-to-point resolution), and a spherical aberration coefficient (Cs) of 2.7 mm. A Scherzer defocus ( $\Delta f = -1000$  Å) condition, and a 37- $\mu$ m objective aperture and a 90- $\mu$ m condenser aperture were used for imaging and selected area diffraction aperture was used for electron diffraction. All micrographs (more than 170) were taken in bright field illumination at magnification of 125,000 $\times$ . Observation and interpretation of phyllosilicate images were performed after Šrodoň et al. (1990).

### RESULTS AND DISCUSSION

#### SEM

Application of the SEM-BSE technique for the examination of transverse section through the lichen-rock interface allowed precise localization of the bioweathered part of the biotite crystal. Figure 1a shows a general view of the transverse section of the biotite crystal (B) colonized by *P. conspersa* thalli (T). Distinct exfoliation and separation of biotite sheets was observed in the direct contact area (1) between the epilithic thallus and biotite. A detailed observation of bioaltered biotite layers penetrated by rhizine (part of *P. conspersa* thallus) demonstrated the presence of apatite grains between biotite sheets. It was noted that some of these apatite grains were in direct contact with hyphae cells, revealing distinct dissolution patterns (white arrows in Figure 1b). Apatite crystal dissolution could be an important source of Ca cations, which may participate in biotite interlayer K exchange reactions, as was demonstrated in Wierchos and Ascaso (1996). However, in these *P. conspersa* thalli the presence of oxalic acid was not detected, but there is perhaps another possibility that should also be considered where

the dissolution of apatite is observed. Lichen fungi may produce other simple organic acids such as citric, gluconic, lactic and/or other proton donors, which could dissolve granitic rock components. Nevertheless, these newly formed salts could be soluble in water or could be easily microbially decomposed and, in consequence, not accumulate within the lichen-rock interface (Jones and Wilson 1985). Several lichen substances such as stictic, norstictic, usnic and constictic acids were detected within the *P. conspersa* thalli (Scriñá 1993). However, their role in the chemical weathering of minerals is still not clear. On the one hand, their limited solubility in water could suggest they do not play an important role in mineral weathering, but, on the other, Ascaso et al. (1976) reported that *P. conspersa* thalli demonstrate the ability to extract cations (including Ca<sup>2+</sup>) when suspended in water minerals and rocks. Also, relatively low pH = 4.5 measured in *P. conspersa* water suspension and pH = 5.3 measured in *P. conspersa*-mica water suspension (Schatz 1963) indicate that chemical weathering processes may occur in granitic rock components. Wierchos and Ascaso (1996) recently demonstrated that the lichen-rock interface could be an important location of chemical changes of biotite. Reported by these authors, biochemical action of *P. conspersa* thallus with biotite leads to the release of 80% K from interlayer positions. At the same time, a 4-fold relative increase in Ca concentration was detected. Thus, the dissolved apatite crystals as a source of the Ca cation can accelerate the K depletion process on lichenized biotite. Microanalytical (EDS) work performed parallel to the lichen-biotite contact zone confirmed previously reported results (Wierchos and Ascaso 1996) and demonstrated that bioaltered biotite sheets exhibit a distinct loss of K content compared to unaffected parts. Biotite on the rock surface but not in contact with saxicolous lichen (area 2 on Figure 1a) has not revealed chemical and/or physical alteration.

#### TEM

Research of bioaltered biotite phases at the nano scale using TEM requires a very elaborate strategy. As a first step, the untreated biotite ultrathin sections proceeding from 3 zones (areas 1, 2 and 3, Figure 1a) were examined. The images of the lattice fringes ob-

Figure 2. HRTEM images of lattice fringes of biotite proceeding from areas 1, 2 and 3 shown in Figure 1a. a) Homogenous aspect of lattice fringes of untreated biotite sections showing stacks of packets made up of unexpanded 10-Å layers proceeding from lichen-biotite contact area 1. b) Diffraction electron pattern of region shown in Figure 2c. c) Lattice fringe image revealing the 10-Å basal spacing (biotite) of the octadecylammonium-ion-treated sample proceeding from area 3. d) Section (area 1) treated with heptylammonium ion showing random arrangement of unexpanded (10-Å) and expanded layers (16- and 17-Å) of interstratified biotite-vermiculite. e, f and g) Ordered bioweathered biotite, interstratified biotite (10-Å) and vermiculite (14-30-Å) phases from the lichen-biotite contact area (1) after octadecylammonium ion treatment. h) Section (area 2) showing stacks of both unexpanded (10-Å) and expanded (14-30-Å) layer components after treatment with Ca and octadecylammonium ion, respectively.

tained for all initial samples clearly demonstrated the high homogeneity of the mineral with regular 10-Å distance between particular sheets, as shown in Figure 2a. The lack of expanded layers in these untreated samples is not sufficient proof of the total absence of weathered biotite phases but does demonstrate the absence of, among others, biogenous or initial chlorite or kaolinite phases (Eggleton and Banfield 1985; Ahn and Peacor 1987; Banfield and Eggleton 1988). However, the HRTEM studies performed by Graf von Reichenbach et al. (1988), Marcks et al. (1989), Ghabru et al. (1989) and Vali and Hesse (1992) also demonstrated a 10-Å basal spacing for weathered biotite considered as vermiculite. Moreover, it was reported that 14-Å interlayer spacing in hydrated vermiculite collapses to 10–12 Å under TEM conditions (Vali and Hesse 1992). Thus, the next step was to treat the extracted samples with an *n*-alkylammonium ion in order to detect bioweathered biotite. Another problem that should be considered is that, in some cases, the longer chain of alkylammonium ions may also cause 10-Å spaced minerals such as illite, glauconite, phlogopite or biotite (Laird et al. 1987; Vali et al. 1991, 1992) to expand potentially, leading to misinterpreted results. The useful distinction between vermiculite and unaltered biotite phases consists of heptylammonium ion treatment. Most of the stable 10-Å *d*(001)-value components do not respond to *n* = 7 alkylammonium treatment (Vali and Hesse 1992) and, for this reason, the 3 groups of samples were first treated with heptylammonium solution. HRTEM examination demonstrated that randomly distributed expanded layers with lattice distance of 16 and 17 Å (Figure 2d) were only observed in samples from the bioaltered area (1). Almost the same (17-Å) interlayer distance was also observed by Vali and Hesse (1990, 1992) on *n* = 7 alkylammonium-treated Jefferson vermiculite (biotite weathering product). Biotite particles from unaltered areas did not respond to heptylammonium treatment, which indicated the absence of weathered biotite phases in samples from areas 1 and 2. However, octadecylammonium ion treatment of all ultrathin sections revealed more distinct differences between compared biotite zones. Figures 2b (electron diffraction pattern) and 2c (HRTEM) demonstrate that a 10-Å distance between sheets was observed for biotite samples proceeding from areas 2 and 3. The lack of expandable layers in these areas after *n* = 18 alkylammonium treatment demonstrates the occurrence of unweathered biotite phases within and on the surface of the fresh parent granitic rock. Nevertheless, HRTEM images (Figures 2e, 2f and 2g) of lattice fringes of biotite taken from the lichen-biotite contact zone after ODA treatment show large areas of both unexpanded (10-Å) and expanded (14–30-Å) layers of phyllosilicates identified as interstratified biotite-vermiculite according to various HRTEM studies (Marcks et al. 1989; Vali and

Hesse 1990; Vali and Hesse 1992; Vali et al. 1992, Vali et al. 1994). Figure 2c shows an ordered distributed 14-Å (occasionally up to 18-Å) expanded layer separated by sequences of packets containing between 4 and 6 layers of biotite corresponding to *R* = 3 structure type (Vali et al. 1994). A similar arrangement of the expanded layers but with an interlayer spacing of between 24 and 30 Å was also observed (Figure 2f). Irregular (Figure 2d) and ordered (Figures 2c and 2f) bioweathered biotite interstratified structures were also accompanied by several zones with almost fully expanded sequences (left part of Figure 2g) consisting of nonpolar layers typical of vermiculite (Vali and Hesse 1992; Vali et al. 1992). However, these usual 22-Å and 14-Å randomly distributed interlayers were accompanied by large zones of unexpanded biotite (10-Å) sheets. According to Banfield and Eggleton (1988), increased weathering correlates with a proportional increase in the number of vermiculite layers and with an increased regularity of interlayering. Observed differences in *d*(001) values (between 14 and 30 Å) for vermiculized phases and in the arrangement of unaltered biotite sequences could be a consequence of heterogeneous, nano-environmental bioweathering conditions, which in turn may vary considerably depending on currently unknown physiological processes related to microorganisms. On the other hand, these differences may be due to radiation damage to the *n*-alkylammonium-treated clay mineral under the electron beam and vacuum condition (Vali and Hesse 1990). Another cause of spacing differences observed in expanded interlayers of both random and *R* = 3 ordered structures of bioweathered biotite could be extensive variation in interlayer charge density, a result of variations in the extent of isomorphous substitution within the T-O-T part of the 2:1 layer silicate (Vali et al. 1994). It was also noted that the number of expanded layers was much lower in the *n* = 7 biotite than in those treated with *n* = 18 alkylammonium ion.

In order to study bioweathering mechanisms, ultrathin sections from unaltered (area 2 on Figure 1a) biotite were examined with HRTEM after initial leaching with Ca and posterior treatment with octadecylammonium ion. The results of this artificial weathering process are shown in Figure 2h. Note the random mixed-layer structure arrangement with unexpanded (10-Å) and expanded (14–30-Å) interlayers. This suggests that depletion of interlayer K by Ca exchange in biotite may be one of the mechanisms responsible for biotite vermiculite interstratified phase formation.

## CONCLUSION

We demonstrate that HRTEM study of the previously examined (Wierzbos and Ascaso 1996) and carefully extracted mineral material appears to be very advantageous in the investigation of biogenically transformed clay minerals. Taking into account the

great heterogeneity of the lichen-rock interface and high probability of contamination by aeolian clay minerals, the method offers a unique possibility to detect the mineralogical transformation on the nanoscale. HRTEM study of bioweathered biotite demonstrates that biogenetic vermiculitization of biotite leads to the formation of random and  $R = 3$  ordered interstratified biotite-vermiculite mineral phases. Even in the first stages of bioweathering, the formation of expandable layers can play a significant role in opening up the biotite structure and can generate the disaggregation of biotite known as the biophysical exfoliation process. We suggest that this biophysical weathering and interlayer ionic exchange of K and subsequent vermiculite phase formation, are the processes responsible for bioweathering of biotite induced by lichen activity.

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