MORPHOLOGICAL AND CHEMICAL FEATURES OF BIOWEATHERED GRANITIC BIOTITE INDUCED BY LICHEN ACTIVITY

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Abstract To study the physico-chemical activity of lichens on micaceous components of granite rocks, samples covered by thallus of Parmelia conspersa (Ehrhrt) Ach. and Aspicilia intermutans (Nyl.) Arn. were collected and examined with Scanning Electron Microscopy (SEM) equipped with a Back Scattered Electron (BSE) detector and an Energy Dispersive Spectroscopy (EDS) microanalytical system. The biophysical activity of both lichen species leads to a deep alteration of biotite, which results in detachment, separation and exfoliation of biotite plates. Chemically, the bioweathering process of biotite in the lichen-mineral contact zone involves considerable depletion of potassium (K) from interlayer positions in biotite and removal of several elements, corresponding to a 9.75% loss in matter. The sequence of the loss of elements is: K > Fe > Ti > Mg. There are also some gains in the order: Ca > Na > Al > Si attributed to dissolution of co-existing Ca and Na-rich minerals. Geochemical mass balance results suggest the transformation of K-rich biotite to scarcely altered biotite interstratified with a biotite-vermiculite intermediate phase in the lichen bioweathered contact zones.

Key Words—Aspicilia intermutans, Biotite, Bioweathering, Granite, Lichens, Parmelia conspersa.

INTRODUCTION

The role of physical and chemical factors in the weathering of micaceous minerals has been adequately documented. A common biotite weathering route is the suppression of K release due to oxidation during synthetic degradation processes (Barshad and Kishik 1968; Rich 1972; Gilkes 1973; Gilkes et al. 1973; Ross and Rich 1974; Goulding 1983; Scott and Aronnete 1988; Diehler and Niederhauke 1994). In those laboratory experiments biotite altered to vermiculite and/or mixed-layer clay minerals. Natural weathering of biotite may also produce kaolinite, halloysite, illite, smectite, chlorite and sesquioxides (Stoekl and Sikora 1976; Gilkes and Siddiquiprakarn 1979; Caw et al. 1982; White et al. 1983; AlDahan and Murad 1986; Murad 1990; Robertson and Eggleton 1991). In contrast to the abundant data on synthetic and natural physico-chemical weathering of micaceous minerals, the involvement of biological alteration processes is not as well understood. Lichens commonly occur on rocks, both in their natural state and also when used as monumental and building stones. Thus, lichen-encrusted rocks provide an ideal environment for studying biological aspects of mineral weathering. The first studies of lichen weathering of rocks led to the conclusion that the effect might almost be entirely ascribed to physical causes. It is known today that the lichen-rock interface is a place of considerable chemical activity, due to extracellular excretion of organic acids and organic compounds with chelating capacity (Jones and Wilson 1985). Biotite bioweathering is of great importance to the study of pedogenetic processes. Biotite bioweathering is important, both for understanding pedogenetic processes and biodeterioration of granitic monumental and building stones. Few works have investigated the morphological and chemical features affecting biotite during biochemical weathering induced by lichens. Iskander and Syers (1972), in laboratory experiments studying metal-complex formation by lichen acids with aqueous suspensions of biotite, granite and basalt observed release of Fe, Al, Ca and Mg from silicates. Chelating properties of lichen acids were investigated later by Ascaso et al. (1976) and Ascaso and Galvan (1976) who reacted mica and other minerals with suspended lichens. Those laboratory works demonstrated that lichens could alter their mineral substrates and provided strong circumstantial evidence that this alteration was mediated by the activity of specific lichens. It was concluded that lichens that produce lichen acids could be significant weathering agents in nature. Depletion of Mg, Fe, K and Al on the mica surface was reported only one time by Wilson and Jones (1983) for naturally lichenized granite.

Given that activities of at least some lichens could lead to deterioration of their immediate micaceous substrates, the question is raised as to the exact nature of the processes involved and to the tendency of mineral transformation in natural conditions.

The aim of this work was to: 1) improve the knowledge of natural biological weathering processes of the micaceous component of granite rocks; and 2) identify pathways for the morphological and chemical changes of biodegraded granitic biotite.

MATERIALS AND METHODS

Pieces of granite rock covered by the foliose thallus of Parmelia conspersa (Ehrhrt) Ach. and crustose As-
*Piptoporia intermutans* (Nyl.) Arn. and coexisting pieces without lichen cover were collected at Buitraguejo de la Sierra, near Madrid. Previous petrographic and X-ray diffraction (XRD) studies of this material showed the presence of quartz, orthoclase and plagioclase in the granite rock as major rock-forming minerals, and biotite, zircon and apatite as accessory minerals (Ascaso 1985). Part of lichen-colonized rocks was processed according to conventional transmission electron microscopy (TEM) procedures for the preparation of lichen material (Ascaso et al. 1986) applying LR White resin as the impregnating medium. Afterward, the blocks were cut and fine polished. Wierzchos and Ascaso (1994) give detailed information concerning this preparation technique. Those samples were then examined with SEM in backscattered electron (BSE) emission mode using a DSM 960 Zeiss apparatus. The subsequent microprobe analysis as points analysis, spatial element distribution and microprobe profile with Energy Dispersive Spectrometry (EDS) Link ISIS microanalytical system were made on the SEM-BSE samples simultaneously during SEM observation operating at 33° take-off angle, an accelerating voltage of 15 kV, a working distance of 25 mm and a specimen current of 1–5 nA. Quantitative mineral analyses were obtained using standard ZAF correction procedures. Muscovite was used as a reference to standardize the analysis condition.

Taking into account multipoint EDS analyses performed on SEM-BSE samples, the geochemical mass balance of the major elements was calculated by the Barth method (1948). The number of ions contained within a single unit cell network based on 22 O atoms has also been transformed into the weights of the corresponding elements and the loss, or gain, of each element, and the total loss of matter has thus been obtained (Lineares et al. 1987; Porzniol et al. 1994).

**RESULTS**

**Scanning Electron Microscopy Observations**

The SEM-BSE micrographs of lichen-micaceous material obtained from transverse sections across the lichen-mineral interface (Figure 1) show various aspects of biophysico-chemical weathering of granite biotite. Figure 1a (general view) and Figure 1b (detail view) and Figure 1c demonstrate the *P. conspersa* biotite interface. Successive detachment and separation of biotite was observed in lichen-micaschists mineral contact zones. An abundance of hyphae masses between biotite sheets were apparent. As the BSE signal is strongly dependent upon mean atomic number of the target (Joy 1991) it was possible to observe different levels of grey in the biowheathered biotite sheets (Figure 1b). Particularly the exfoliated sheets demonstrate a deeper shade of grey, indicating the mean atomic number in this zone was less than in the coexisting unaffected one.

Similar exfoliation of biotite was also observed for the case of granitic mica covered by crustose *A. intermutans* (Figures 1a and 1c). Some biotite particles were curved (Figure 1d; lower left part) and others were detached and surrounded by fungal hyphae (Figure 1e). Figure 1f demonstrates the physical action of *A. intermutans* hyphae packed into a deep fissure (3 mm below surface) between biotite sheets. Detachment of biotite plates from fissure walls was observed.

**Microprobe Examinations**

In Figure 2, EDS X-ray images demonstrate the spatial distribution of Fe and K on biowheathered biotite. The Fe spatial distribution maps exactly record the forms and shapes of micaceous material shown on the BSE images (Figures 1b, 1d, 1e, 1f). However, an evident lack of K in the biotite sheets attached to the hyphae cells was observed. Figure 2a shows a large, approximately 350 μm, K-depletion zone in the central part of the exfoliated granitic biotite. The K-depletion effect observed in Figures 2b and 2c occurred more intensively in the approximate area of cracks and narrow fissures between separated biotite layers. The next Fe and K distribution maps (Figure 2d) were taken in the fissure filled with hyphae, which occur at 3 mm distance from the granite rock surface. Loss of K was observed in detached packets of biotite layers and also in the fissure walls zones. In the case of finely exfoliated biotite layers as shown in the BSE image (Figure 1c), K-depletion can be easily demonstrated by the EDS microprobe line profile (Figure 3). The relative concentration of Al was more or less constant (Figure 1c line), and a slight decrease of Fe was observed in separated biotite layers. However, the relative concentration of K was distinctly smaller for exfoliated biotite sheets. The substitution of microprobe line profile for Fe and for K shown in the bottom of Figure 3, indicates a new of K release occurring in separated biotite plates.

**EDS microanalysis also permits determination of chemical and mineralogical features within biowheathered biotite. Multipoint EDS analyses from the unaffected K-rich zone (white shade) and from the coexisting, K-depleted (grey shade on the BSE image—Figure 1b) area were performed. Results of quantitative analyses as wt% of oxides and calculation of structural formulae on the basis of 22 oxygen per unit cell are displayed in Table 1. Moreover, results of the geochemical mass balance, based upon EDS data for major elements for both examined zones are set out in Table 2. Quantitatively, the percentage of element losses during biowheathering (1 → 2) was K⁺ ⇌ Fe⁴⁺ > Ti⁴⁺ ≈ Mg²⁺ with total losses of mass on biowheathered biotite 47.7 g/22 O. The gain sequence was Ca²⁺ > Na⁺ ⇌ Al³⁺ > Si⁴⁺. Nevertheless, changes in mass...
of Ti⁺⁺, Mg²⁺ and Si⁺⁺ contents were insignificant, indicating that these elements were conserved during bioalteration. We also examined biotite grains with no lichen cover on the surface or fissures with SEM-BSE and EDS. These zones lacked characteristic bioalteration features.

Figure 2. Elemental spatial distribution of Fe and K. 2a, 2b, 2c, and 2d correspond to Figures 1b, 1d, 1e and 1f respectively. EDS measurements.

DISCUSSION AND CONCLUSIONS

Detachment, separation and exfoliation of granitic biotite plates in adhesion zones of epilithic foliaceo- crustose lichen thalli confirm the strong physical action of lichens. Similar biophysical effects of the endolithic \textit{Lecidea auricula} thalli were also observed by Ascaso and Wierzchos (1994). Hyphae penetration and expansion and contraction processes generated by alternate wetting and drying cycles led to biophysical weathering of biotic. Chemical changes demonstrated by microprobe analyses also suggest biochemical weathering of biotic. Lichen thalli can form characteristic chemical microenvironment and specific weathering conditions (microclimate) affecting the immediate substratum surface. Syers and Iskandar (1973) suggested 3 possible processes for such bioweathering effects involving carbonic acids, lichen acids and oxalic acids. The possible mechanisms and results of chemical action of these lichenic substances as acid attack and/or chelating effects have been discussed in detail by Jones and Wilson (1985) and Wilson (1995). However, those authors concluded that these processes had not been conclusively demonstrated in natural samples. In this work, distinct depletion of interlam-

Figure 3. Microprobe line profile across line drawn in Figure 1c. EDS measurement.

Figure 1. SEM-BSE images of the lichen-granitic biotite contact zone. Figures 1a and 1c: general view of the \textit{Parmelia compressa}-biotite interface. Key: T = thallus; A = algal layer; m = mycelium. Arrows indicate rhizine in longitudinal section (K) and fragments of rhizine (r) attached to biotite (B). Figure 1b: detail of Figure 1a. Figures 1d and 1e: interface zone between the \textit{Aspilia interna} thalli and biotite sheets. Key: H = hyphae. Figure 1f: fissure in the biotite grain filled by hyphae (H).
Table 1. Comparison of elemental composition between co-existing K-rich (white part) and K-poor (gray part) zones of the biotite shown in Figure 1b. (Oxide wt%, FeO represents total Fe).

<table>
<thead>
<tr>
<th>Element</th>
<th>K-rich (14 analyses)</th>
<th>K-poor (14 analyses)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std. dev.</td>
</tr>
<tr>
<td>SiO₂</td>
<td>38.17</td>
<td>0.57</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.44</td>
<td>0.23</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.37</td>
<td>0.18</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>25.08</td>
<td>0.29</td>
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<tr>
<td>MgO</td>
<td>0.60</td>
<td>0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>7.72</td>
<td>0.21</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.33</td>
<td>0.04</td>
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<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>CaO</td>
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<td>0.01</td>
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Element ratios based on 22 O

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<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>150.6</td>
<td>151.2</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>74.0</td>
<td>95.0</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>153.7</td>
<td>126.8</td>
</tr>
<tr>
<td>Mg</td>
<td>40.1</td>
<td>39.3</td>
</tr>
<tr>
<td>Mn</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Ti</td>
<td>12.0</td>
<td>11.5</td>
</tr>
<tr>
<td>Ca</td>
<td>0.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Na</td>
<td>2.1</td>
<td>8.9</td>
</tr>
<tr>
<td>K</td>
<td>56.9</td>
<td>7.4</td>
</tr>
<tr>
<td>Sum</td>
<td>494.7</td>
<td>446.5</td>
</tr>
</tbody>
</table>

Total losses (%) = 0.7

Table 2. Geochemical mass balance of the K-rich (1) and K-poor (2) biotite zones according to results shown in Table 1.

\[ \text{Gain} \]

The geochemical mass balance data showed in Table 2 indicates that loss of Fe as total Fe was observed. The application of microprobe analysis does not permit determination of the valence of the Fe cations, but according to Pozzuoli et al. (1994) more intensive decreases in Fe<sup>3+</sup> than gains in Fe<sup>2+</sup> during the first stage of natural weathered biotite can be suspected. Moreover, an increase in Ca<sup>2+</sup> and Na<sup>+</sup> in the interlayer spacing was observed. This gain is probably due to the dissolution of fragments of coexisting Ca and Na rich (apatite and feldspars) minerals in the granitic rock and deposition of these cations in interlayer spaces.

As has been shown by Mortland et al. (1956), bioite can alter to vermiculite if interlayer K is used as a nutritional source by plants. The transformation of mica into vermiculite has been observed in laboratory experiments by Weed et al. (1969) as a result of K exchange by cations present in nutrient solution, and soil fungi shifted the equilibrium in this reaction by absorption of K<sup>+</sup> cations. According to recent studies carried out by Pozzuoli et al. (1994), natural weathering of biotite to vermiculite occurred in a localized and heterogeneous way. These authors found out that even small samples are normally characterized by different spatial concentrations of biotite, vermiculite and an intermediate interstratified phase in dependency to the alteration grade. Our results for the geochemical mass balance (Table 2) as element losses or gains and total loss of mass of the bioweathered biotite zone were in good agreement with data obtained by Pozzuoli et al. (1994) and suggest the transformation biotite to scarcely altered biotite with a biotite-vermiculite intermediate interstratified phase. However, additional work remains to be done to confirm the occurrence of this mineralogical transformation of biotites in the lichen-mineral interface. Nevertheless, it is reasonable to conclude that the physico-chemical action of lichens can accelerate weathering rates of biotite.
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REFERENCES


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