

EFFECT OF OXIDATION AND REDUCTION ON POTASSIUM EXCHANGE OF BIOTITE*

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Abstract—The selectivity of K over Ca of Amelia biotite increased sharply upon oxidation by H_2O_2 at pH 6.0. This increase in K selectivity was only partially reversible upon reduction by $Na_2S_2O_4$. Oxidation by H_2O_2 of the Ca-form of this biotite resulted in a loss of no more than 2.8 and 0.4 per cent of the total Fe and Al, respectively, and caused a small and perhaps insignificant decrease in layer charge. Although 95 per cent of the structural Fe^{2+} of the Ca-form of this biotite was oxidized by H_2O_2 , only 17 per cent was reduced again by four treatments with $Na_2S_2O_4$.

The evidence indicates that under the conditions of this experiment the loss of protons from structural hydroxyls was the dominant mechanism by which electroneutrality in the biotite was maintained during oxidation of structural Fe^{2+} . Because this mechanism increases the bond strength of interlayer K, it explains the increased K selectivity of biotite upon H_2O_2 oxidation. The relatively small reduction by $Na_2S_2O_4$ of structural Fe^{3+} to Fe^{2+} , which implies an equally small reprotonation of structural hydroxyls, explains the incomplete reversibility of K selectivity by $Na_2S_2O_4$ treatment.

INTRODUCTION

Oxidation of octahedral Fe^{2+} in biotite decreases the replaceability of K with another cation. This has been attributed to an increased inclination of OH dipoles away from the normal to the basal plane which results in a more electronegative environment of K and consequently in a stronger bonding of K (Barshad and Kishk, 1968; Robert and Pedro, 1968; Juo and White, 1969; Farmer *et al.*, 1971; Gilkes *et al.*, 1973). Farmer *et al.* (1971) showed that chemical oxidation of Fe-rich vermiculites and vermiculitized biotites was associated with a conversion of OH to O ions. This was followed by a loss of Fe^{3+} ions from the octahedral sheet resulting in an increased number of octahedral vacancies. Both these mechanisms reduce the screening effect of hydroxyl H on interlayer K, which results in a stronger bonding of K. Unlike the irreversible loss of octahedral Fe, the loss of protons may be reversible upon reduction (Farmer *et al.*, 1971).

Although the increase of K selectivity of oxidized high-Fe biotites and vermiculites has been amply documented, the effect of reduction on K selectivity is less well established. Barshad and Kishk (1968, 1970) concluded that the increase in K fixation in oxidized

biotite was reversible upon reduction. It is likely, however, that this reversibility is influenced by the amount of iron ejected during oxidation and by the extent of Fe^{3+} to Fe^{2+} reconversion during reduction. This investigation was designed, therefore, to determine K selectivity of biotite after oxidation and reduction and to relate changes in K selectivity to losses of octahedral cations and to changes in oxidation status of octahedral Fe.

MATERIALS AND METHODS

Micas

The biotite used was from Amelia, Virginia. For comparison a phlogopite, containing almost no Fe^{2+} , was used in some of the experiments. The structural formulas are shown below*. Although it came from the same locality, the biotite had a somewhat different composition than the biotite used in previous experiments by LeRoux *et al.* (1970) and Ross and Rich

* The structural formula for Amelia biotite is:
($Al_{0.01}Ti_{0.09}Fe_{0.07}^{3+}Fe_{1.13}^{2+}Mg_{1.64}$)($Si_{2.80}Al_{1.20}$)
 $O_{10}(OH)_2[K_{0.96}Na_{0.08}Ca_{0.01}]$;
and for Loughborough phlogopite it is:
($Al_{0.16}Fe_{0.07}^{3+}Fe_{0.04}^{2+}Mg_{2.77}$)($Si_{2.60}Al_{1.40}$) $O_{10}(OH)_2$
[$K_{0.97}Na_{0.04}Ca_{0.04}$].

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(1973). Only the 54–75 μm fraction was used which was obtained by wet-grinding and subsequent wet-sieving.

Potassium replaceability and K depletion of micas

Potassium replaceability by Ca, or K selectivity over Ca, was determined in 0.2 N CaCl_2 which was adjusted to a pH of 6.0 by addition of $\text{Ca}(\text{OH})_2$. A K-free CaCl_2 stock solution was prepared by dissolving CaCO_3 in HCl. Samples of 40 mg each were added to 200 ml 0.2 N CaCl_2 in 250 ml polypropylene bottles which were placed in a water bath having a constant temperature of 75°C. To determine K exchange in oxidizing conditions, 2 ml of 30 per cent H_2O_2 also at pH 6 were added to some bottles at the start of the reaction. Release of K was followed by periodically withdrawing 1 ml aliquots which were diluted 6 times with H_2O and subsequently analyzed for K by atomic absorption spectrophotometry.

A number of samples were completely K depleted by changing the CaCl_2 solution every 3 days. Four solution changes were required to achieve complete K-depletion. Some of the completely K-depleted samples were oxidized during an additional extraction period by adding 2 ml 30 per cent H_2O_2 to the exchange solution.

Reduction of partially and completely K-depleted micas

After 40 days, when it was certain that K for Ca exchange equilibrium was obtained, the partially K-depleted, H_2O_2 -treated samples were centrifuged and the samples were extracted with sodium dithionite-citrate solution according to the method of Mehra and Jackson (1960). Separate experiments with similarly K-depleted, oxidized samples showed that precipitated hydrous iron oxide was removed during the first $\text{Na}_2\text{S}_2\text{O}_4$ extraction but that significant amounts of K were released not only during the first, but also during the subsequent extractions. Therefore, to minimize K release during reduction, the samples in this experiment were extracted only once with $\text{Na}_2\text{S}_2\text{O}_4$ and then returned to their CaCl_2 solutions. Exchange of K at 75°C of these $\text{Na}_2\text{S}_2\text{O}_4$ -treated samples was again measured by periodically withdrawing 1 ml aliquots.

Chemical analyses

The extracted Fe, Al, Mg and K were determined directly in the $\text{Na}_2\text{S}_2\text{O}_4$ extracts by atomic absorption spectrophotometry since preliminary experiments had shown that digestion of the extracts was unnecessary if standards comparable to the sample solutions were used. Samples of the biotite were digested in HF/HClO_4 solution before and after the K exchange experiments and K, Ca, Na, Fe, Mg and Al were determined by atomic absorption. The layer charges of the micas were estimated from their interlayer cation

population. The content of FeO in the original and treated biotite samples were determined by the method of Reichen and Fahey (1962). This is a relatively simple method which gave reproducible results. Silicon and Ti were determined by the procedure of Jackson (1962).

Infrared absorption and X-ray diffraction analyses

I.R. absorption spectra were recorded on K-resaturated samples heated at 180°C for 6 hr in a heating cell mounted on a Beckman IR 12 spectrophotometer. Some samples were dispersed in KBr disks and others were dried from suspensions in aluminum dishes to form self-supporting thin films.

X-ray diffraction results were obtained on randomly oriented specimens for 060 reflections and on basally oriented specimens for 001 reflections. A Philips diffractometer with Fe-filtered Co radiation was used.

RESULTS

Figure 1 shows the amounts of K exchanged by Ca and the corresponding K concentrations in the CaCl_2 solutions. The equilibrium concentrations of K were 6 ppm for the biotite treated with H_2O_2 and 10 ppm for the biotite not treated with H_2O_2 . Adding H_2O_2 to the reacting solution of phlogopite did not measurably affect its equilibrium concentration of K which is explained by the low (0.67 per cent) FeO content of the mica. The results show that the lower equilibrium K concentration for H_2O_2 -treated biotite was due to oxidation of Fe^{2+} to Fe^{3+} and not to other factors such as diminished particle size or decreased particle thickness which might result from exfoliation during the H_2O_2 treatment.

The K release curves after 40 days reaction in Fig. 1 show the change in K selectivity after extracting the samples once with $\text{Na}_2\text{S}_2\text{O}_4$ solutions. An almost identical change, not shown here, was recorded when a H_2O_2 -oxidized biotite sample was extracted once with $\text{Na}_2\text{S}_2\text{O}_4$ after 2 days reaction in CaCl_2 . The equilibrium K concentration of the biotite which had been 40 per cent K-depleted in the presence of H_2O_2 increased to 8 ppm as compared with an increase to 9.7 ppm for the biotite sample which had been 40 per cent K-depleted in the absence of H_2O_2 . There was only a small increase of 0.3 ppm in the equilibrium K concentrations of the phlogopite samples which had been 39 per cent K-depleted with and without H_2O_2 . The results for phlogopite serve to verify that the marked increase in K concentration for the H_2O_2 -oxidized biotite after $\text{Na}_2\text{S}_2\text{O}_4$ treatment was related to the reduction of Fe^{3+} to Fe^{2+} and probably also to the removal of precipitated hydrous iron oxides but not to other factors as, for example, the formation of new

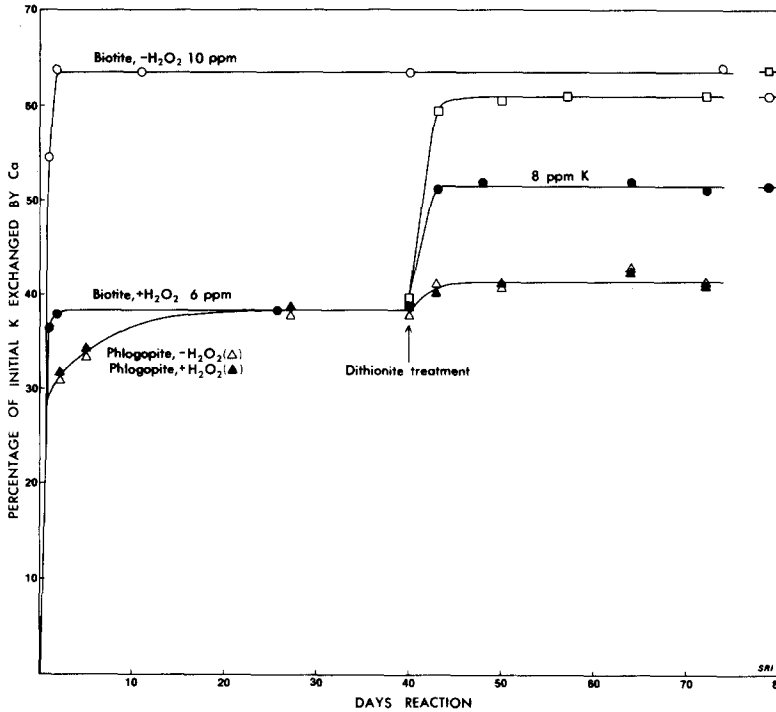


Fig. 1. Amounts of K exchanged by Ca and corresponding equilibrium K concentrations before and after $\text{Na}_2\text{S}_2\text{O}_4$ treatment. The symbol \square is for a biotite sample which had been 40 per cent K depleted in the absence of H_2O_2 prior to $\text{Na}_2\text{S}_2\text{O}_4$ treatment. The disconnected symbols show the amounts of K exchanged as determined by HF/HClO_4 decomposition of the samples after the experiment.

exchange wedges or exchange sites by $\text{Na}_2\text{S}_2\text{O}_4$ treatment. The amounts of K released as determined after decomposing the samples in HF/HClO_4 (shown by the disconnected symbols) agree fairly well with the amounts of K released as determined by analysis of the CaCl_2 reacting solutions (shown by the connected symbols). Ideally, for the $\text{Na}_2\text{S}_2\text{O}_4$ -treated samples the amounts indicated by the disconnected symbols should be about 6 per cent higher than the amounts indicated by the connected symbols, because, according to Fig. 2, about 6 per cent K was extracted in one $\text{Na}_2\text{S}_2\text{O}_4$ treatment.

Figure 2 shows the amounts of cations extracted by repeated $\text{Na}_2\text{S}_2\text{O}_4$ treatments from the samples which had been completely and partially K-depleted in the presence and absence of H_2O_2 . The samples which were K-depleted in the absence of H_2O_2 were nevertheless partly oxidized (Table 1). The clear break in the curves indicates that surface- and inter-layer hydroxides were dissolved during the first extraction and that the small amounts dissolved in the subsequent extraction periods were due to dissolution of the sample. Thus the quantities of cations liberated by H_2O_2 oxidation were obtained by extrapolation to zero extrac-

tion periods. Accordingly, 2.8 per cent of the initial Fe and 0.4 per cent of the initial Al were ejected from the 100 per cent K-depleted oxidized biotite (Fig. 2A) and 0.9 per cent of the initial Fe and 0.2 per cent of the initial Al from the 40 per cent K-depleted, H_2O_2 -treated biotite (Fig. 2B). About 0.2 per cent of the initial Mg was released by the $\text{Na}_2\text{S}_2\text{O}_4$ treatment, which is attributed to dissolution of the sample during this treatment. An additional 0.5 per cent of the total Mg was released from the biotite samples during K depletion by CaCl_2 . This amount was the same for the samples depleted in the presence and absence of H_2O_2 and is therefore also attributed to a slight dissolution of the samples during K depletion. The pH of the CaCl_2 solution during K depletion and oxidation remained the same, which is further evidence that Mg release was small. The rate of K exchange with Na in the $\text{Na}_2\text{S}_2\text{O}_4$ solutions was lower for the 40 per cent K-depleted, H_2O_2 -treated biotite than that for the corresponding sample not treated with H_2O_2 (Fig. 2B). This corroborates the incomplete increase of the equilibrium K concentration of the H_2O_2 -treated biotite after $\text{Na}_2\text{S}_2\text{O}_4$ treatment (Fig. 1). A slight dissolution of the phlogopite samples due to $\text{Na}_2\text{S}_2\text{O}_4$ treatment is indicated by the small but

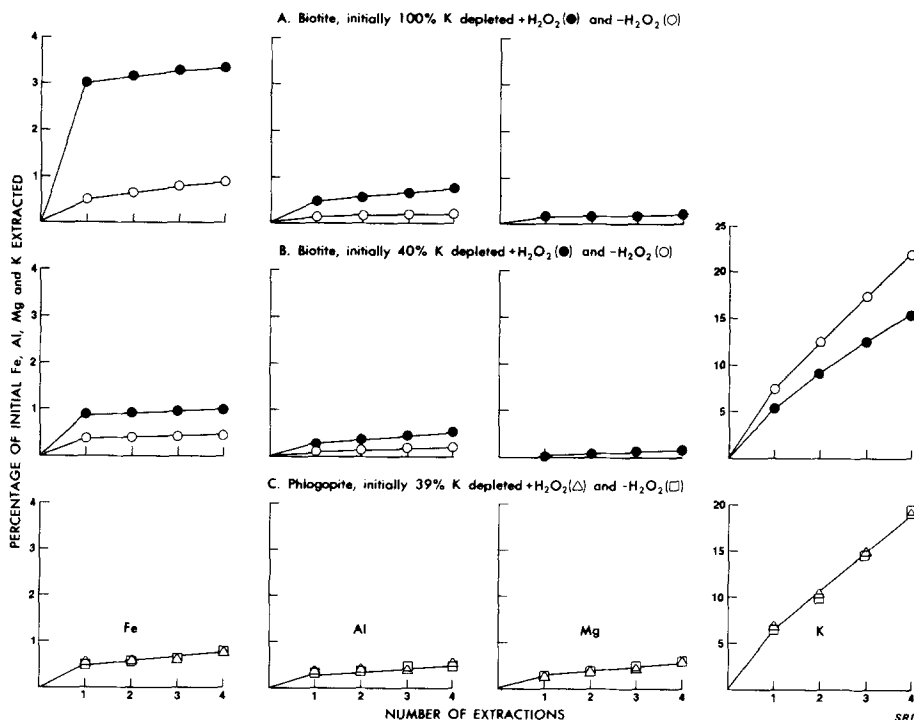


Fig. 2. Loss of Fe, Al, Mg and K by successive $\text{Na}_2\text{S}_2\text{O}_4$ extractions of the indicated samples.

equal release of octahedral cations from the sample which had been treated with and without H_2O_2 (Fig. 2C). The K exchange of these samples by Na in the $\text{Na}_2\text{S}_2\text{O}_4$ solutions was also the same which substantiates the equal equilibrium K concentration of the corresponding samples after $\text{Na}_2\text{S}_2\text{O}_4$ treatment in Fig. 1.

Table 1 shows additional data for the biotite and phlogopite samples. For the 100 per cent K-depleted biotite there was a considerable decrease in layer charge (50 m-equiv/100 g) during K-depletion, but only a small further decrease of 6 m-equiv/100 g during H_2O_2 oxidation. A subsequent increase of 10 m-equiv/100 g was

Table 1. Layer charges and iron contents of Loughborough phlogopite and Amelia biotite*

| | Layer charge† (m-equiv/100 g) | Fe^{2+} as per cent of sample weight | Fe^{2+} oxidized to Fe^{3+} as per cent of original Fe^{2+} |
|--|-------------------------------|---|--|
| Loughborough phlogopite, original ($\text{Fe}^{2+} = 0.54\%$) | 243 | | |
| 100% Ca-form, K-depleted without H_2O_2 | 220 | | |
| Amelia biotite, original ($\text{Fe}^{2+} + \text{Fe}^{3+} = 14.5\%$) | 220 | 13.3 | |
| 100% Ca-form, K-depleted without H_2O_2 | 170 | 8.3 | 37 |
| 100% Ca-form, K-depleted with H_2O_2 | 164 | 0.7 | 95 |
| 100% Ca-form, K-depleted with H_2O_2 then reduced once | 174 | 2.3 | 83 |
| 100% Ca-form, K-depleted with H_2O_2 then reduced four times | 188 | 2.9 | 78 |
| 40% Ca-form, partially K-depleted without H_2O_2 | 203 | 12.4 | 6 |
| 40% Ca-form, partially K-depleted with H_2O_2 | 198 | 7.1 | 46 |
| 40% Ca-form, partially K-depleted with H_2O_2 then reduced once | | 8.9 | 33 |
| 40% Ca-form, partially K-depleted without H_2O_2 then reduced four times | | 9.0 | 32 |

* Sample weights of hydrated forms based on weights at 200°C since TGA analysis showed that loss of interlayer water was complete at this temperature.

† Layer charges of Ca-forms based on weights of corresponding K-forms.

recorded after one $\text{Na}_2\text{S}_2\text{O}_4$ treatment and a further increase of 14 m-equiv/100 g after four $\text{Na}_2\text{S}_2\text{O}_4$ treatments. These increases after $\text{Na}_2\text{S}_2\text{O}_4$ reduction are similar to those reported by Farmer *et al.* (1971) and may be significant. There was also a significant decrease in layer charge of the phlogopite (23 m-equiv/100 g) during K-depletion. This decrease, combined with the small reduction in layer charge during H_2O_2 oxidation of the K-depleted biotite, indicates that reactions other than oxidation decreased the layer charge during K-depletion. Such a reaction may be the absorption of protons into the structure (Rosenqvist, 1963; Raman and Jackson, 1966; Newman and Brown, 1966; Leonard and Weed, 1970). Even in the absence of H_2O_2 37 per cent of the original Fe^{2+} was oxidized during K depletion and nearly all (95 per cent) Fe^{2+} was oxidized in the presence of H_2O_2 . A small decrease to 78 per cent in the oxidized Fe^{2+} occurred after four $\text{Na}_2\text{S}_2\text{O}_4$ treatments which indicates that reduction of oxidized structural Fe by $\text{Na}_2\text{S}_2\text{O}_4$ is relatively ineffective. The changes in layer charge and Fe^{2+} contents of the 40 per cent K-depleted biotite samples are half or less than those of the corresponding 100 per cent K-depleted samples. This reflects the fact that only the expanded portion of the sample is subject to oxidation by H_2O_2 and to subsequent reduction by $\text{Na}_2\text{S}_2\text{O}_4$.

Infrared absorption analysis of K-depleted and then K-resaturated biotite samples did not show significant differences resulting from H_2O_2 oxidation. Differences in direction of OH dipoles caused by H_2O_2 oxidation were apparently not sufficient to be observed by the techniques used in this experiment.

Oxidation of the K-depleted, Ca-saturated biotite by H_2O_2 decreased the 060 spacing from 1.538 to 1.534 Å. This corresponds to a decrease in *b*-dimension from 9.23 to 9.20 Å which is somewhat smaller than the decreases in *b*-dimensions reported by Farmer *et al.* (1971). The biotite samples which were partially K-depleted in 0.2 N CaCl_2 with and without H_2O_2 gave 14.8 and 10.0 Å d_{001} spacings indicating discrete expanded and unexpanded components. There was no evidence for a regularly-interstratified hydrobiotite structure in the H_2O_2 -treated samples. Such a structure might develop when K in biotite is replaced by a hydrated cation under certain experimental conditions of oxidation and K exchange (Farmer and Wilson, 1970).

DISCUSSION

The selectivity of K over Ca of the biotite used in this experiment increased sharply upon oxidation by H_2O_2 . This increase in K selectivity was only partially reversible upon $\text{Na}_2\text{S}_2\text{O}_4$ treatment. Oxidation by

H_2O_2 caused only a small decrease in layer charge of this biotite. Similarly, oxidation of this biotite at pH 6.0 resulted in a loss of no more than 2.8 and 0.4 per cent of the total Fe and Al, respectively. The small amount of Fe^{3+} which was reduced to Fe^{2+} by $\text{Na}_2\text{S}_2\text{O}_4$ indicates little reconversion of O to OH.

The quantity of octahedral cations ejected from the biotite oxidized at pH 6 in our experiment is much smaller than the losses reported by Farmer *et al.* (1971) and Gilkes *et al.* (1973) for biotites oxidized under more acid conditions. This suggests that the loss of octahedral cations versus the loss of hydroxyl protons is strongly influenced by pH.

As has been pointed out by Farmer *et al.* (1971), there are three possible mechanisms by which electroneutrality in biotite is maintained during oxidation of structural Fe. These are: (a) loss of protons from structural hydroxyls; (b) loss of octahedral cations; and (c) decrease in layer charge. Under the conditions of our experiment it appears that loss of protons from structural hydroxyls was the major mechanism which balanced the change in charge due to oxidation of Fe^{2+} to Fe^{3+} .

The conversion of structural OH to O eliminates the screening effect of H on K near the deprotonated hydroxyls which should result in a stronger bonding of K at these locations. This mechanism, therefore, explains the increase in K selectivity of the H_2O_2 -oxidized biotite in our experiment. The limited reduction by $\text{Na}_2\text{S}_2\text{O}_4$ of structural Fe^{3+} to Fe^{2+} , which implies a proportionally limited reconversion of O to OH, explains the incomplete reversibility of K selectivity after $\text{Na}_2\text{S}_2\text{O}_4$ treatment. This reversibility actually seems greater than expected from the small change of Fe^{3+} to Fe^{2+} after $\text{Na}_2\text{S}_2\text{O}_4$ reduction. This suggests that the increased K selectivity of H_2O_2 -oxidized biotite may be partly due to a blocking of K exchange by precipitated hydrous oxides of Fe and Al in the inter-layer.

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Résumé—La sélectivité de la biotite d'Amélia pour K vis à vis de Ca, augmente brutalement lors de l'oxydation à pH 6,0 par H_2O_2 . Cette augmentation de sélectivité pour K est seulement partiellement réversible lors de la réduction par $Na_2S_2O_4$. L'oxydation par H_2O_2 de la forme Ca de cette biotite entraîne une perte de Fe et Al qui ne dépasse pas 2,8 pour cent de Fe total et 0,4 pour cent de Al total, et une petite diminution, peut être non significative, de la charge du feuillet. Bien que 95 pour cent de Fe^{2+} de constitution de la forme Ca de cette biotite soient oxydés par H_2O_2 , seuls 17 pour cent en sont réduits après quatre traitements par $Na_2S_2O_4$.

Il est donc évident que dans les conditions de cette expérience, la perte de protons venant des hydroxyles de constitution est le mécanisme principal qui maintient l'électronéutralité de la biotite pendant l'oxydation de Fe^{2+} du réseau. Comme ce mécanisme augmente la force de rétention de K interfeuillet, il explique l'augmentation de sélectivité de la biotite pour K lors de l'oxydation par H_2O_2 . La diminution relativement faible de Fe^{3+} qui se transforme en Fe^{2+} par traitement $Na_2S_2O_4$, implique une reprotonation également petite des hydroxyles de constitution et explique la réversibilité incomplète de la variation de la sélectivité pour K lors des traitements $Na_2S_2O_4$.

Kurzreferat—Die Selektivität von Amelia Biotit für K gegenüber Ca stieg nach Oxidation mit H_2O_2 bei pH 6,0 scharf an. Dieser Anstieg der K-Selektivität war nach Reduktion mit $Na_2S_2O_4$ nur teilweise reversibel. Die Oxidation durch H_2O_2 hatte bei der Ca-Form dieses Biotits einen Verlust von nicht mehr als 2,8 Prozent Gesamt-Fe und 0,4 Prozent Gesamt-Al zur Folge und rief eine geringe und vielleicht nicht signifikante Abnahme der Schichtladung hervor. Obwohl 95 Prozent des Gitter- Fe^{2+} der Ca-Form dieses Biotits durch H_2O_2 oxidiert wurde, wurden nur 17 Prozent durch vier Behandlungen mit $Na_2S_2O_4$ wieder reduziert.

Dieser Nachweis zeigt, daß unter diesen Bedingungen dieses Versuches der Verlust von Protonen aus Gitterhydroxylionen der vorherrschende Mechanismus ist, mit dem die Elektronneutralität in Biotit während der Oxidation von Gitter- Fe^{2+} aufrecht erhalten wird. Da dieser Mechanismus die Bindungsstärke des Zwischenschicht-K erhöht, erklärt er die Zunahme der K-Selektivität von Biotit als Folge der H_2O_2 -Oxidation. Die verhältnismäßig geringe Reduktion des Gitter- Fe^{3+} zu Fe^{2+} durch $Na_2S_2O_4$, die eine gleich geringe Reprotonierung der Gitterhydroxylionen beinhaltet, erklärt die unvollständige Reversibilität der K-Selektivität durch $Na_2S_2O_4$ -Behandlung.

Резюме — Избирательность биотита Амелия по K над Ca резко повышается при окислении посредством H_2O_2 при pH 6,0. При восстановлении $Na_2S_2O_4$ это повышение избирательности по K только частично обратимо. Окисление H_2O_2 формы Ca этого биотита повело к потере не менее, чем 2,8 и 0,4 процента общего содержания Fe и Al, соответственно, и причинило малое, а может быть незначительное, понижение заряда слоев. Хотя, 95 процентов структурного Fe^{2+} формы Ca этого биотита подвергалось окислению посредством H_2O_2 , только 17 процентов было восстановлено четырьмя переработками $Na_2S_2O_4$.

Полученные данные указывают, что при этом эксперименте потеря протонов из структурных гидроксиллов является преобладающим механизмом удержания электронейтральности биотита во время окисления структурного Fe^{2+} . Так как, этот механизм усиляет связь межслойного K, это объясняет увеличение избирательности биотита по K при окислении H_2O_2 . Сравнительно малое восстановление Fe^{3+} в Fe^{2+} посредством $Na_2S_2O_4$, означает также малую репротонацию структурных гидроксиллов, и объясняет неполную обратимость избирательности по K при переработке $Na_2S_2O_4$.