Orientation of the Dipole Moments of Hydroxyl Groups in Oxidized and Unoxidized Biotite

Abstract. *Observations of the infrared absorption bands attributed to the stretching vibrations of hydroxyl groups in biotite containing predominantly ferrous iron show that the dipole moments of the hydroxyls associated with ferrous iron are oriented perpendicular to the cleavage plane of the lattice. Oxidation in the biotite from ferrous iron to ferric iron results in the disappearance of the infrared absorption bands due to the hydroxyls associated with ferrous iron. The dipole moments of the hydroxyls associated with ferric iron in the oxidized biotite have been shown to be in an inclined position with respect to the cleavage plane. Our experiments confirm the hypothesis of Barshad and Kishk regarding the effect of oxidation on the replaceability of interlayer potassium ions in biotite by ammonium ions.*

Barshad and Kishk (*1*) have showed that oxidation of octahedral ferrous to ferric iron in biotite increases the difficulty of replacing interlayer K^+ in the mineral by NH_4^+ ions. They explained this effect on the basis of a change in the orientation of the dipole moments of the octahedral hydroxyls but offered no experimental evidence. They assumed that the dipole moments of the hydroxyl groups are perpendicular to the cleavage plane when iron is in the ferrous state, whereas in the oxidized biotite, where iron is in the ferric state, the orientation of the dipole moments of the hydroxyls is changed to an inclined position with respect to the cleavage plane. Such a change may place the interlayer K^+ in a more electrically negative environment; in other words, the interlayer K^+ becomes more strongly held by the surrounding oxygens in the oxidized biotite (*2*). Studies of the infrared absorption bands of hydroxyls in biotite in relation to chemical composition and weathering (*3–5*) have showed that OH groups associated with ferric iron give infrared absorption bands at frequencies lower than those associated with ferrous iron.

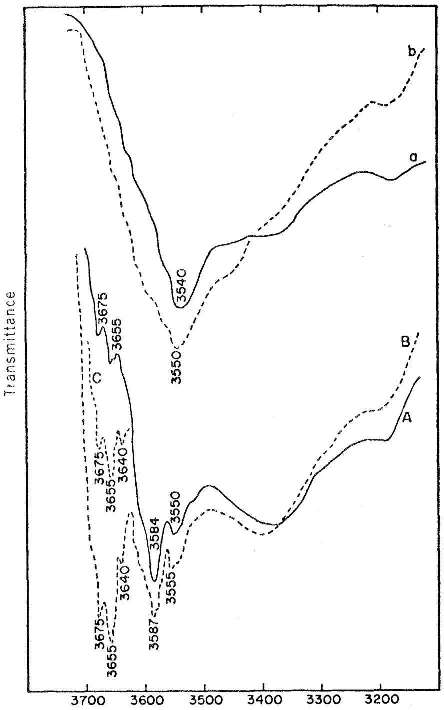

Fig. 1. Stretching vibrations of hydroxyls in oxidized and unoxidized biotites. (Curve *A*) Natural biotite scanned at normal position; (curve *B*) natural biotite scanned at 45° rotation; (curve *C*) natural biotite scanned at 30° rotation; (curve *a*) biotite oxidized by treatment with sodium hypochlorite scanned at normal position; (curve *b*) biotite oxidized by treatment with sodium hypochlorite scanned at 45° rotation.

To test the validity of Barshad and Kishk's hypothesis, we observed the infrared absorption bands of the stretching vibrations of hydroxyls in unoxidized and oxidized biotite. The biotite used (*6*) contained predominantly ferrous iron. Biotite was oxidized by treating the sample ($< 5\ \mu$) repeatedly with 5 percent sodium hypochlorite at 80°C, and the oxidized biotite was resaturated with K^+ according to the procedure of Barshad and Kishk (*1*). Oriented films of both the treated and untreated biotites were made by depositing the sample on an Irtran-2 window (Eastman Kodak). The air-dried films were then covered with Nujol to reduce scattering of the infrared radiation. Infrared spectra were recorded on a grating spectrometer (Perkin-Elmer model 421) at × 5 scale expansion.

The infrared spectrum of the untreated biotite in the region of OH stretching vibrations is given in Fig. 1 (curve *A*). The two strong and distinctive bands at 3584 cm^{-1} and 3550 cm^{-1}, and the two weak but sharp bands at 3675 cm^{-1} and 3655 cm^{-1}, are attributed to the vibrations of the various types of octahedral hydroxyls in the biotite lattice (*3, 4*).

Rotating the sample film 45° with respect to the normal scanning position resulted in the following changes in the infrared spectrum (Fig. 1, curve *B*): The intensity of the bands at 3655 cm^{-1} and 3675 cm^{-1} greatly increased, even though the positions of these bands remained unchanged. A third band appeared at a frequency of 3640 cm^{-1}. The intensities of these three bands were found to increase further as the sample film was rotated to a greater angle with respect to the normal scanning position. This effect indicates that the hydroxyls which give rise to these bands are oriented in a position perpendicular to the cleavage plane of the biotite lattice. The bands at 3550 cm^{-1} and 3584 cm^{-1} in the spectrum scanned at normal position shifted slightly to higher frequencies when the spectrum was scanned at 45°, but their intensities remained unaffected.

The infrared spectrum of the biotite oxidized by treatment with sodium hypochlorite and saturated with K^+ is given in Fig. 1 (curve *a*). Only one strong band at 3540 cm^{-1} is seen in the OH stretching region of the oxidized biotite. This band may be attributed mainly to the OH associated with the ferric iron in the octahedral layer. The disappearance as a result of oxidation of the three bands of the untreated biotite at 3640 cm^{-1}, 3655 cm^{-1}, and 3675 cm^{-1} suggests that these OH groups, which are oriented perpendicular to the cleavage plane, are associated with the ferrous iron in the structure. Rotating the sample film to 45° caused the band of the oxidized biotite at 3540 cm^{-1} to shift to a slightly higher frequency, but its intensity remained unaffected (Fig. 1,

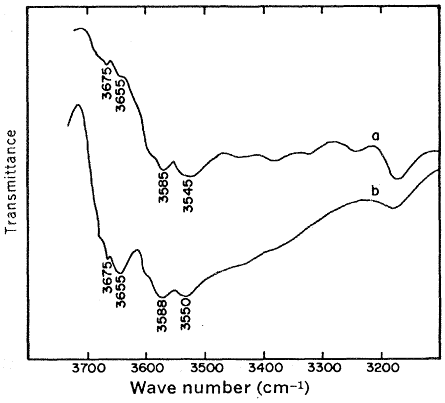

Fig. 2. Stretching vibrations of biotite oxidized by treatment with H_2O_2 in the presence of excess K^+. (Curve *a*) Scanned at normal position; (curve *b*) scanned at 45° rotation.

curve *b*). No recognizable band appeared in the vicinity of 3650 cm^{-1} when the sample film was scanned at a rotation of 45°. However, a shoulder appeared between 3600 cm^{-1} and 3700 cm^{-1} which may indicate the presence of a small amount of hydroxyl perpendicular to the cleavage plane of the oxidized biotite. The decrease in intensity of the band near 3380 cm^{-1} on rotating the spectrum 45° may suggest that the water molecules at the immediate surface of the mineral are well oriented (*7*). It is difficult to recognize the presence of the band at 3584 cm^{-1} in the spectrum of the oxidized biotite (Fig. 1, curve *a*); this appeared to be the strongest band in the untreated biotite spectrum (Fig. 1, curve *A*). This band may still be present in the oxidized biotite but may be overlapped by the increase in intensity of the band at 3540 cm^{-1} as a result of oxidation, or it may have disappeared during oxidation; presumably, it is also associated with the ferrous iron in the structure.

Farmer *et al.* (*3, 4*) assigned the band of a weathered biotite flake at 3550 cm^{-1} to the OH groups associated with the ferric iron; the principal band of the unoxidized biotite at 3658 cm^{-1} was ascribed to OH associated with ferrous iron. Farmer *et al.* assigned this band (3658 cm^{-1}) to $(Mg_2Fe)^{2+}$, $(MgFe_2)^{2+}$, and $(Fe_3)^{2+}$ groupings, but they were unable to resolve individual bands. With the aid of thinner oriented films recorded at × 5 scale expansion, we obtained more detailed spectra of these biotite samples in the region of the OH stretching vibrations.

On the basis of the results reported here and by others, it may be concluded that the OH bands of the untreated biotite at 3675 cm^{-1}, 3655 cm^{-1}, and 3640 cm^{-1} may be assigned to OH associated with the groupings $(Mg_2Fe)^{2+}$, $(MgFe_2)^{2+}$, and $(Fe_3)^{2+}$, respectively, in the octahedral layer. These OH groups are oriented perpendicular to the cleavage plane of the biotite crystal. The OH band of the untreated biotite at 3550 cm^{-1} indicates the presence of ferric iron. The band of the untreated biotite at 3587 cm^{-1} may be due to the OH groups associated with other cations such as Al^{3+} (*3*). Oxidation of ferrous to ferric iron in biotite by sodium hypochlorite results in the disappearance of the OH bands associated with the ferrous iron; the band at 3540 cm^{-1} is the only significant lattice OH stretching vibration observed in the spectrum of the oxidized biotite.

Only partial oxidation of ferrous to ferric iron occurred when the biotite powder sample was treated repeatedly at 80°C with 30 percent H_2O_2 containing 0.2*M* KCl. The bands at 3655 cm^{-1} and 3675 cm^{-1} persisted after H_2O_2 treatment (Fig. 2, curve *a*). However, their intensities relative to that of the band at 3550 cm^{-1} were reduced considerably (Fig. 2, curve *b*) as compared with those of the untreated biotite (Fig. 1, curve *B*). This suggests that the presence of an excess amount of K^+ in the solution during the oxidation process would prevent layer expansion of the biotite. Thus, only the Fe^{2+} ions present at the broken edges of the octahedral layer or in other easily accessible sites have been oxidized to Fe^{3+} under this condition, whereas, in the case of oxidation with sodium hypochlorite, the Na^+ ions may replace the interlayer K^+ and cause the layers to expand. Consequently, the Fe^{2+} ions inside the octahedral lattice were made more available for oxidation.

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References and Notes

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Oral Contraceptives: Long-Term Use Produces Fine Structural Changes in Liver Mitochondria

Abstract. Liver biopsies from two groups of women receiving oral contraceptives from 1 to 6 months and from 12 to 30 months, respectively, were examined by electron microscopy. The fine structure of the liver cells from the first group appeared normal, except for an increase in the amount of smooth endoplasmic reticulum. In the second group, however, there were many cases with striking changes—altered shape, increase in size, and presence of paracrystalline inclusions—in the mitochondria. No significant correlation between mitochondrial changes and alterations in liver function was detected.

Chronic administration of oral contraceptives can occasionally interfere with various aspects of hepatic function, resulting in a decreased excretory capacity for bromosulfonphthalein (BSP), cholestatic jaundice, and a transient increase in serum aminotransferases (*1*). Little data is available, however, on the fine structure of the hepatic cell during long-term treatment with these hormonal agents. We studied two groups of women who regularly had used oral contraceptives (*2*). In group 1 (15 patients) the treatment lasted from 1 to 6 months, while in group 2 (13 patients) treatment was from 12 to 30 months. All the women (ages 19 to 40 years) were clinically normal. None had a history of chronic drug ingestion, heavy alcohol intake, or malnutrition.

To evaluate the liver function the following standard clinical tests were performed: serum bilirubin, serum aminotransferases, alkaline phosphatase concentrations and BSP excretion (45-minute retention and the clearance constant K_1). A liver biopsy was obtained from each patient with the Menghini needle. No patients were biopsied during menstruation, but otherwise the samples represented all stages of the cycle. The tissue was fixed in 4 percent formaldehyde for light microscopy, and in 2 percent osmium tetroxide buffered with Veronal acetate for electron microscopy (*3*). Sections embedded in Epon (*4*) were stained with uranyl acetate and lead citrate (*5*).

Liver-function tests in both groups were normal except for BSP excretion, which, in a few cases, was prolonged. No significant difference was found when both groups were compared statistically. By light microscopy, sections of the hepatic tissue appeared normal in all cases. By electron microscopy,