

OXIDATION AND REDUCTION OF STRUCTURAL IRON IN CHLORITE AT 480°C

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Abstract—An iron-rich chlorite, ripidolite, was oxidized by air-heating at 480°C, i.e., below the dehydroxylation temperature and subsequently reduced in hydrogen at the same temperature. On the basis of chemical, differential thermal, infrared, Mössbauer, and X-ray powder diffraction analyses, Fe(II) seems to be present only in the 2:1 layer of the original chlorite in a type of site similar to that of Fe(II) in biotite, with OH in *cis*-positions. These data also suggest that octahedral Al and Fe(III) are located in the hydroxide sheet of the original chlorite. The structural changes of the mineral due to the oxidation and the subsequent reduction appear limited to minor structural rearrangements and, perhaps, to the introduction of OH in both *cis*- and *trans*-positions. The results of the investigation are in agreement with a reaction of the form: $[\text{Fe(II)OH}]^+ \rightleftharpoons [\text{Fe(II)O}]^+ + \text{H}(\text{H}^+ + \text{e}^-)$.

Key Words—Chlorite, Infrared spectroscopy, Iron, Mössbauer spectroscopy, Oxidation, Reduction.

INTRODUCTION

The alteration of chlorite to vermiculite is considered to take place via an oxidation and subsequent removal of structural iron from the hydroxide interlayer (Makumbi and Herbillon, 1972; Ross, 1975; Ross and Kodama, 1974, 1976; Goodman and Bain, 1979). The two processes may be separated by thermal oxidation of the iron succeeded by acid dissolution of the hydroxide interlayer (Ross and Kodama, 1974; Goodman and Bain, 1979). During dry thermal oxidation, the layer charge remains constant by the release of one hydrogen atom per oxidized Fe(II), as suggested in the oxidation of biotite (Vedder and Wilkins, 1969; Farmer *et al.*, 1971; Veith and Jackson, 1974; Hogg and Meads, 1975; Tripathi *et al.*, 1978; Bagin *et al.*, 1980), chlorite (Makumbi and Herbillon, 1972; Goodman and Bain, 1979), and smectite (Rozenon and Heller-Kallai, 1976a, 1976b). For chlorite, the mechanism of this hydrogen release is obscure, as is the reversibility of the oxidation step. Furthermore, the distribution of the cations between the two octahedral sheets in chlorite is not completely clear.

In the present investigation an iron-rich chlorite (ripidolite) was heated below the dehydroxylation temperature at 480°C in the presence of oxygen. The oxidized chlorite was subsequently reduced by hydrogen

or carbon monoxide. The oxidation and reduction mechanisms of the chlorite were investigated by chemical, differential thermal, infrared, Mössbauer, and X-ray powder diffraction analyses.

EXPERIMENTAL

Material

Ripidolite (CCa-1) of the polytype I1b from Flagstaff Hill, El Dorado County, California, obtained from The Clay Minerals Society, was studied. Chlorites from this area have been described by Post and Plummer (1972). The sample was hand ground and passed through a 0.25-mm sieve. A chemical analysis by the HF method (Bernas, 1968) gave: 12.1% Si, 10.8% Al, 19.1% Fe, and 10.5% Mg. The minor element content as determined by X-ray fluorescence was: 0.71% Ti, 0.08% Cr, 0.06% Mn, 0.04% Ni, 0.006% Cu, 0.003% Ga, and 0.002% Zn. Loss on ignition was 9.3%. The Fe(II)/Fe(III) ratio determined by Mössbauer spectroscopy (see below) was 10.8, giving the half-cell formula:



According to Post and Plummer (1972), differential thermal analysis showed no sign of dehydroxylation below 500°C.

Oxidation-reduction

The chlorite was oxidized by heating it in air in an open crucible in a furnace at $480^\circ \pm 6^\circ\text{C}$. Samples were removed after heating periods of a few hours to 1680 hr. After heating the chlorite for 1680 hr, Mössbauer spectroscopy (see below) showed that nearly all of the Fe(II) was oxidized. During the

heating the color changed from grayish green to grayish brown. The original and the oxidized (1680 hr at 480°C) chlorite were also heated at 480°C in a sealed glass tube filled with nitrogen. The oxidized chlorite was reduced in a glass tube under a hydrogen (or carbon monoxide) pressure of 106 kPa at 480°C. The reduction was followed by a color change from grayish brown to grayish black.

Chemical analysis

The original and the oxidized (heated 1680 hr at 480°C) chlorite were treated by dithionite-citrate-bicarbonate as described by Gilkes *et al.* (1972) and by prolonged EDTA extraction in weakly alkaline solutions as described by Borggaard (1979). Extracted Fe and Mg were determined by atomic absorption spectrophotometry.

Differential thermal analysis and evolved gas analysis

A Stanton-Redcroft 673-4 differential thermal analysis (DTA) apparatus was used with Pt-Rh thermocouples and platinum crucibles. The water evolved was detected by an Analytical Development Co. infrared H₂O-analyzer having sensitivity ranges 0–1000 ppm and 0–10,000 ppm. Only evolved water was detected. Al₂O₃ was used as a reference material. Atmospheres of N₂ (analytical quality) and O₂ (analytical quality) in N₂ were used.

Infrared spectroscopy

The infrared (IR) spectra were recorded on pressed KBr discs (1 mg chlorite in 300 mg KBr) on a Perkin-Elmer Model 457 spectrometer.

Mössbauer spectroscopy

Mössbauer spectra were obtained by use of a constant acceleration spectrometer with a 25 mCi source of Co⁵⁷ in Rh. The spectrometer was calibrated with a 10- μ m absorber of α -Fe which yielded a linewidth, full width at half maximum (FWHM), of 0.25 mm/sec. Isomer shifts are given relative to the centroid of the spectrum of α -Fe at room temperature. To avoid texture effects which may result in different line areas of the two lines in the quadrupole doublets, the measurements were carried out in a geometry with the normal of the absorber plane forming an angle of 54.7° with the gamma ray direction (Ericsson and Wäppling, 1976).

Scanning electron microscopy

Scanning electron micrographs (SEMs) were obtained by use of a J.S.M.-U3 scanning electron microscope. The powdered samples were studied at 100 to 30,000 times magnification.

Weight loss

The weight loss during the oxidation was determined on a sample heated first at 300°C for 83 days and then heated at 480°C in an open crucible. The preheating at 300°C resulted in a weight loss of approximately 0.3%, but no oxidation could be detected after this treatment.

X-ray powder diffraction

X-ray powder diffraction (XRD) studies were carried out using a Philips goniometer PW 1050/80, with channel control and proportional counter PW 1390 and a Co normal-focus tube PW 2236/20. A Fe beta filter before the sample and pulse height selection were used for monochromatization, as the use of an AMR E3-202 curved graphite monochromator resulted in intense low-angle scatter, in accordance with Klug and Alexander (1974). Randomly oriented specimens were analyzed. Quartz with a particle size less than 0.063 mm was used as external standard.

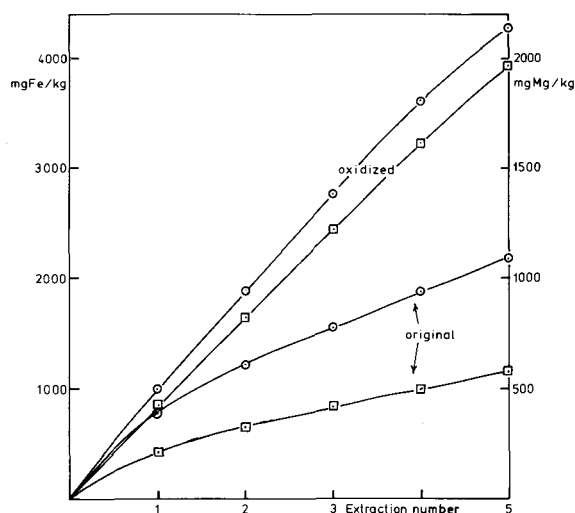


Figure 1. Dithionite-citrate-bicarbonate extractable iron (○) and magnesium (□) as a function of extraction number for original chlorite and oxidized chlorite (heated in air at 480°C for 1680 hr).

RESULTS

Chemical analysis

Iron and magnesium extracted by the dithionite-citrate-bicarbonate method by repeated extractions for the original and the oxidized chlorite (Figure 1) show that although the extracted amounts are small, the oxidized sample is clearly more labile than the original chlorite. The absence of a break on the extraction curve of the oxidized chlorite indicates that almost no iron oxides are present on the mineral surface. The prolonged EDTA-extraction data are shown in Figure 2. Here also the extraction curves of the original and the oxidized chlorite are different. The amount of iron extracted from the former is independent of pH (8.5 to 10.3), the solid:solution ratio (1:500 to 1:100), the EDTA concentration (0.02 M to 0.01 M), and the extraction time (up to 9 months) after approximately 3 months of extraction. This result corresponds to earlier findings (Borggaard, 1976, 1979), indicating extraction of only a surface coating of iron oxides, presumably noncrystalline iron oxides. The break on the extraction curve of the original chlorite in Figure 1 also indicates a surface coating of iron oxides. The results for oxidized chlorite shown in Figures 1–2 indicate a commencing dissolution of the mineral.

Original and oxidized chlorite were also extracted with HCl (Ross and Kodama, 1974) to remove the interlayer hydroxide sheet. Less Al, Fe, and Mg was mobilized by this treatment than by the EDTA extraction.

Differential thermal analysis and evolved gas analysis

The DTA curve (Figure 3A) of the chlorite in 40% O₂ is similar to the curve obtained by Post and Plummer

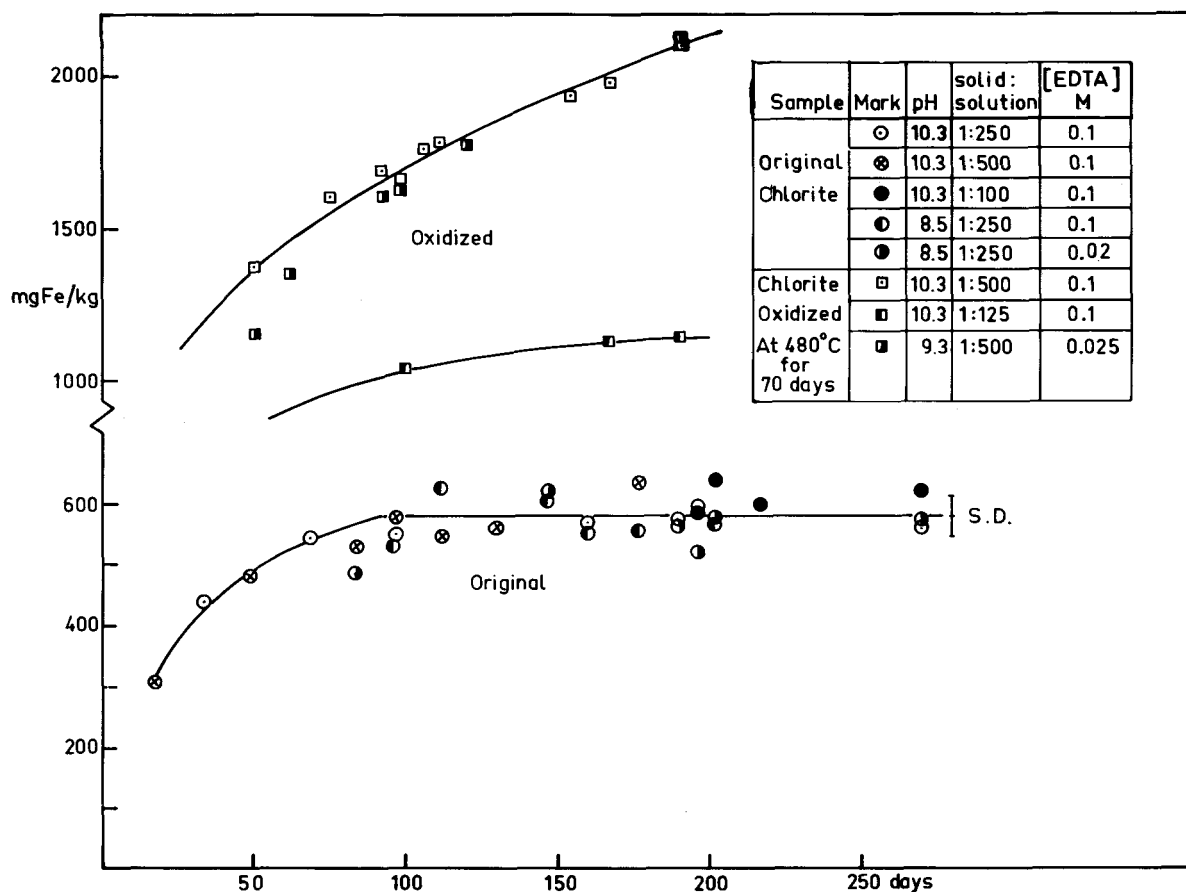


Figure 2. The amounts of iron extracted by various EDTA solutions plotted against the extraction time for original chlorite and oxidized chlorite (heated in air at 480°C for 1680 hr).

(1972) and has a sharp dehydroxylation peak at 610°C and a sharp recrystallization peak at 810°C. The evolved gas analysis (EGA) curve shows a small water release at 100°C, a large amount of water evolved at 610°C, and a small amount of water evolved at 810°C. The curve shows that small amounts of water are evolved from 440° to 810°C, corresponding to a deflection on the DTA curve at 470°C. If the temperature increase is stopped at 470°C, the water release and the endothermic deflection is steadied at small, positive values, and thus this small water release is probably due to one, slow process.

The curves of the original chlorite in N₂ (Figure 3B) are similar to those run in 40% O₂, except that the small water-release from 440° to 810°C did not occur. A sample was then heated in N₂ to 650°C, i.e., just above the main dehydroxylation peak, and then cooled. When this sample was heated to 1000°C in 40% O₂, the small water-release from 440° to 810°C was observed. Thus, this small water-release occurring only in the oxidizing atmosphere seems to be independent of the main dehydroxylation process.

The curves obtained in 40% O₂ for the oxidized chlo-

rite (Figure 3C) are similar to those for the original chlorite, except that the small water-release from 440° to 810°C did not occur. The curves obtained with 40% O₂ for the chlorite reduced in H₂ (Figure 3D) are entirely different from those of the original and the oxidized samples. There is no sharp recrystallization peak at 810°C, but one strong and sharp, three medium and sharp, and one weak and broad endothermic peaks were detected. The DTA curve obtained in 40% O₂ for the chlorite reduced in CO (not shown) is blurred; the only significant peak is a broad one at 590°C. The corresponding EGA curve shows two sharp peaks at 590° and 835°C. For all the curves shown in Figure 3, the amount of water evolved followed the endothermic peaks, indicating the same process for all of the endothermic peaks. The large endothermic peak of the original chlorite at 610°C is generally accepted to be due to dehydroxylation, and thus all endothermic peaks shown in Figure 3 might be due to dehydroxylation of separate layers or specific atom groups within each layer.

The large dehydroxylation peak at 610°C of the original sample is probably due to dehydroxylation of the

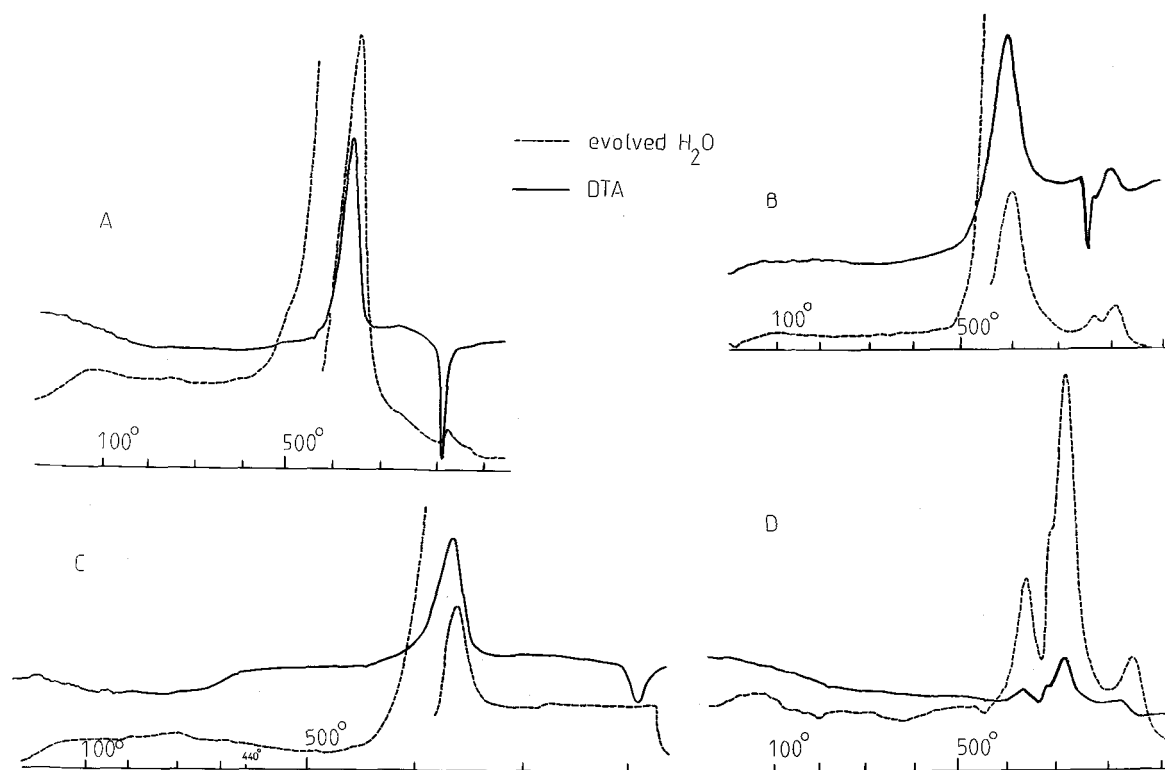


Figure 3. Differential thermal-evolved gas analyses of various chlorite samples. A: original chlorite in 40% O₂; B: original chlorite in N₂; C: oxidized chlorite (heated in air at 480°C for 1680 hr) in 40% O₂; D: reduced chlorite (oxidized chlorite heated in H₂ at 480°C for 504 hr) in 40% O₂. Gas flows: A and D: 300 ml/min; B and C: 400 ml/min. Heating rates: 10°C/min, except for C 5°C/min from 440°C (base line shift of the DTA curve at 440°C in C is due to this change). Sensitivities: DTA: 50 μV; EGA: A, B, and C: 1000 ppm until main peak, 10,000 ppm upwards; D: 1000 ppm.

interlayer hydroxide, as proposed by Caillère and Hénin (1956). This assignment is also supported by the large amount of water evolved. XRD of samples heated to 650°C in N₂ or O₂ showed an intensity increase of the (001) reflection, whereas the (002) reflection almost disappeared; the XRD spectra showed the chlorite structure to be largely intact. These results show that the dehydroxylation water easily diffused out of an almost intact structure. The slow process starting at 470°C in the original chlorite in O₂ is the reaction during which Fe(II) is oxidized and might, as mentioned above, be a dehydroxylation, but might also be a hydrogen liberating process in which the hydrogen reacts with oxygen to form water. However, the oxidation of Fe(II) does not occur in N₂, supporting an oxygen uptake by Fe(II) that might then be coupled with a dehydroxylation. Such an oxygen uptake has been suggested by Caillère and Hénin (1956) based on thermogravimetric curves for thuringite.

The small water release at 810°C is probably due to dehydroxylation of some groups in the 2:1 layer, causing the dehydroxylation of this chlorite to resemble that for other chlorites, with a second dehydroxylation step close to the recrystallization.

Infrared spectroscopy

Selected IR spectra of the various samples are shown in Figure 4. The assignments follow those proposed by Hayashi and Oinuma (1965, 1967) and Farmer (1974).

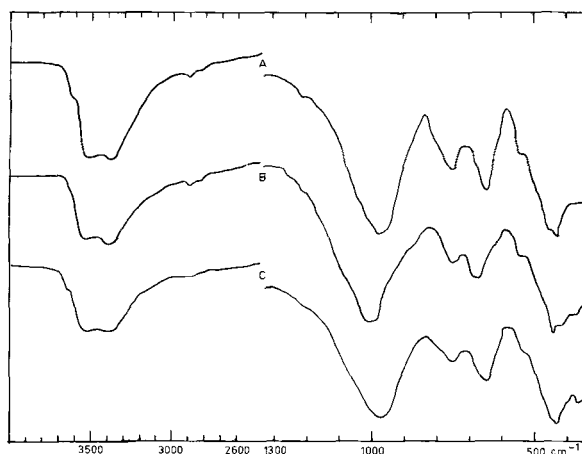


Figure 4. Infrared spectra of various chlorite samples. A: original chlorite; B: oxidized chlorite (heated in air at 480°C for 1680 hr); C: reduced chlorite (oxidized chlorite heated in H₂ at 480°C for 504 hr).

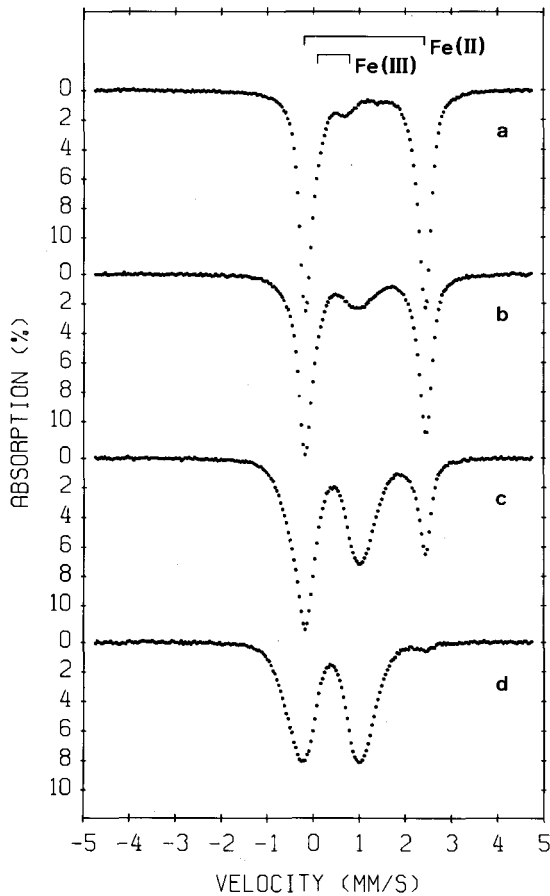


Figure 5. Room temperature Mössbauer spectra of the chlorite obtained after various times of oxidation in air at 480°C. a: 0 hr; b: 8 hr; c: 120 hr and d: 1680 hr. The spectra were obtained with the absorber normal at an angle of 54.7° with the gamma ray direction.

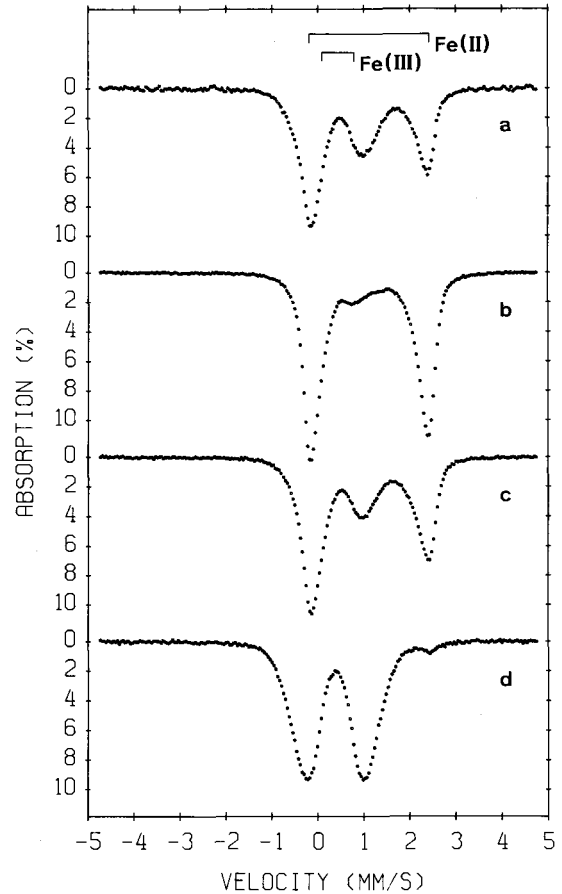


Figure 6. Room temperature Mössbauer spectra of oxidized chlorite after various types of reduction at 480°C. a: 22 hr in H₂; b: 504 hr in H₂; c: 120 hr in CO; d: 168 hr in N₂. The spectra were obtained with the absorber normal at an angle of 54.7° with the gamma ray direction.

The spectra of the oxidized and the oxidized + reduced chlorite appear more blurred than the spectrum of the original chlorite. The shoulder near 3650 cm⁻¹ corresponding to OH in the 2:1 layer is weaker in the oxidized sample than in the original and the reduced samples. The bands near 3400 and 3540 cm⁻¹ corresponding to OH in the hydroxide sheet seem to be nearly unaltered by the oxidation. In contrast, the Si-O bands of the original chlorite near 980 and 425 cm⁻¹ have moved to higher frequencies upon oxidation. The band at 425 cm⁻¹ is probably due to octahedral Fe-O-Si vibrations. The band at 650 cm⁻¹ also moves to a higher wave number after oxidation but the intensity of the band is slightly reduced compared to the intensities of the original and the reduced samples. This band is considered to be a composite due to Si-O vibrations and OH vibrations in both the 2:1 layer and the hydroxide sheet. The band near 755 cm⁻¹ and the shoulder near 540 cm⁻¹ seem independent of the oxidation state of the structural iron. The assignment of these bands is difficult. Farmer

(1974) assigned chlorite bands near 760 cm⁻¹ to tetrahedral Al-O vibrations, and Hayashi and Oinuma (1965) assumed the shoulder near 540 cm⁻¹ to be due to octahedral Al-O-Si vibrations. Other assignments are, however, possible. The spectrum of a partly dehydroxylated sample (not shown) obtained by heating the chlorite four days at 680°C shows no bands in the 900 to 500 cm⁻¹ region, except for a very broad shoulder around 650 cm⁻¹. This result indicates that the bands at 775, at 540, and (at least partly) at 650 cm⁻¹ arise from OH vibrations.

Reduction of the structural iron of the oxidized sample results in a spectrum where the bands have moved back to their original positions and the shoulder at 3650 cm⁻¹ seems to be more intense.

Mössbauer spectroscopy

Figure 5 shows room temperature Mössbauer spectra of chlorite samples obtained after different times of oxidation. Figure 5a is a spectrum of the original sample

Table 1. Mössbauer parameters of chlorite after various treatments.

Heat treatment (480°C)	T (°C)	Fe (II)				Fe (III)			
		ΔE_Q (mm/sec)	δ_{Fe} (mm/sec)	$v_{1/2}$ (mm/sec)	Relative area	ΔE_Q (mm/sec)	δ_{Fe} (mm/sec)	$v_{1/2}$ (mm/sec)	Relative area
Original sample	25	2.60 ± 0.02	1.13 ± 0.02	0.32 ± 0.02	0.91 ± 0.02	0.58 ± 0.1	0.39 ± 0.1	0.29 ± 0.1	0.05 ± 0.02
		0.84 ± 0.1	0.52 ± 0.1	0.46 ± 0.1	0.04 ± 0.02				
Original sample	-196	2.83 ± 0.02	1.25 ± 0.02	0.35 ± 0.02	0.91 ± 0.02	0.70 ± 0.1	0.38 ± 0.1	0.34 ± 0.1	0.06 ± 0.02
		0.84 ± 0.1	0.58 ± 0.1	0.36 ± 0.1	0.03 ± 0.02				
8 hr in air	25	2.61 ± 0.02	1.13 ± 0.02	0.33 ± 0.02	0.75 ± 0.02	0.84 ± 0.1	0.45 ± 0.1	0.43 ± 0.1	0.12 ± 0.02
		1.48 ± 0.1	0.44 ± 0.1	0.56 ± 0.1	0.13 ± 0.02				
120 hr in air	25	2.62 ± 0.02	1.12 ± 0.02	0.30 ± 0.02	0.32 ± 0.02	0.98 ± 0.1	0.42 ± 0.1	0.40 ± 0.1	0.33 ± 0.05
		1.64 ± 0.1	0.37 ± 0.1	0.50 ± 0.1	0.35 ± 0.05				
1680 hr in air	25	2.6 ± 0.1	1.1 ± 0.1	0.3 ± 0.1	0.02 ± 0.01	1.04 ± 0.1	0.39 ± 0.1	0.39 ± 0.1	0.45 ± 0.05
		1.63 ± 0.1	0.36 ± 0.1	0.51 ± 0.1	0.53 ± 0.05				
1680 hr in air + 22 hr in H ₂	25	2.60 ± 0.03	1.11 ± 0.03	0.27 ± 0.02	0.23 ± 0.03	0.98 ± 0.1	0.41 ± 0.1	0.42 ± 0.1	0.27 ± 0.02
		2.18 ± 0.05	1.12 ± 0.05	0.47 ± 0.05	0.26 ± 0.03	1.59 ± 0.1	0.40 ± 0.1	0.51 ± 0.1	0.24 ± 0.02
1680 hr in air + 504 hr in H ₂	25	2.61 ± 0.02	1.12 ± 0.02	0.29 ± 0.02	0.48 ± 0.04	0.83 ± 0.1	0.37 ± 0.1	0.39 ± 0.1	0.08 ± 0.02
		2.20 ± 0.05	1.11 ± 0.05	0.46 ± 0.05	0.36 ± 0.04	1.25 ± 0.1	0.53 ± 0.1	0.58 ± 0.1	0.08 ± 0.02
1680 hr in air + 120 hr in CO	25	2.59 ± 0.03	1.11 ± 0.03	0.34 ± 0.02	0.35 ± 0.04	0.99 ± 0.1	0.38 ± 0.1	0.44 ± 0.1	0.16 ± 0.03
		2.10 ± 0.05	1.08 ± 0.05	0.45 ± 0.05	0.27 ± 0.04	1.30 ± 0.1	0.49 ± 0.1	0.62 ± 0.1	0.22 ± 0.03

δ_{Fe} isomer shift; ΔE_Q quadrupole splitting; $v_{1/2}$ line width (FWHM).

which, as indicated, contains both a Fe(II) component and a Fe(III) component. Spectra (b), (c), and (d) were obtained after oxidation in air at 480°C for 8, 120, and 1680 hr, respectively. These spectra clearly show that the relative area of the Fe(III) component increases with increasing oxidation time at the expense of the Fe(II) component. The lines of the Fe(III) components in all of the spectra are considerably broader than those of the Fe(II) component, which are slightly broader than those of the standard α -Fe absorber.

The spectra were computer fitted with one Fe(II) quadrupole doublet and two Fe(III) quadrupole doublets. The line widths and the line intensities of the two lines in each doublet were made equal. The Mössbauer parameters obtained from the computer fits are given in Table 1. The position of the low-velocity line of the Fe(II) doublet in the spectra of the most oxidized samples can not be determined unambiguously. However, the Fe(II) line at about 2.4 mm/sec is not changed during oxidation and this indicates that the quadrupole splitting and the isomer shift of the Fe(II) doublet is unaffected by the heating. The broad lines of the two Fe(III) doublets in all the spectra suggest the presence of broad distributions in Fe(III) quadrupole splittings, but the fits with only two Fe(III) doublets can be used for an investigation of the changes in the hyperfine parameters of the Fe(III) component during oxidation and for a determination of the Fe(II)/Fe(III) area ratios.

The results in Table 1 show that the parameters of the Fe(III) component gradually change during oxidation indicating that the Fe(III) component formed by the oxidation of Fe(II) is different from the original Fe(III) component and, therefore, the Fe(III) parameters of the partly oxidized samples presumably repre-

sent averages between those of the original sample and those of the Fe(III) component formed by oxidation of Fe(II).

Mössbauer spectra of samples oxidized at 480°C in air for 1680 hr and heated in H₂, CO, or N₂ at 480°C are shown in Figure 6. The spectra show that Fe(III) is reduced to Fe(II) in both H₂ and in CO. The re-formed Fe(II) component has broader lines than the original Fe(II) component and, moreover, the lines have become asymmetric. The spectra of the reduced samples were therefore fitted with two Fe(II) doublets and two Fe(III) doublets (Table 1). One of the Fe(II) doublets has parameters identical to those of the original Fe(II) doublet, whereas the other has a smaller quadrupole splitting. It is interesting that the Fe(III) component also changes during reduction and gradually becomes more similar to the Fe(III) component in the spectrum of the original sample. This result suggests that the Fe(III) ions in the original sample are unaffected by the heating of the samples in air, H₂, or CO. Measurement on a non-oxidized sample heated in H₂ at 480°C for 48 hr showed in accordance with this that the Fe(III) ions in the original sample were not reduced during heating in H₂. The Mössbauer spectra of original and oxidized samples were found to be unaffected by heating at 480°C in N₂ for 504 hr and 168 hr, respectively.

Measurement on a few samples at -196°C showed that the area ratio of Fe(II) and Fe(III) components is essentially independent of temperature, suggesting that the f-factors are identical. Therefore, the relative area of the Fe(II) component can be considered to be equal to the fraction of iron in the divalent state. Mössbauer results for the fraction of the original amount of Fe(II) that remained in the divalent state after various times

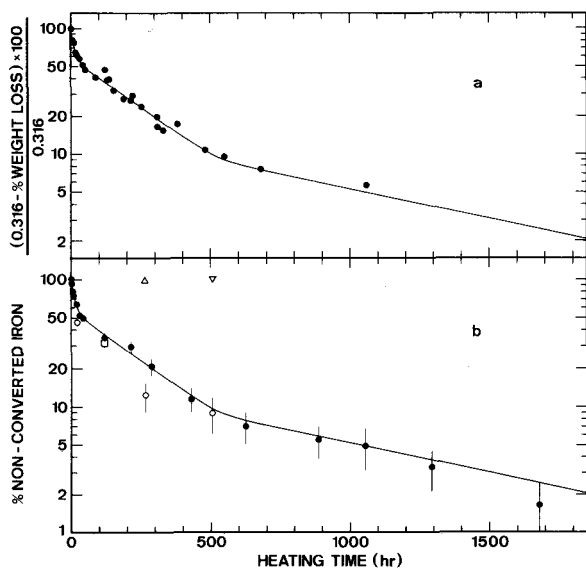


Figure 7. The weight loss (a) and percent non-converted iron (b) for the chlorite plotted against heating time at 480°C. Original chlorite heated in air (●) or N₂ (▽). Oxidized chlorite (heated in air at 480°C for 1680 hr) heated in CO (□), H₂ (○) or N₂ (△). The curves in (a) and (b) are identical and drawn according to the percent non-converted iron vs. heating time results for oxidation of chlorite in air.

of oxidation are shown in Figure 7, which also shows results for the kinetics of reduction of chlorite that has first been oxidized in air for 1680 hr at 480°C. These data give the relative amount of reducible Fe(III) that remained in trivalent state after various times of reduction, i.e., the ~9% non-reducible iron which was present in the original sample has been subtracted from the

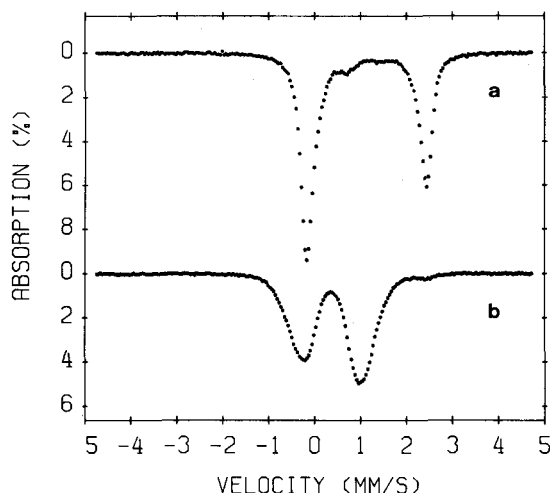


Figure 8. Room temperature Mössbauer spectra of chlorite obtained with the absorber plane perpendicular to the gamma ray direction. (a): original chlorite; (b): after oxidation in air at 480°C for 1680 hr.

Table 2. X-ray powder diffraction data for original chlorite, oxidized chlorite (heated in air at 480°C for 1680 hr), and reduced chlorite (oxidized chlorite heated in H₂ at 480°C for 504 hr).

(hkl)	Original chlorite		Oxidized chlorite		Reduced chlorite	
	d (Å)	I	d (Å)	I	d (Å)	I
(001)	14.2	3400	14.2	5200	14.0	5000
(002)	7.09	10,400	7.11	6100	7.04	5500
		6.52		120		
(003)	4.72	3800	4.73	1500	4.71	1400
(020)	4.64	40	4.58	40	4.60	20
(021)*	4.36	40				
		4.29		20		
(022*, 111)	3.91	70	3.93	20	3.90	10
(112)*	3.61	40				
(004)	3.54	8000	3.56	4900	3.54	3700
(023)*	3.27	80	3.29	30	3.27	20
(005)	2.831	1600	2.841	1400	2.83	1000
(024)*	2.76	20			2.78	30
		2.678		10	2.670	20
		2.62		20	2.628	10
		2.600		100	2.574	65
(131, 202̄)	2.600	100	2.574	65	2.593	100
(132̄, 201)	2.556	120	2.532	50	2.549	105
(132, 203̄)	2.452	120	2.430	120	2.447	160
(133̄, 202)	2.392	100	2.373	65	2.398	90
(006)			2.333	10		
		2.268		80	2.249	50
		2.235		60		
(133, 204̄)	2.235	60				
		2.07		10	2.062	20
(134, 205̄)	2.024	240	2.028	140	2.024	100
(007)	2.009	200	1.990	120	2.006	180
(135, 204)	1.887	80	1.879	70	1.885	80
(135, 206)	1.827	60	1.822	40	1.826	40
(136̄, 205)	1.720	10	1.71	20	1.72	20
(136, 207)	1.663	60	1.66	30	1.664	40
(137, 206)	1.574	80	1.579	40	1.576	40
(009)	1.568	180	1.564	120	1.568	160
(137, 208̄)	1.547	80	1.532	50	1.546	60
(060, 331)	1.52	20				
(062, 331)	1.51	40			1.51	25
(0·0·10)	1.416	240	1.421	100	1.418	80
(208)	1.395	200	1.394	120	1.396	140

* Corresponds to own assignment.

total amount of Fe(III) before calculating the fractions of non-reduced iron given in Figure 7. The rate of reduction in H₂ or CO is similar to the rate of oxidation in air.

Mössbauer spectra of the original sample and the sample oxidized in air for 1680 hr at 480°C shown in Figure 8 were obtained with the absorber plane perpendicular to the gamma ray beam. The texture-induced asymmetry of the Fe(III) component in the oxidized sample is opposite to that of the Fe(II) component in the original sample.

Scanning electron microscopy

The original sample and the sample oxidized in air at 480°C for 1680 hr were found by SEM to consist of plate-like grains with a size in the range 10–100 μm. Thus, the grain size did not change significantly during

oxidation, nor did oxidation create visible defects or cleavage at the edges of the grains.

Weight loss

To present the weight loss and the Mössbauer results on the same scale, the data in Figure 7 are expressed as: $[(0.316 - \% \text{ weight loss}) \times 100]/0.316$, where 0.316 is the weight loss proportion corresponding to the complete oxidation of the Fe(II) (17.5%) in the chlorite and assuming the release of one hydrogen atom per oxidized Fe(II). The data are composed of several series, each started from a fresh chlorite portion (83 days at 300°C) and a resetting of the furnace at 480°C.

X-ray powder diffraction

Using the criteria of Bailey (1975, 1980) and the monoclinic indices of Shirozu (1958), the chlorite is a monoclinic polytype IIb, in agreement with the results of Post and Plummer (1972). No changes in the diffractograms were found after heating the chlorite at 300°C in air or at 480°C in N₂. After oxidation the b-dimension (measured from d(060)) decreased from 9.28 Å to 9.19 Å, and d(001) (measured from d(0·0·10)) increased from 14.16 Å to 14.21 Å (Table 2). Changes in the b- and c-dimensions following oxidation of chlorites were noted by Shirozu (1958). Also I(001)/I(002) increased from 0.3 to 0.9, and I(001)/I(003) increased from 1 to 3. Following reduction of oxidized (at 480°C for 1680 hr) chlorite, the b-dimension returned to 9.28 Å, and d(001) decreased to 14.18 Å. However, the intensity ratios did not return to their original values. Considerable line-broadening was present after oxidation and remained after reduction.

During oxidation at least two phases could be detected, one resembling the original chlorite that decreased in amount with time, and another resembling the oxidized chlorite that increased in amount with time.

DISCUSSION

Location of octahedral cations

From XRD analysis it is difficult to determine the distribution of the four cations (Al, Fe(II), Fe(III), and Mg) between the two octahedral layers (Goodman and Bain, 1979). The Mössbauer spectra of the original and the oxidized samples may, however, clarify this point. In the original chlorite the Fe(II) component has relatively narrow lines both at 25°C and at -196°C. Therefore, all of the Fe(II) ions are located in sites with nearly identical surroundings. The Mössbauer parameters of the Fe(II) component are in accord with those obtained in previous studies of chlorite (Taylor *et al.*, 1968; Hayashi *et al.*, 1972; Ericsson *et al.*, 1977; Goodman and Bain, 1979; Blaauw *et al.*, 1980), and are similar to those of Fe(II) in the *cis*-positions in the 2:1 layer in biotite (Hogg and Meads, 1975; Tripathi *et al.*, 1978; Goodman and Bain, 1979). It is therefore likely that Fe(II) is present in similar *cis*-positions in chlorite. The

line width is slightly larger than that observed in the spectrum of a thin α -Fe absorber. This is, however, not surprising because the individual Fe(II) ions in this layer have slightly different surroundings depending on the distribution of Fe(II) and Mg at the nearest neighbor cation sites. The line width may also be slightly affected by the substitution of Si by Al in the tetrahedral sites and by substitution of Mg by Al and Fe(III) at nearby sites in the hydroxide layer. The presence of trivalent ions in the 2:1 layer would result in a significant change in the quadrupole splitting of neighboring Fe(II) atoms, and therefore a broadening of the lines. The narrow Fe(II) Mössbauer lines thus suggest that the 2:1 layer in the non-oxidized state is occupied only by divalent ions (Fe(II) and Mg), and not by Al and Fe(III).

The IR results are in agreement with this allocation of Fe(II). The movement of the Si-O bands at 980 and 425 cm⁻¹ to higher frequencies upon oxidation and back again to the original wave numbers after subsequent reduction shows a close connection between the original Fe(II) and Si. Oxidation of Fe(II) located in the hydroxide sheet is not expected to produce such an effect on the Si-O bands. For various smectites, Rozenson and Heller-Kallai (1976a, 1976b) and Russell *et al.* (1979) found the Si-O band near 1000 cm⁻¹ to shift to lower frequencies after treatment with reducing agents. Furthermore, the insensibility of the bands near 3400 and 3540 cm⁻¹ corresponding to OH in the hydroxide interlayer toward oxidation and reduction seems to preclude Fe(II) in the hydroxide sheet. Chemical analysis shows that Fe(II) is unlikely in the hydroxide sheet because the amounts of Al, Fe, and Mg extracted after oxidation are much smaller than those extracted by Makumbi and Herbillon (1972) and Ross (1975) from chlorites which they considered to contain Fe(II) in the hydroxide sheet. The DTA-EGA data, showing no correlation between the oxidation processes and the main dehydroxylation peak of the hydroxide interlayer at 610°C, also support the assignment of original Fe(II) to the 2:1 layer.

If the original Fe(II) is present only in the 2:1 layer, octahedral Al and Fe(III) must be placed in the hydroxide sheet, an assignment that is in accord with the suggestion of Blaauw *et al.* (1980), but which seems to disagree with the allocation suggested by Goodman and Bain (1979) assuming Fe(II) first to occupy the hydroxide sheet. The location of original Fe(III) in tetrahedral coordination may be ruled out because the measured isomer shift of the Fe(III) component in the Mössbauer spectra is significantly larger than the isomer shift typical of tetrahedral Fe(III). Thus, Fe(III) ions seem to be located in the hydroxide sheet. The insensitivity of the Fe(III) component in the Mössbauer spectra of the original chlorite to heat treatment at 480°C in H₂ also shows that the location of these Fe(III) ions is different from that of the Fe(III) ions formed upon oxidation of the Fe(II), supporting the above interpretation. The broad lines of the Fe(III) component of the original

chlorite are also consistent with this location of Fe(III), because the hydroxide layer will contain a distribution of divalent ions (Mg) and trivalent ions (Fe(III) and Al) close to an Fe(III) ion, resulting in different quadrupole splittings of the Fe(III) ions.

Structural changes during oxidation and reduction

The very broad Mössbauer lines of the Fe(III) component formed upon oxidation suggest a random distribution of Mg and Fe(III) ions in the 2:1 layer, because the quadrupole splitting of an Fe(III) ion will depend on the number and the distribution of neighboring divalent and trivalent ions in the nearest neighbor sites in the 2:1 layer. Different configurations of oxygen and hydroxyl anions in the oxidized samples may also contribute to the line broadening of the Fe(III) component (Bagin *et al.*, 1980).

The Mössbauer parameters of the Fe(II) component formed upon reduction of the oxidized sample are of particular interest. About 50% of these Fe(II) ions are located in surroundings similar to those of the original Fe(II), whereas the remaining Fe(II) ions show a smaller quadrupole splitting (see Table 1). It is noteworthy that the parameters of this new Fe(II) doublet are similar to those of Fe(II) in the *trans*-positions in biotite (Ericsson *et al.*, 1977; Bagin *et al.*, 1980). The result therefore suggests that during the reduction of the oxidized sample the original structure is almost restored, but some disorder of the OH-groups is introduced so that both *cis*- and *trans*-positions exist. However, other interpretations are also possible.

If Fe(II) is assumed to be located exclusively in the 2:1 layer, oxidation must result in a contraction of this layer due to the size difference between Fe(II) and Fe(III). XRD analysis shows a contraction along the b-axis. The Fe(II)-free hydroxide sheet is not subjected to the same effect, but because of the attractive electric forces between the 2:1 layer and the hydroxide sheet, the sheet must also decrease in the b-dimension. Whereas contraction may result in an overall expansion of the c-dimension, an increase in $d(001)$ from 14.16 Å to 14.21 Å is actually seen. Alternatively, this expansion may be explained by a reduction of the difference in charge between the negative 2:1 layer and the positive hydroxide sheet that is due to the oxidation of Fe(II) in the 2:1 layer together with a release of a proton from the hydroxide sheet, as proposed by Steinfink (1958).

The contraction along the b-axis may create tensions within the crystal structure leading to the observed increase in the susceptibility of the oxidized sample toward chemical treatments. The oxidized chlorite was found to be attacked even by EDTA, which is considered (Borggaard, 1976, 1979) a very mild extractant. The increase in susceptibility toward chemical treatments after oxidation of the structural iron in chlorites has been demonstrated several times (Makumbi and

Herbillon, 1972; Ross, 1975; Ross and Kodama, 1974, 1976; Goodman and Bain, 1979). The broadening of the IR bands and the XRD peaks is in line with a distortion of the crystal lattice.

It is interesting that the asymmetry of the Mössbauer spectra obtained in the 90° geometry is opposite for the original and the oxidized samples (Figure 8). Because SEMs show that the shape of the crystallites is essentially unchanged by the oxidation, similar textures must be present in the two Mössbauer absorbers. The results show that the electric field gradients of Fe(II) in the original sample and Fe(III) in the oxidized sample have opposite signs. The contribution to the quadrupole splitting of Fe(II) from the electrons of the atom itself is larger than the lattice contribution and of an opposite sign, whereas the quadrupole splitting of Fe(III) is solely determined by the lattice contribution. Therefore the spectra shown in Figure 8 indicate that the Fe(II) in the original sample and the Fe(III) in the oxidized samples are present in sites of similar symmetry. Thus, the Mössbauer spectra in Figure 8 indicate that only limited structural changes take place during the oxidation.

The small structural changes taking place during the oxidation and the reduction are difficult to explain in detail. DTA and XRD indicate dehydroxylation during the oxidation. However, dehydroxylation is followed by a substantial weight loss that corresponds only to one hydrogen atom per oxidized Fe(II) (Figure 7). A release of one hydrogen atom per oxidized Fe(II) seems necessary to maintain charge balance. Electroneutrality may also be preserved by ejection of octahedral cations (e.g., Fe), as found during wet oxidation of biotites (Farmer *et al.*, 1971; Gilkes *et al.*, 1972; Veith and Jackson, 1974). In the present investigation the chemical analysis rules out this possibility. The intensity changes in XRD reflections can, however, not be explained by a hydrogen release alone due to the low scattering ability of hydrogen. Because the basal reflection intensities are generally changed, and because the structure remains I1b and reverses to the same dimensions after reduction, the scattering ability of the two octahedral layers must be changed relatively e.g., by displacement of atoms heavier than hydrogen, such as oxygen.

Mechanism of oxidation

Only a reaction scheme of the form: $[\text{Fe(II)OH}]^+ \rightleftharpoons [\text{Fe(III)O}]^+ + \text{H}$ (or $\text{H}^+ + \text{e}^-$) seems compatible with the results presented in Figure 7. The stoichiometry reflected by this reaction scheme, i.e., a release of one hydrogen atom per oxidized Fe(II), has also been suggested in the oxidation of biotite (Vedder and Wilkins, 1969; Farmer *et al.*, 1971; Veith and Jackson, 1974; Hogg and Meads, 1975; Tripathi *et al.*, 1978; Bagin *et al.*, 1980), chlorite (Makumbi and Herbillon, 1972; Goodman and Bain, 1979), and smectite (Rozenson and Heller-Kallai, 1976a, 1976b). The released hydrogen may react with oxygen at the edges of the crystallites forming water or (at least theoretically) the

water may be formed within the crystals if oxygen is able to diffuse into the 2:1 layer and react with Fe(II) and hydrogen. Diffusion of water from the structure of various micas gives rise to only minor structural rearrangements (Vedder and Wilkins, 1969). The sharp dehydroxylation peak at 610°C, as seen from Figure 3, proves that water easily can move out of a structure, which, after the reaction, was found to be largely intact by XRD. Diffusion of oxygen into crocidolite (Addison *et al.*, 1962) and into biotite, phlogopite, and vermiculite (Tripathi *et al.*, 1978) is, however, considered unlikely.

In agreement with the results in Figure 7, the reaction scheme also indicates the oxidation-reduction process to be reversible, although, as discussed above, minor structural changes occurred. At least a part of the structural iron in biotite and smectite is believed to be able to undergo reversible oxidation and reduction (Vedder and Wilkins, 1969; Farmer *et al.*, 1971; Veith and Jackson, 1974; Rozenson and Heller-Kallai, 1976a, 1976b; Russell *et al.*, 1979).

The Mössbauer results showing that the line positions and line width of the Fe(II) component are unchanged during oxidation also show that the oxidation of Fe(II) does not take place at random Fe(II) sites in the grains. Such a reaction would result in broadening of the lines of the remaining Fe(II) ions. The results rather suggest that two phases are present during oxidation, namely an oxidized phase and the original phase. The data in Figure 7 may be fitted by three straight lines corresponding to three parallel first-order reactions. This fitting of the data only represents a proposal for the rate expression, as other mathematical equations corresponding to other reaction mechanisms may fit the data equally as well. Further speculations on this point must await experiments with more uniform chlorite particles. Bagin *et al.* (1980) reported that the oxidation of single biotite plates occurred in steps.

CONCLUSIONS

It is possible to oxidize nearly all of the structural Fe(II) in a chlorite by prolonged thermal treatment in air at 480°C, i.e., below the main dehydroxylation temperature. The oxidized chlorite can be reduced by heating in hydrogen or carbon monoxide at the same temperature.

Essentially all of the Fe(II) of the original chlorite seems to be located in the 2:1 layer in sites similar to those of Fe(II) in biotite with OH in *cis*-positions. Octahedral Al and original Fe(III) must exist solely in the hydroxide sheet.

Despite the profound oxidation, only limited structural changes seem to take place; reduction of the chlorite seems to recreate the original XRD spacings and the main surroundings of atoms of the original mineral. Small structural changes take place, but the nature of these changes is obscure, except, perhaps, for the in-

roduction of OH in both *cis*- and *trans*-positions in the reduced sample.

The conversion of iron from Fe(II) to Fe(III) appears to be reversible, and the oxidation of Fe(II) seems to be associated with a release of one hydrogen atom per oxidized Fe.

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Резюме—Хлорит богатый в железо, рипидолит, был окислен путем нагрева в воздухе при 480°C, то есть ниже температуры дегидроксиляции. Окисленный хлорит был последовательно восстановлен в водороде при такой же температуре. По данным химического, термодифференциального, инфракрасного, Мессбауэровского, и рентгеновского анализов кажется, что Fe(II) существует только в 2:1 слоях исходного хлорита в местах, похожих на те, которые Fe(II) занимает в биотите, с группами OH в положениях *cis*. Эти данные указывают также на то, что октаэдрические Al и Fe(III) расположены в гидроокисных пластах исходного хлорита. Структурные изменения минерала, возникающие в результате окисления и последовательного восстановления кажутся быть ограниченными до небольших структурных перестроек, и, возможно до введения групп OH в обоих *cis* и *trans* положениях. Результаты исследований согласны со следующей формой реакции: $[\text{Fe(II)OH}]^+ \rightleftharpoons [\text{Fe(III)O}]^+ + \text{H}(\text{H}^+ + \text{e}^-)$. [E.C.]

Resümee—Ein eisenreicher Chlorit, Ripidolith, wurde durch Erhitzen auf 480°C an der Luft, (d.h. unter die Dehydratationstemperatur) oxidiert und anschließend im Wasserstoff bei der gleichen Temperatur reduziert. Aufgrund chemischer Analysen, Differentialthermo-, Infrarot-, Mössbauer- und Röntgendiffraktometer-Untersuchungen scheint das Fe²⁺ nur in der 2:1 Schicht des ursprünglichen Chlorites vorhanden zu sein, wobei die Art des Platzes, den das Fe²⁺ besetzt, dem des Fe²⁺ in Biotit ähnelt und das (OH) in *cis*-Stellung ist. Diese Ergebnisse deuten weiters darauf hin, daß oktaedrisches Al und Fe³⁺ in den Hydroxidschichten des ursprünglichen Chlorits sind. Die strukturellen Veränderungen des Minerals aufgrund der Oxidation und der darauf folgenden Reduktion scheinen auf geringe strukturelle Neuordnungen und, vielleicht, auf die Einführung von (OH) sowohl in *cis*- als auch in *trans*-Stellung beschränkt zu sein. Die Ergebnisse dieser Untersuchung stimmen mit folgender Reaktion überein: $[\text{Fe}^{2+}\text{OH}]^+ \rightleftharpoons [\text{Fe}^{3+}\text{O}]^+ + \text{H}(\text{H}^+ + \text{e}^-)$. [U.W.]

Résumé—Une chlorite riche en fer, la ripidolite, a été oxidée par échauffement à l'air à 480°C, c'est à dire sous la température de déshydroxylation, et la chlorite oxidée a subséquemment été réduite dans l'hydrogène à la même température. Basé sur des analyses chimiques, thermales différentielles, infrarouges, de Mössbauer, et de diffraction poudrée aux rayons-X, Fe(II) ne semble être présent que dans la couche 2:1 de la chlorite originale, dans un genre de site semblable à celui de Fe(II) dans la biotite, avec OH dans les positions-*cis*. Ces données suggèrent aussi qu'Al octaédral et Fe(III) sont situés dans la feuille hydroxide de la chlorite originale. Les changements structuraux du minéral causés par l'oxidation et la réduction subséquente semblent limités à des réarrangements mineurs, et peut-être à l'introduction d'OH dans les positions-*cis* et-*trans*. Les résultats de l'investigation s'accordent avec une réaction de la forme: $[\text{Fe(II)OH}]^+ \rightleftharpoons [\text{Fe(III)O}]^+ + \text{H}(\text{H}^+ + \text{e}^-)$. [D.J.]