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THE 5-M-NaOH CONCENTRATION TREATMENT FOR IRON OXIDES IN SOILS

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Abstract—The boiling 5-M-NaOH treatment was found to aid in the identification and characterization of goethite and hematite by effectively concentrating the two Fe oxides in kaolinitic-gibbsitic soil clays. No transformations of goethite to hematite or hematite to goethite were detected, but poorly crystalline, highly Al-substituted goethite was found to dissolve and recrystallize into a more well-crystalline, less Al-substituted goethite in samples low in Si. The Si released from kaolinite was sufficient to block goethite dissolution and recrystallization in kaolinitic samples, but noncrystalline silica had to be added to samples rich in gibbsite to minimize this effect.

Key Words—Aluminum, Gibbsite, Goethite, Hematite, Iron, Kaolinite, Leaching.

INTRODUCTION

Poor crystallinity and low concentrations of Fe oxides in soils and sediments are generally responsible for the difficulty in their identification and quantification. This difficulty has hampered our knowledge about this important group of minerals in the weathering environment. In order to concentrate Fe oxides from such materials, Norrish and Taylor (1961) used a boiling 5-M-NaOH treatment for kaolinitic-goethitic samples to remove kaolinite and were thus able to determine the degree of Al substitution of the goethites. Since then, this method has been used only occasionally (Janot *et al.,* 1971; Fölster, 1971; Davey *et al.,* 1975; Resende, 1976; Bigham *et al.,* 1978; Kitagawa and Möller, 1979; Torrent *et al.,* 1980), perhaps because of the possibility that the rather drastic treatment might alter the Fe oxides with respect to form, crystallinity, and substitution. This possibility was supported by work on synthetic and natural Fe oxides (Kojima, 1963; Petit *et al.,* 1964; Janot *et al.,* 1971) in which transformations and increased crystallinity of goethite were observed. On the other hand, a milder treatment using 1.25 M NaOH at 75°C (Mendelovici *et al.,* 1979) did not remove kaolinite completely.

It seems desirable, therefore, to test the 5-M-NaOH method in some detail to find out the possible alterations of Fe oxides by this treatment. Therefore, the effect of the NaOH treatment on the form, crystallinity, and Al substitution of natural and synthetic goethite, hematite, ferrihydrite, and lepidocrocite was studied, and efforts to improve the method in such a way as to avoid possible alterations were made.

MATERIALS AND METHODS

Materials

Synthetic Fe oxides. Synthetic Fe oxides were prepared as follows: Goethite DL 18 was prepared by air oxidation at pH 7 and 25°C of a 0.05 M $FeCl_2$–0.05 M $NaHCO_3$ mixed solution; Al-goethite G2B3II (31 mole % Al), by slow air oxidation at 25°C of a 0.05 M $FeCl_2$–0.025 M $AlCl_3$ mixed solution brought to pH 11.2 with KOH; goethite GNK2, by storing a 0.1 M $Fe(NO_3)_3$ solution at pH 13 for 14 days at 25°C; Al-hematite HNK3 (10 mole % Al), by storing a 0.1 M $Fe(NO_3)_3$–0.011 M $Al(NO_3)_3$ mixed solution at pH 7 and 50°C for 90 days; ferrihydrite FhNK1, by precipitating a 0.1 M $Fe(NO_3)_3$ solution at pH 13 and 25°C with 5 M NaOH and immediate washing; and lepidocrocite P23, by oxidizing a 0.1 M $FeCl_2$ solution at pH 7 with air at room temperature. The purity of the synthetic samples was checked by X-ray powder diffraction (XRD).

Natural Fe oxides. Hematitic-goethitic-kaolinitic clay fractions of Inceptisols, Ultisols, and Oxisols and a gibbsitic-goethitic saprolite were used, all from basalt in Southern Brazil (Kämpf, 1981).

Si sources. Kaolinite from Rosenthal, FRG, and noncrystalline silica Cab-o-Sil from Cabot GmbH, Hanau, FRG, with 1.83% H_2O (110°C), were used as Si sources.

Methods

5-M-NaOH treatment (Norrish and Taylor, 1961). One hundred milliliters of 5 M NaOH was added to a 1-g sample in a covered 150-ml Teflon beaker. The mixture was boiled for 60 min on a sandbath and after cooling transferred to centrifuge tubes. The sample was spun down, the clear liquid was discarded, and the sample was washed once with 5 M NaOH, once with 0.5 M HCl

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(15–20 min of contact) to dissolve sodalite, twice with 1 N $(NH_4)_2CO_3$ to remove NaCl, and twice with distilled water to remove excess NH_4 and CO_3. The sample was then transferred to a glass beaker and dried at 110°C overnight to volatilize the remaining $(NH_4)_2CO_3$. The $(NH_4)_2CO_3$ step was preferred over ethanol or acetone washing because of better flocculation.

1.25-M-NaOH treatment (Mackenzie and Robertson, 1961). One hundred milliliters of 1.25 M NaOH was added to a 400-mg sample in 250-ml centrifuge tubes and heated to 75°C in a waterbath. For treatments up to 14 days, the samples were kept in closed plastic bottles in an oven. After treatment, the samples were washed and dried as in the 5-M-NaOH treatment.

X-ray powder diffraction (XRD). Powder samples mounted on Perspex plastic holders and pressed against filter paper were examined on a Philips diffractometer equipped with a graphite monochromator using CoKα radiation at ½°2θ/min (25 mA, 35 kV; 2-sec time constant; 1° divergence slit, 0.2-mm receiving slit, 1° scatter slit). The goethite/hematite ratio was estimated from the integrated intensity of the goethite 110 and the hematite 102 peak. The d-values of the 111 line of goethite and the 110 line of hematite were used for estimating the amount of Al substitution with an error of ± 2 mole % Al (±0.05°2θ).

Transmission electron microscopy (TEM). Samples suspended in ethanol were spread on carbon-coated grids and air dried. The samples were examined on a Zeiss-EM-10A/B electron microscope.

Fe extraction. Total oxidic Fe was determined by extraction with dithionite (Fe_d) after Mehra and Jackson (1960) and oxalate extractable Fe(Fe_o) after Schwertmann (1964).

RESULTS

Synthetic Fe oxides

The 5-M-NaOH treatment of goethite DL 18 produced stronger and sharper XRD peaks (Table 1) indicating recrystallization of the rather ill-defined, lath-shaped goethite crystals (Figure 1a) into well-defined, larger, rectangular crystals (Figure 1b). The addition of 30 mole % Al reduced this recrystallization; the addition of 50 wt. % kaolinite was even more effective (Figure 1c, Table 1). As d(111) did not change (Table 1), no Al was apparently taken up by the goethite because of the extremely high OH concentration (Lewis and Schwertmann, 1979). A decrease in the ratio of oxalate-extractable to dithionite-extractable Fe (Fe_o/Fe_d) also indicates the improvement of crystallinity, whereas when kaolinite was added, a smaller reduction in the Fe_o/Fe_d ratio was noted (Table 1).

Table 1. Effect of the 5-M-NaOH treatment on synthetic goethite DL18.

Treatment	110 line			d(111) (Å)	Fe_d (%)	$\frac{Fe_o}{Fe_d}$[3]
	$I_{obs.}$[1]	$I_{rel.}$[1]	WHH[2] (°2θ)			
Untreated	340	100	1.35	2.451	51.6	0.064
5 M NaOH	463	136	0.95	2.451	54.8	0.014
5 M NaOH + 30 mole % Al	410	121	1.10	2.451	n.d.	n.d.
5 M NaOH + 50% kaolinite	351	103	1.20	2.451	48.8	0.032

[1] $I_{obs.}$ = Observed intensity. $I_{rel.}$ = Peak intensity relative to untreated sample.

[2] WHH = Width at half height.

[3] Fe_o, Fe_d = oxalate, dithionite extractable Fe.

That the recrystallization proceeded via solution is shown by the behavior of Al-goethite G2B3II. The newly formed, well-defined crystals (cf. Figures 2a and 2b) had only 10% Al substitution as compared to 31% in the original goethite (Table 2). Here also the addition of large amounts of kaolinite was very effective in reducing recrystallization (Figure 2c) and Al loss (Table 2). In contrast, with Al-hematite HNK3 neither the Al substitution nor the width at half height (WHH) of the 104 (0.33°2θ) and 110 (0.20°2θ) lines were changed by the NaOH treatment. However, an increase in I(104)/I(110) from 0.95 to 1.27 took place. If one of these reflections were to be used for a quantitative estimation of hematite in mixtures, this change in intensity might be interpreted as a change in hematite proportion (see next paragraph). However, the change in the I(104)/I(110) ratio can easily be interpreted as a dispersion effect of NaOH on the hematite crystals which results in some orientation of the hematite platelets on the sample holder and to an enhancement of the near-basal 104 reflection as opposed to the non-basal 110 reflection (Schwertmann *et al.*, 1968). This interpretation is supported by the fact that a sample taken from the suspension after a NaOH dispersion treatment at room temperature also showed a higher I(104)/I(110) ratio (1.37) than a sample taken from the flocculated sediment at the bottom (1.05).

The poorly crystalline, synthetic ferrihydrite transformed to hematite on 5-M-NaOH treatment (Figure 3). The addition of 50% kaolinite, however, completely

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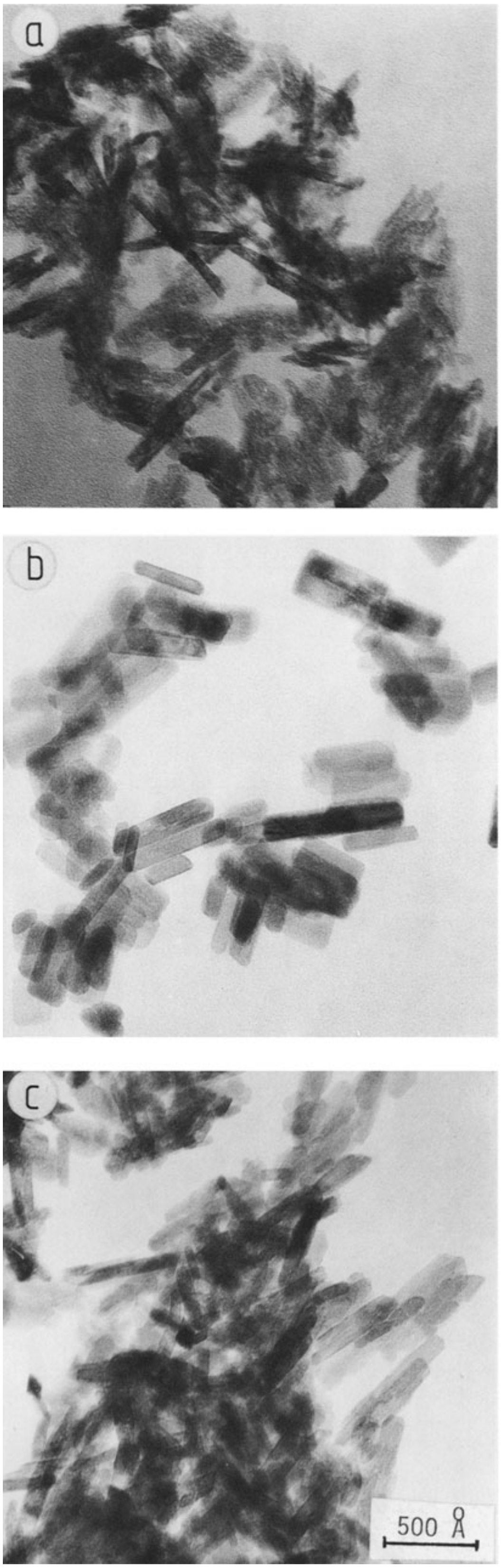
Figure 1. Left. Electron micrographs of a pure synthetic goethite (DL 18) (a) before and (b) after treatment with 5 M NaOH, and (c) after treatment with 5 M NaOH + 50% kaolinite.

Figure 2. Right. Electron micrographs of a synthetic Al-substituted goethite (G2B3II) (a) before (b) after treatment with 5 M NaOH, and (c) after treatment with 5 M NaOH + 50% kaolinite.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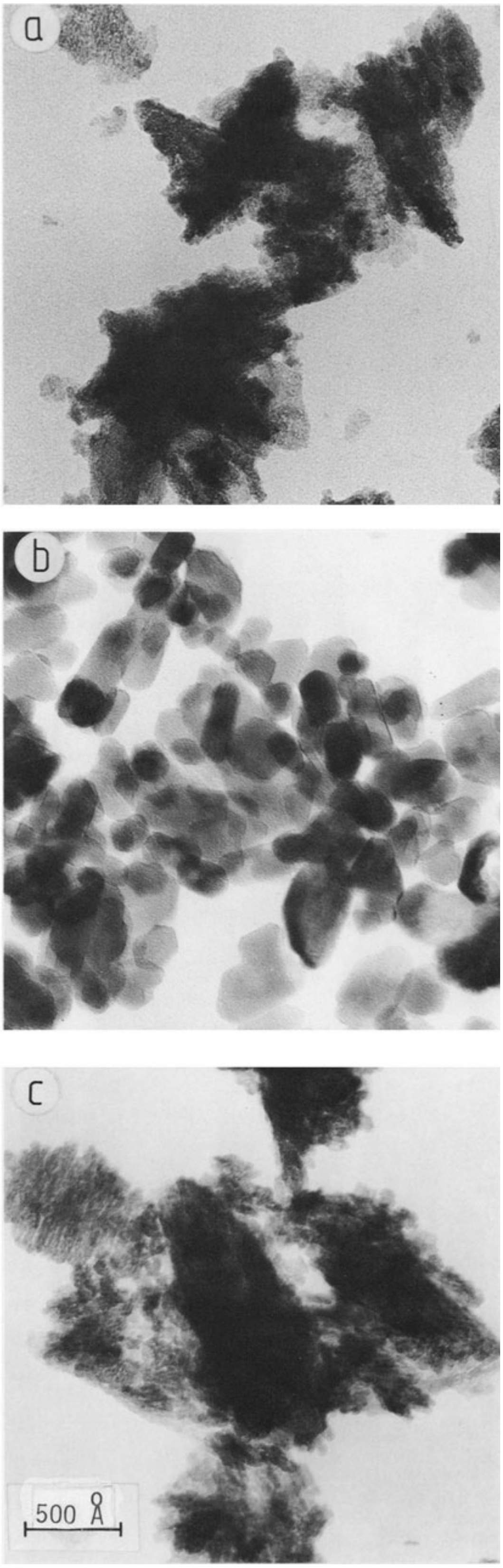
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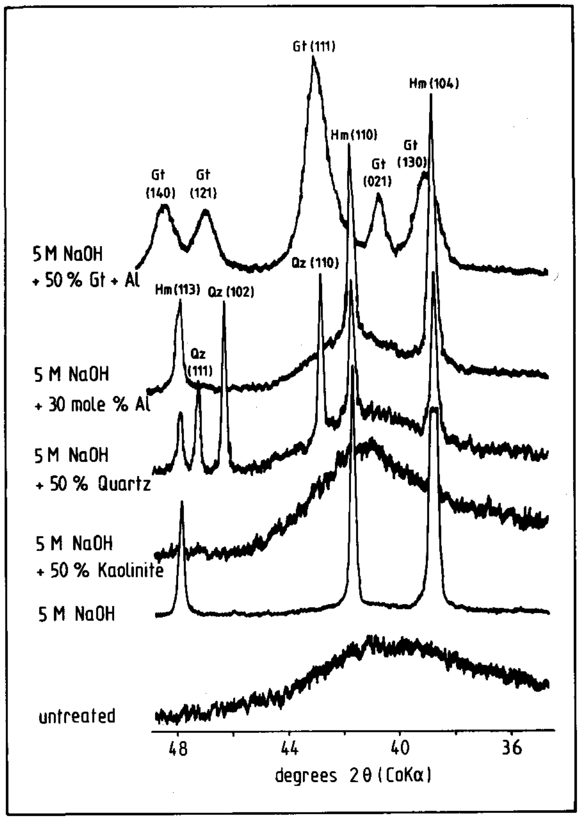

Figure 3. Effect of various treatments on the X-ray diffractogram of synthetic ferrihydrite FhNK1. Gt = goethite; Hm = hematite; Qz = quartz.

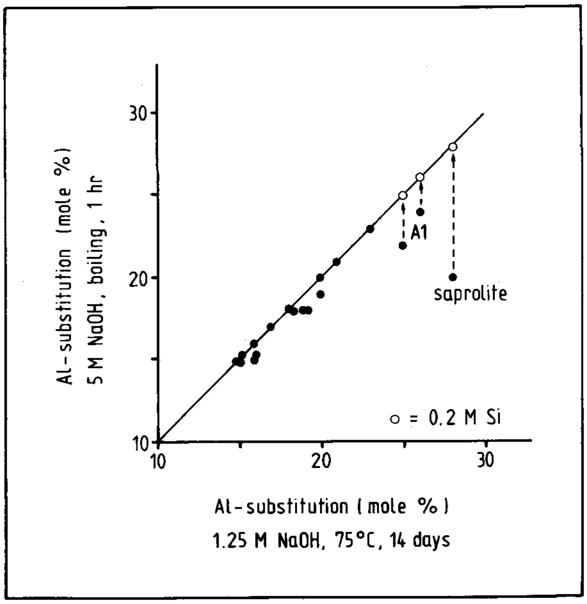

Figure 4. Al-substitution of soil goethites after a mild (1.25 M, 75°C, 14 days) and a strong (5 M, boiling, 1 hr) NaOH treatment.

blocked this transformation. Only the crystallinity of the ferrihydrite improved slightly, as indicated by a slight shift, a narrowing, and an enhancement of the main ferrihydrite peak at ~2.5 Å. Adding 50% quartz caused only partial inhibition of the transformation to hematite, probably because the Si concentration in solution produced by quartz is much lower than that produced by kaolinite. This result shows that dissolved Si is possibly the blocking agent for recrystallization and is in agreement with earlier observations on such an effect on the formation of lepidocrocite (Schwertmann and Thalmann, 1976) and goethite (Schwertmann and Taylor, 1972). The addition of 30 mole % Al also retarded the transformation to hematite but no Al was taken up by the hematite. When 50% synthetic goethite was added, the ferrihydrite converted solely to goethite instead of hematite. Goethite obviously has a strong nucleation effect and thereby accelerates the formation of new goethite to such an extent that hematite no longer forms, even in the presence of Al. Al is here also not taken up by the goethite.

Table 2. Effect of the 5-M-NaOH treatment on synthetic Al-goethite G2B3II.

Treatment	WHH(110)[1] (°2θ)	d(111) (Å)	Al-substitution[2] (mole %)
Untreated	0.47	2.410	31 ± 4[3]
5 M NaOH	0.40	2.438	10
5 M NaOH + 50% kaolinite	0.50	2.421	22
5 M NaOH + 80% kaolinite	0.50	2.415	29

[1] WHH = Width at half height.

[2] Based on Vegard rule (Vegard, 1921).

[3] 95% confidence interval.

Thus, ferrihydrite in natural samples or ferrihydrite formed from Fe in kaolinite after its dissolution in 5 M NaOH will not transform to goethite and/or hematite as long as the concentration of Si in solution is sufficiently high.

Lepidocrocite P23 transformed more readily than goethite or hematite. In a 1:1 mixture of goethite and lepidocrocite, the lepidocrocite was completely converted by the 5-M-NaOH treatment into a mixture of 82% goethite and 18% hematite. The addition of 50% kaolinite produced a 60:40 mixture of goethite and lepidocrocite, indicating that kaolinite retarded the transformation to goethite and inhibited the transformation to hematite, in agreement with earlier results on the influence of Si on the lepidocrocite to goethite transformation (Schwertmann and Taylor, 1972).

Goethite/hematite ratio

Preliminary tests showed that the composition of a 50/50 goethite-hematite mixture changed to a ratio of

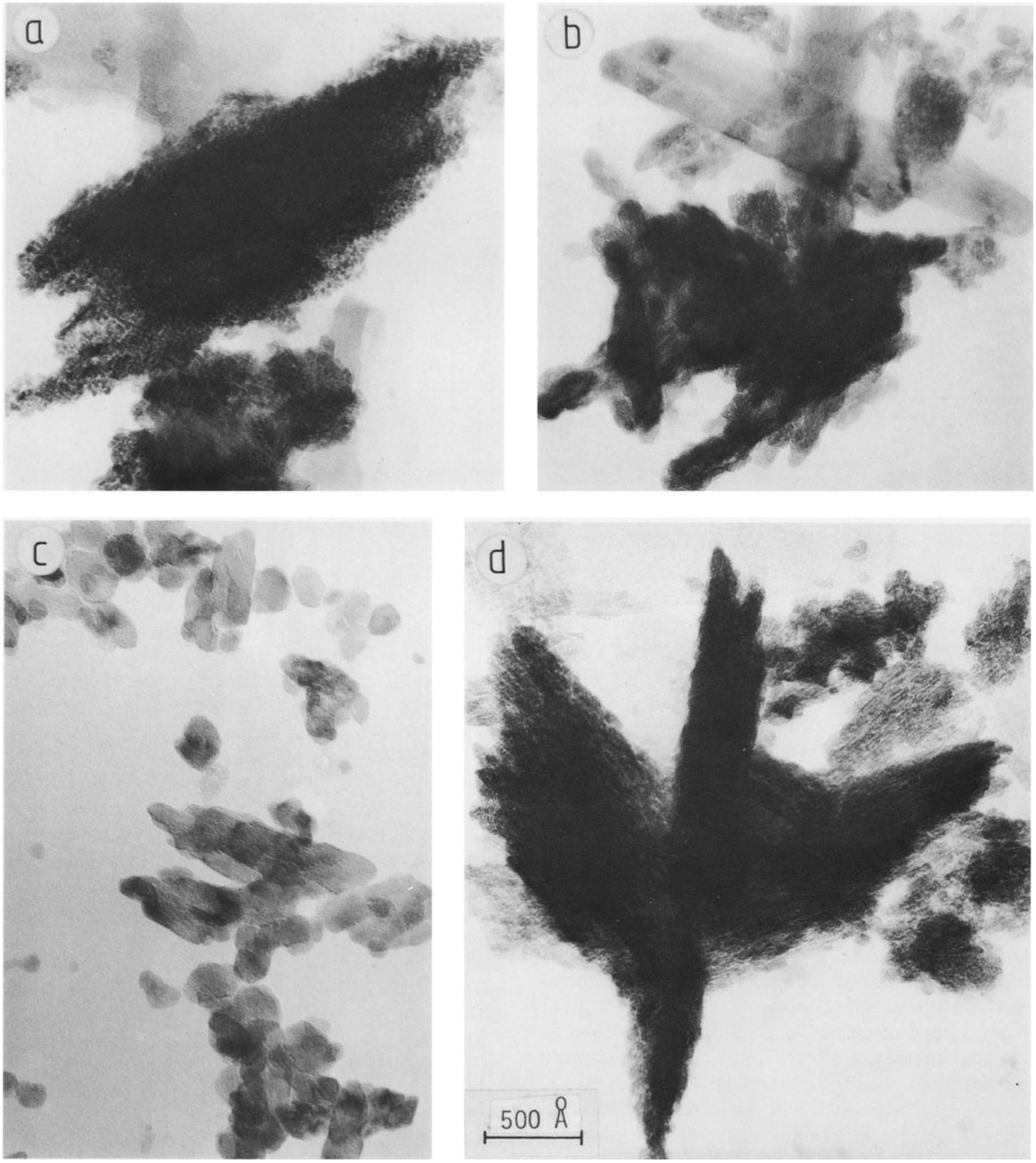

Figure 5. Electron micrographs of a natural Al-substituted goethite (GP3I) (a) before, (b) after one treatment with 5-M-NaOH, (c) after three 5-M-NaOH treatments and (d) after treatment with 5 M NaOH + 50% kaolinite.

53/47 and 52/48 after a 5-M-NaOH treatment without or with an addition of 50% kaolinite, respectively. These values are within experimental error. With 50/50 mixtures of synthetic hematite HNK3 and either synthetic goethite GNK2 or the natural goethite GP3I, slight changes of the Gt/(Gt + Hm) ratios did occur even after the addition of 50% kaolinite. However, because a transformation of goethite to hematite or vice versa did not occur with the single synthetic phases, it is most likely that these changes are due to variations in line intensity resulting from either recrystallization of goethite or dispersion effects of hematite as described above. A transformation of goethite to hematite is also unlikely because the added hematite did not change its Al substitution and WHH which could be expected if neoformation of hematite had occurred.

Table 3. Effect of the 5-M-NaOH treatment on two 1:1 goethite-hematite mixtures.

	Goethite (110)			Hematite (102)			Intensity ratio[1]
	$I_{obs.}$[2] (cps)	$I_{rel.}$[2]	WHH[3] (°2θ)	$I_{obs.}$[2] (cps)	$I_{rel.}$[2]	WHH[3] (°2θ)	
Goethite GNK2 + Hematite HNK3							
Untreated	190	100	0.65	51	100	0.25	0.50
5 M NaOH	251	132	0.53	45	88	0.24	0.60
5 N NaOH + 50% kaolinite	312	112	0.55	48	94	0.25	0.54
Goethite GP3I + Hematite HNK3							
Untreated	221	100	0.77	103	100	0.24	0.50
5 M NaOH	269	121	0.50	129	125	0.23	0.49
5 M NaOH + 50% kaolinite	199	90	0.55	108	105	0.25	0.46

[1] Goethite (110)/goethite (110) + hematite (102), calculated using $I_{rel.}$.

[2] $I_{obs.}$ = observed intensity. $I_{rel.}$ = intensity relative to untreated sample.

[3] WHH = width at half-height.

Table 4. Effect of NaOH treatment on natural goethite GP3I.

Treatment	111 line		Al-substitution[1] (mole %)
	d (Å)	WHH[2] (°2θ)	
0.5 M NaOH, 2.5 min, boiling	2.417	0.55	25 ± 4[3]
1.25 M NaOH, 60 min, 75°C	2.416	0.55	26
1.25 M NaOH, 14 days, 75°C	2.416	0.54	26
5 M NaOH, 60 min first treatment	2.427	0.56	18
5 M NaOH, 60 min second treatment	2.434	0.58	13
5 M NaOH, 60 min third treatment	2.439	0.58	9
5 M NaOH, 60 min + 50% kaolinite	2.418	0.60	24
5 M NaOH, 120 min	2.428	0.58	17
5 M NaOH, 120 min + 50% kaolinite	2.420	0.57	23

[1] Based on Vegard rule (Vegard, 1921).

[2] WHH = Width at half-height.

[3] 95% confidence interval.

Soil iron oxides

Al substitution was compared before and after treatment because the degree of Al substitution proved to be a more sensitive measure of the effect of the NaOH treatment than the transformation of goethite or hematite. The exact position of the 111 line of goethite could, however, not be ascertained unless most of the interferring kaolinite had been removed. This was accomplished by a comparably mild treatment (1.25 M NaOH at 75°C for 14 days) which removed most of the kaolinite, but, as concluded from the natural goethite GP3I (see below), did not change Al substitution. This treatment was therefore taken as a reference.

Only 3 of 18 goethites with the highest Al substitution showed a significant decrease in substitution after the 5-M-NaOH treatment (Figure 4). Making the 5-M-NaOH solution 0.2 M in Si by adding noncrystalline silica completely prevented the Al loss.

The mechanism of the alteration of goethites was, therefore, studied in more detail with two goethites from a hematite-free saprolite consisting only of goethite, gibbsite, some magnetite (which was removed by magnetic separation) and ilmenite. There was no difference in Al substitution between a 0.5-M-NaOH boiling treatment for 2.5 min and a 60-min, 1.25-M-NaOH treatment at 75°C (Table 4). Most likely, those treatments which removed gibbsite completely (but not kaolinite) left the goethite practically unaltered. This is also supported by TEM micrographs (not shown). In contrast, one, two, or three consecutive 1-hr treatments with boiling 5 M NaOH increasingly removed the Al in the goethite down to 9 mole % Al. In a goethite sample from another saprolite the Al substitution dropped from 21 to 12 mole % after a single treatment. TEM photos show that the original highly serrated crystals (Figure 5a) dispersed into many subrounded, smaller crystals (Figure 5c), along with larger lath-shaped crystals (Figure 5b).

Fifteen minues after starting the boiling 5-M-NaOH treatment, the Fe concentration in solution was 2.60 mg/liter corresponding to 0.047% of the goethite in the sample. The Al substitution dropped from 25 to 17–18 mole % and remained practically constant during the whole 2-hr treatment. Obviously the build-up of Al released from gibbsite blocked further Al loss from goethite. Only after replacing the extracting solution with a fresh one was additional Al released (see second and third treatments in Table 4). As with the synthetic goethite, the addition of 50% kaolinite effectively prevented most of the Al loss. Recrystallization was also inhibited by Si in solution, and crystal morphology remained essentially the same (Figure 5d).

To determine the Si concentration necessary to prevent a change in Al substitution, the natural and synthetic Al-goethites were treated with 5 M NaOH solutions with Si concentrations between 0 and 0.19 M. With

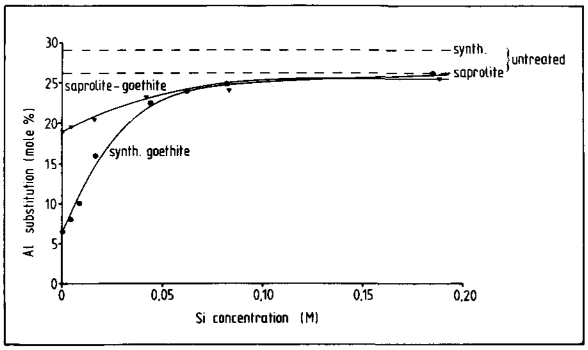

Figure 6. Effect of Si concentration of the 5-M-NaOH solution on Al-substitution after 5-M-NaOH treatment of a synthetic and a natural goethite.

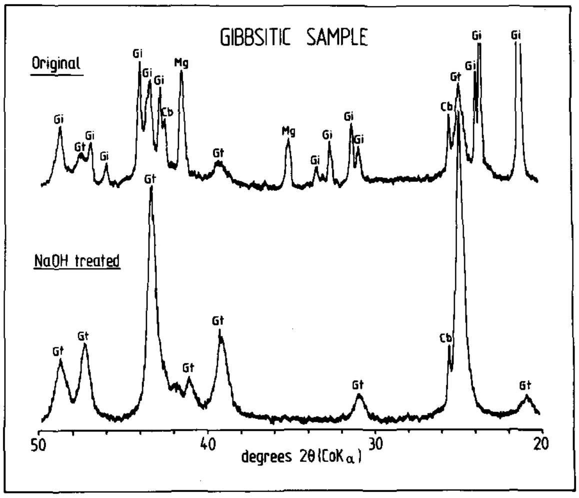

Figure 7. Effect of a 5-M-NaOH treatment on the mineralogy of a gibbsitic sample (Gt = goethite, Hm = hematite, Gi = gibbsite, Cb = cristobalite, K = kaolinite, Qz = quartz, An = anatase, Mg = magnetite, removed by a magnet in the NaOH-treated sample).

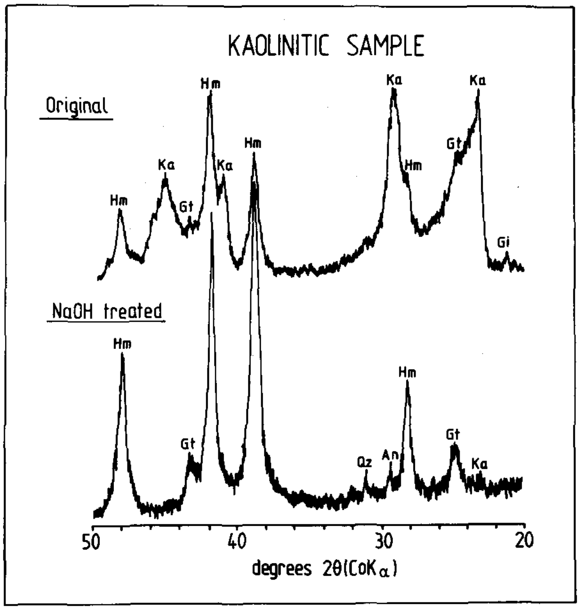

Figure 8. Effect of a 5-M-NaOH treatment on the mineralogy of a kaolinitic sample (Abbreviations as in Figure 7).

increasing Si concentration, loss of Al was continuously reduced (Figure 6). Thus, the mechanism responsible for this effect is the inhibition of goethite nucleation in solution by soluble Si.

No evidence of hematite formation during the treatment of goethite GP3I was observed even after 3 consecutive treatments. The temperature (109°C) of the boiling 5 M NaOH was obviously not high enough for the transformation. Petit *et al.* (1964) and Janot *et al.* (1971) observed a transformation of goethite to hematite only at 138°C and 145°C, respectively.

Concentration effect of the treatment

The concentration of iron oxides by the NaOH treatment in different clay fractions was between 3- and 20-fold. Examples of XRD traces before and after treatment are given for a gibbsitic sample containing goethite and some cristobalite (Figure 7) and a kaolinitic sample with hematite, goethite, and some quartz (Figure 8). Kaolinite and gibbsite were completely dissolved, whereas quartz and cristobalite remained. The resulting XRD traces easily permit quantitative determination of goethite and hematite in these soils for pedogenetic studies (Kämpf and Schwertmann, 1982). The concentration effect was much smaller in clay fractions dominated by 2:1 layer silicates. However, in a smectitic sample from a Vertisol with 1% Fe_d, the treatment concentrated the Fe oxides sufficiently to identify goethite. Concentration factors of 2.5–3 were obtained in illitic-smectitic soils clays from Germany (Schwertmann *et al.*, 1982).

CONCLUSIONS

The 5-M-NaOH boiling treatment of Norrish and Taylor (1961) is a useful method to concentrate Fe oxides in soil clays for further identification and characterization and does not change the relative proportions of goethite and hematite. No change in crystallinity or in Al substitution occurs as long as the Si concentration in the treating solution is sufficiently high. With kaolinitic samples, sufficient Si is supplied by the dissolution of kaolinite. If the kaolinite concentration is low, however, noncrystalline silica (e.g., Cab-o-Sil) should be added to achieve an Si concentration of approximately 0.2 M in the 5 M NaOH solution. Since it was introduced by Norrish and Taylor in 1961 the method has been used successfully to identify and characterize goethite and hematite in a range of soils.

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Резюме—Найдено, что обработка килящим раствором 5-M-NaOH облегчала идентификацию и характеризацию гетита и гематита путем эффективной концентрации двух окисей Fe в каолинито-гиббситовых почвенных глинах. Не наблюдались трансформации гетита в гематит или обратно, но найдено, что слабо-кристаллический, высоко Al-подставленный гетит растворяалься и рекристаллизовался в более хорошо-кристаллический, менее Al-подставленный гетит в образцах с низким содержанием Si. Количество Si, освобожденного из каолинита было достаточно, чтобы предотвратить растворение гетита и рекристаллизацию в каолинитовых образцах, но в этом случае нужно было добавить некристаллический кремнезем до образцов богатых в гиббсит, чтобы минимизировать этот эффект. [E.C.]

Resümee—Die Behandlung mit kochendem 5 M NaOH erwies sich als sehr geeignet zur Anreicherung von Goethit und Hämatit in kaolinitisch-gibbsitischen Bodentonen. Umwandlungen zwischen Goethit und Hämatit durch diese Behandlung wurden nicht beobachtet. Schlecht-kristallisierter hoch-Al-substituierter Goethit kann sich jedoch auflösen und zu gut-kristallisiertem weniger Al-substituierten Goethit umkristallisieren, falls die Probe arm an Si ist. Das aus dem sich lösenden Kaolinit stammende Si reicht in der Regel aus, um diese Veränderungen des Goethits zu blockieren. Bei kaolinitarmen oder -freien Proben (gibbsitische Proben) ist dagegen amorphes Si-oxid zuzusetzen.

Résumé—On a trouvé que le traitement par ébullition 5-M-NaOH aidait dans l'identification et la caractérisation de goethite et d'hémitate en concentrant de manière effective les deux oxides Fe dans des argiles de sols kaolinitiques-gibbsitiques. On n'a détecté aucune transformation de goethite en hématite ou d'hématite en goethite, mais on a trouvé qu'une goethite pauvrement cristalline et fortement substituée avec Al s'était dissoute et recristallisée en une goethite mieux cristalisée et moins substituée avec Al dans des échantillons pauvres en Si. La Si provenant de la kaolinite était suffisante pour bloquer la dissolution et la recristallisation de la goethite dans des échantillons kaolinitiques, mais de la silice non-cristalline a dû être ajoutée aux échantillons riches en gibbsite pour minimiser cet effet. [D.J.]