

LOSS OF K-BEARING CLAY MINERALS IN FLOOD-IRRIGATED, RICE-GROWING SOILS IN JIANGXI PROVINCE, CHINA

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Abstract—The loss of K-bearing clay minerals has been observed over an 80 y cultivation period in Chinese rice paddies despite the use of NKP fertilizers. Clay mineral determinations were made in flood-irrigated paddies cultivated for 3, 10, 15, 30 and 80 y in clayey (45 wt.%), red soils derived from red Quaternary sediments. Three clay minerals are initially present in these soils: illite-mica, magnesian chlorite and an interstratified mica-aluminous chlorite mineral. This last phase was identified using computer simulations. The K-bearing phases (discrete mica and illite as well as interstratified mica layers) are to a large extent lost while the Fe content decreases in the soil as a whole and increases in the chlorite. The mica component in the mixed-layer mineral decreases also. These changes in clay mineralogy and relative abundance suggest a loss of potassic minerals and an increase in the formation of less siliceous, more ferro-magnesian chlorite. These changes occur over 30 y or less, a rather rapid, irreversible transformation of soil clay minerals. Such loss of potassic minerals renders the cultivation more dependent on fertilizer amendment.

Key Words—Clay Mineral, Irrigation, Mica-chlorite Interlayer, Potassium.

INTRODUCTION

Clay mineral changes in flood-irrigated soils have rarely been investigated although there are a few studies (Chen *et al.*, 1994; Ionue, *et al.*, 1977; Prikhod'ko *et al.*, 2000; Pharande *et al.*, 2000). The process of flood irrigating is one in which surface evaporation is very important in the evacuation of water in contrast to normal culture methods where most of the water in pores is evacuated by downward flow to the water table. Strong evaporation creates changes in pH and salt content of the water of the soils. In desert environments, where intense rain events produce hydrologic effects similar to those of flood irrigation, there is clear formation of the magnesian minerals, sepiolite and palygorskite (magnesian silicates) formed from the aluminous clay minerals illite, kaolinite and smectites (Velde, 1985). The magnesian minerals are also among the more silica-poor in surface clay minerals. Similar changes are seen in Indian irrigated soils (Pharande *et al.*, 2000) where palygorskite replaces smectite in the cultivated soils after 30 y of flood irrigation. The clay minerals and the physical properties of the soils are altered drastically.

The present study concerns flood-irrigated soils in southern China and attempts to observe the effect of flood irrigation agriculture on soils developed from Quaternary red clays in Jiangxi Province.

In China, soils often contain chlorite, vermiculite and mica minerals as separate phases or as interstratified clay minerals (Jiang *et al.*, 1982; Shanmei *et al.*, 1988;

Zhang and He-Zhen, 1992; Deng and Xu, 1990; Chen and Liu, 1994). These minerals are found in the area of study selected here, Jiangxi Province in south central China. This mineralogy is very different from most other temperate-climate non-mountainous areas where soils contain smectite or interstratified illite-smectite minerals such as found in the Central Plains area of the USA (Velde, 2001).

The question asked here is whether irrigation will produce the same types of clay mineral changes in Chinese irrigated soils (containing chlorite and mica) as those observed in desert soils or Indian irrigated soils where aluminous clays (smectite, kaolinite, illite) are transformed into low-silica, Mg silicates.

MATERIALS AND METHODS

The red clays in Jiangxi Province represent ~20% of the soils in the province where red soils represent 70% of the total. The plots investigated are several hundreds of meters apart and have been cultivated for different periods of time ranging from 3 to 80 y. The agriculture consists of double cropping of rice. Using this material we hoped to observe the effect of such cultivation practices on the clay minerals in the soils used to grow the rice crops. Thus the source soils were very similar and the climate virtually the same.

Samples

Samples from three locations were taken at two depths (0–10 and 10–20 cm) from sites where the soil was not cultivated and from plots cultivated for different lengths of time (3, 10, 15, 30 and 80 y). The plow zone extends to 17–25 cm depth. The cultivation practices

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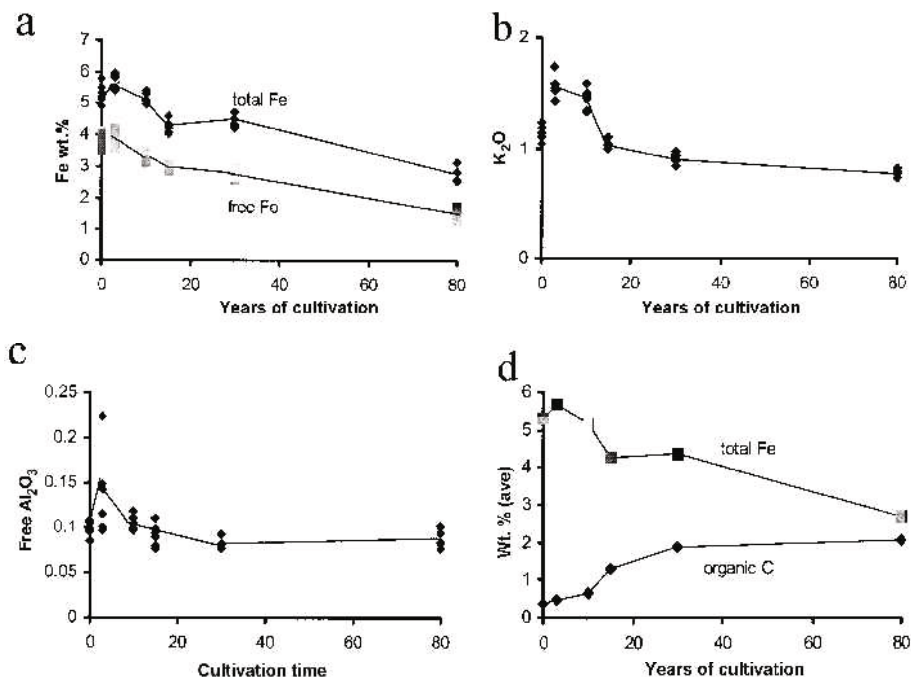


Figure 1. Chemical data for the rice-paddy plots investigated. (a) Comparison of free, extractable and total Fe, (b) K content, (c) free, extractable Al, (d) comparison of average values for C and total Fe.

were the same, double cropping using flood irrigation and NKP fertilizer (Ca, Mg phosphate – 4500 kg ha⁻¹; urea – 1500 kg ha⁻¹, KCl – 1500 kg ha⁻¹ per season). Average yields for plots of different cultivation periods increase from 22,000 kg ha⁻¹ in the youngest plots (3 y cultivation) to 43,000 kg ha⁻¹ each year in the oldest plots (80 y). Also, the average organic carbon content increases. The average pH increases initially and then decreases. Total and free Fe decrease, and K content increases initially but then decreases. Free Al decreases with length of cultivation period. These data are presented in Figure 1.

The average soil colors (Munsell chart) change as indicated in Table 1. The colors change from bright red in the initial material to dark gray in soils under cultivation for 80 y. The clay fraction (<2 μm) decreases with cultivation time as shown in Figure 2.

Clay mineral determinations

Experimental method. X-ray diffraction (XRD) was used to determine the clay mineralogy of the <2 μm soil fraction. No chemical treatment was used to eliminate Fe and Al oxides or organic matter. This is contrary to methods usually used in soil analysis outlined by Bertsch and Bloom (1996) and Loeppert and Inskeep (1996). This choice was made in order to minimize the potential

disturbance of the hydroxy-interlayer materials which are present (10–14 Å aluminous chlorite-mica mixed-layer minerals). Examples of the XRD patterns for soil samples submitted to different periods of cultivation are shown in Figure 3. Samples were Sr saturated and run in the air-dried state. The positions of obvious peaks are shown and zones where others are probably present are indicated by arrows.

Clay fractions (<2 μm) were Sr or K saturated, oriented on glass slides and X-rayed under air-dried conditions and ethylene glycol treatment using a Philips diffractometer with a step-scanning program. K-saturated samples were heated to 200°C for 4 h. Sharp peaks were identified at 14.5, 10.2, 7.2, 3.46 and 3.26 Å. Other larger peaks or shoulders were observed at ~12.9, 7.5, 4.7 and 3.3 Å. The different treatments did not affect the XRD patterns and no further peak shifts were observed after heating the K-saturated specimens to 200°C.

CLAY MINERALS

Mineral identification procedure

Identification of diffraction peaks. Visual inspection indicates the presence of several minerals. However, large shoulders and wide peaks indicate the presence of others (Figure 3). In order to identify all of the minerals

Table 1. Average colors (Munsell chart) of soils as a function of years of cultivation.

Years	0	3	10	15	30	80
Color	7.5YR7-7	7.5YR7-6	10YR8-4	2.5YR7-2	2.5YR5-2	2.5YR7-2

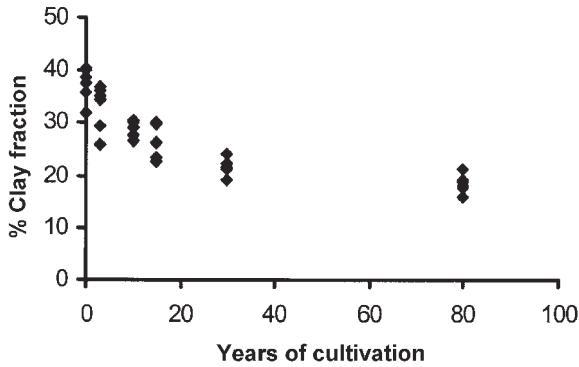


Figure 2. Clay content (<2 μm fraction) related to years of cultivation.

present, a decomposition program (Lanson, 1997) was used after smoothing the digital intensity patterns on a 7-point interval and subtracting the background. Convergence of the fitting routine to 98% concordance was used as a reasonable criterion for identifying the peak position and intensity. The method uses the following guidelines: a phase should be visually present before, during and after the operations. Micas and chlorites show peaks with invariable positions and they are narrow (width at half height, $\text{WWH} \leq 0.5^\circ 2\theta$). In the samples investigated it is clear that there are several sharp peaks which are always present, at or near 14.5 \AA , at 10.0 \AA and near 7.2 \AA . Figure 4 indicates the steps which can be used to fit and identify the peaks in the diagrams of the Chinese red soils. The 14.5, 10 and 7.2 \AA peaks can be modeled easily using decomposition procedures (Figure 4b). Once these peaks are established as a first hypothesis for the fitting routine, others are added according to findings from past studies. First, there is usually an illite-mica peak pair in most clays (Gharrabi *et al.*, 1998; Velde, 2001). The illite has a slightly larger basal spacing (near 10.3 \AA) and is wider than the sharp mica peak. Peaks at 14.5 and 7.2 \AA can initially be assumed to belong to chlorite and perhaps part of the 7.2 \AA , to kaolinite. These are seen in Figure 4b. However, it is clear that parts of the XRD trace, one near 12 \AA and the other near 7.5 \AA have significant residual diffraction intensity when the initial peaks (mica-illite and chlorite) are subtracted from the total diffraction intensity (Figure 4c). It is clear that after subtraction, two symmetric peaks remain. These two new peaks are added to the initial fitting hypothesis. Figure 4d shows the results of such decomposition and subtraction routines. In Figure 5 the numerical results of decomposition of the spectra are shown for four samples, from 3, 10, 15 and 30 y cultivation plots.

Attribution of diffraction peaks to clay minerals. In Figure 4d the narrow peaks near 10, 14 and 7.2 \AA indicate the presence of mica and chlorite. A wider peak at >10 \AA indicates the presence of illite. The two broad

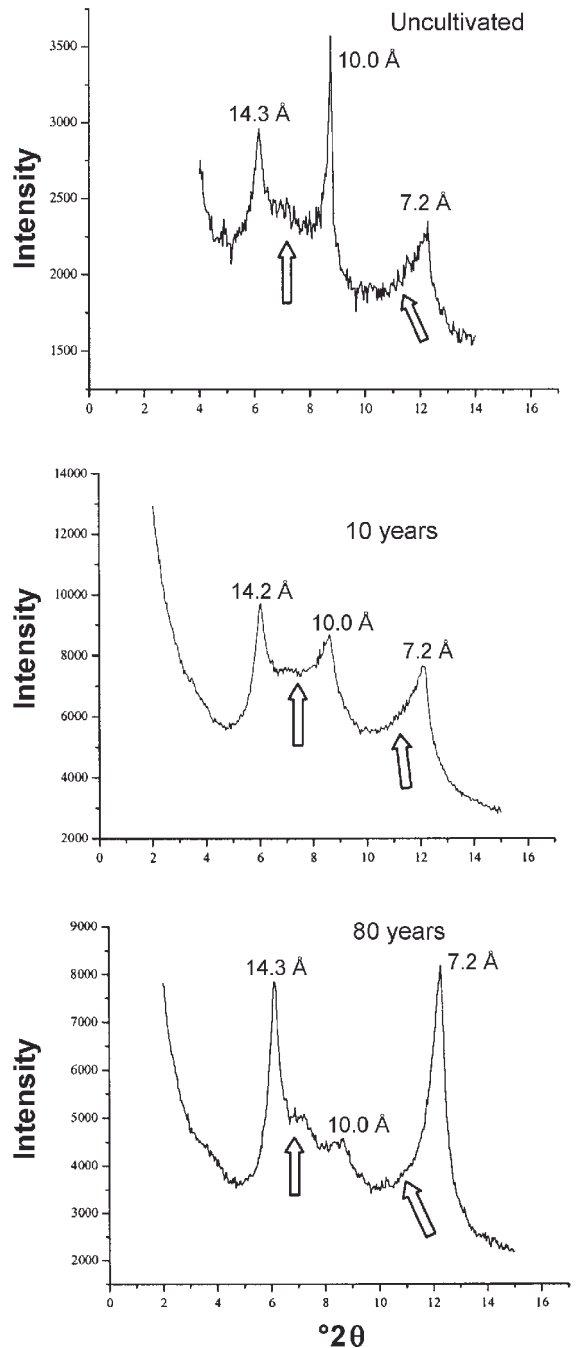


Figure 3. Representative XRD patterns for different cultivation periods. Arrows indicate low-intensity shoulders which overlap sharper peaks. The samples were in a Sr-saturated, air-dried state.

peaks near 11–13 \AA and 7.5 \AA must be attributed to another phase. Given the similar, large peak widths, we attribute these two peaks to the same phase. The positions, however, indicate a non-rational series of diffraction maxima which, according to Moore and Reynolds (1997), could be attributed to a mixed-layer mineral. As the peak positions do not change with glycol

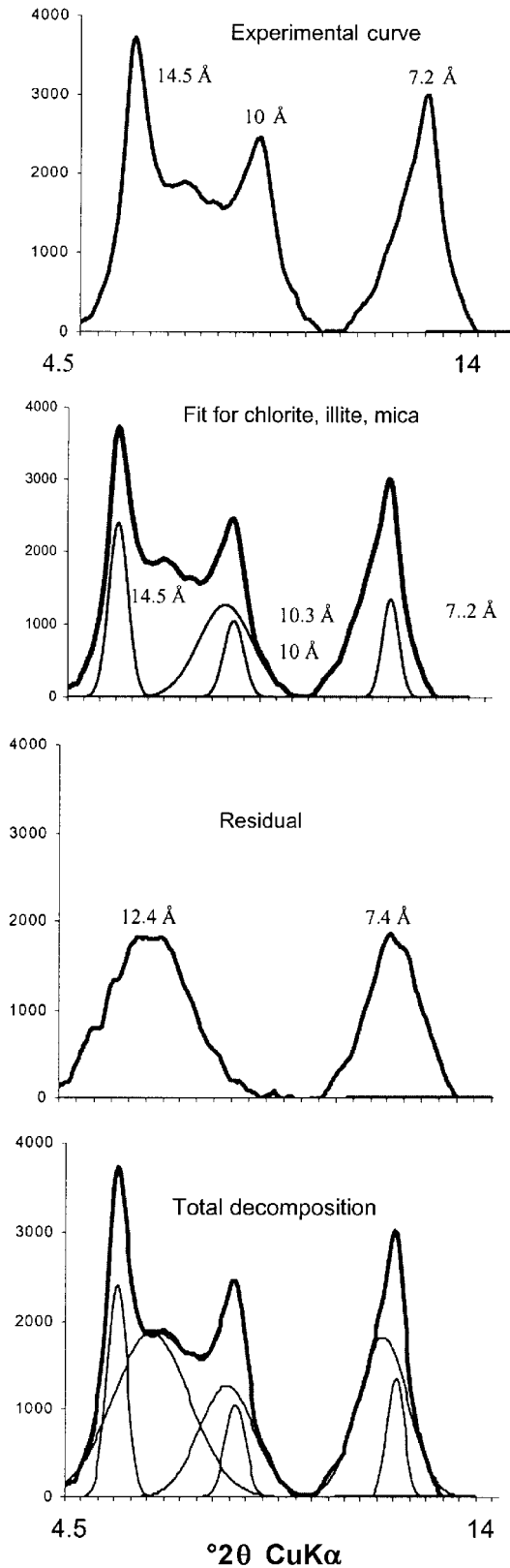


Figure 4. Demonstration of decomposition identification of the low-intensity peaks found near 12 and 7.4 Å. The darker curve represents the experimental data.

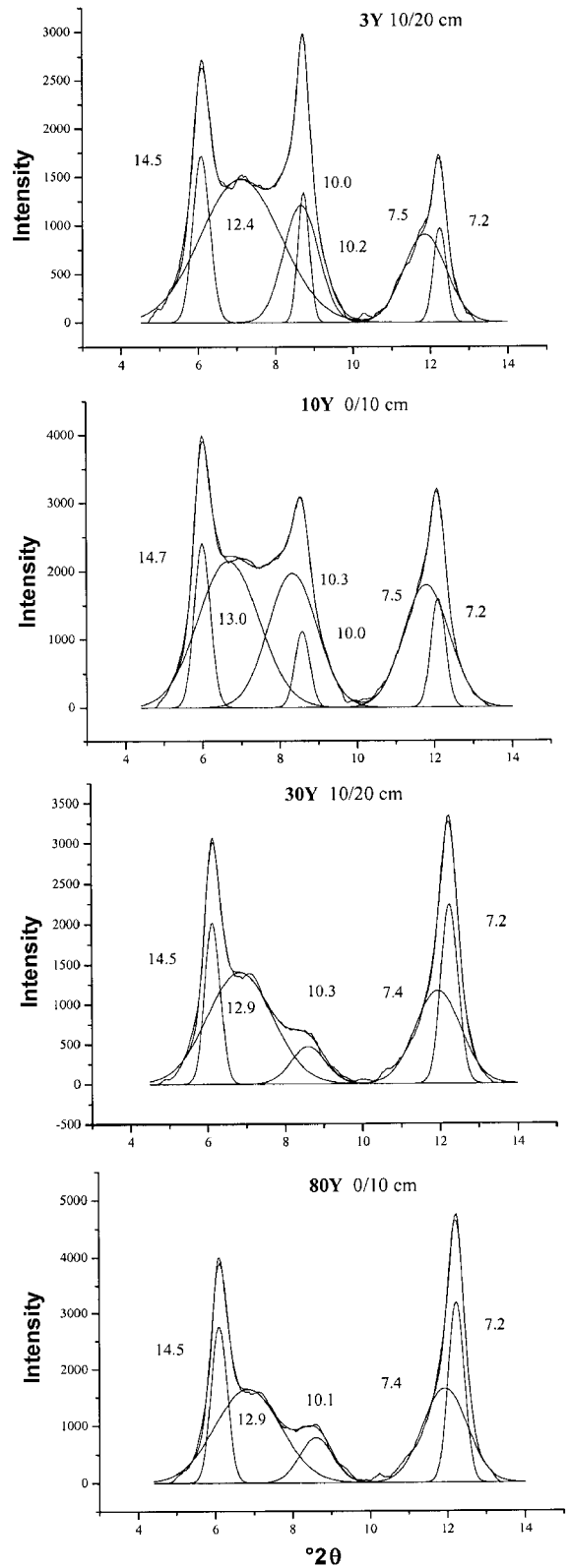


Figure 5. Peak positions (Å) revealed by decomposition analysis for four cultivation periods, 3Y = three years, 10Y = 10 years, 30Y = 30 years, 80Y = 80 years.

treatment, K saturation and heating, one can assume that no smectite (expandable) phase or collapsible interlayer unit is present. Using the NEWMOD program (Reynolds, 1985) it is clear that the mixed-layer mineral matches patterns of 10 and 14 Å mixed-layer clay units. When a trioctahedral mineral or vermiculite (hydroxy-smectite) model is used as a hypothesis, the 13–14 Å peak is very intense compared to the 7 Å peak. As seen in Figure 4c, this is not the case for our samples. Given the options of tri-trioctahedral or di-dioctahedral minerals, the best fit for peak intensities and width is one of a mica-di-dioctahedral chlorite. In order to maintain relatively similar intensities for the 7 and 12.5 Å peaks, a low Fe content in the chlorite hydroxy interlayered site is required. These simulated peaks are wide ($3-1.3^{\circ}2\theta$ WHH for the 11–13 Å peaks, and $1.2-1.4^{\circ}2\theta$ for the 7.5 Å peaks). Figure 6 shows the peak position and intensity ratios for different simulations using a low Fe content of the components (no Fe in the mica and 1–2 Fe in the octahedral sites of the chlorites).

The results of curve fitting for the different peaks for the rice-paddy samples are given in Table 2. In the first four columns the relative surface areas are given, considering 14, 12.5, 10.3 and 10 Å peaks. The intensity ratio for the chlorite-mica mixed-layer mineral first- and second-order peaks is given in column 5, the intensity ratio for the 7.2–14.5 Å chlorite peaks is given in column 6, and the position of the mixed-layer chlorite-mica mineral is given in column 7.

Characteristics of minerals identified

Illite-mica. The peaks near 10 Å can be attributed to mica (probably detrital) and illite near 10.2 Å (Gharabbi *et al.*, 1998). The mica gives a sharp peak ($\sim 0.2^{\circ}2\theta$ width at half height or WHH) and the illite a peak near $1^{\circ}2\theta$ WHH. These are typical values for sedimentary and soil materials (Moore and Reynolds, 1997).

Chlorite. Sharp peaks ($<0.4^{\circ}2\theta$ WGG) at or near 14.2 and 7.2 Å identify chlorite. The 14 Å peak is generally more intense than the 7 Å peak in the initial materials and the reverse is true in the soils cultivated for 80 y (Table 2, column 6). Using the NEWMOD models, these chlorites would initially have a slight defect (vacancy) in the hydroxide sheet sites in a dominantly trioctahedral magnesian mineral. Increase in cultivation time changes the intensity ratio of the 001 and 002 peaks indicating an increase in Fe content.

Mixed-layer minerals. The peaks at 11 to 13 Å and 7.5 Å show an irrational series which are wide ($3-1.3^{\circ}2\theta$ WHH for the 11–13 Å peaks, and $1.2-1.4^{\circ}2\theta$ for the 7.5 Å peaks). As stated above, any combination of trioctahedral minerals gave very high intensity 12 Å peaks relative to the 7 Å peaks indicating a poor simulation for the peak intensities observed in the decomposition results. In the mica-di-dioctahedral chlorite mixed-layer mineral simulations using NEWMOD, the peaks are wide ($1.5^{\circ}2\theta$ or more) and the intensities of the 12 and 7 Å peaks are similar. This chlorite structural unit can be considered to be a dioctahedral Fe,Mg,Al hydroxy mineral whose composition is dominated by Al ions with an Fe-Al hydroxy complex in the interlayer position. This would be similar to a kaolinite with an aluminous hydroxy ferromagnesian interlayer unit.

Compositional variations can occur in the mica and in two sites in the dioctahedral chlorite layers. It is expected that the mica is close to a muscovite in composition and hence little change in the XRD intensities would occur. The Fe content is the most important chemical variable for peak intensity which would occur in the chlorite layers. However, the existence of a full hydroxide sheet in the chlorite is also extremely important for relative peak intensity. Since all of these factors (6) can vary simultaneously, it

Table 2. Results of curve-fitting for different peaks for rice-paddy samples as a function of period of cultivation. chl = chlorite; mi = mica, % = area percent for first-order chlorite, mixed-layer chlorite-mica, illite and mica peaks, I = intensity of peaks.

Years		14 Å chl %	chl-mi %	illite %	mica %	$I_{7.5}/I_{12}$ Å	$I_{7.2}/I_{14.5}$ Å	chl-mi pos Å
0	av	14	57	19	10	0.5	0.5	12.4
	range	3	10	7	4	0.3	0.4	0.8
3	av	13	58	20	9	0.6	0.4	12.3
	range	6	9	7	6	0.4	0.2	0.4
10	av	18	51	25	6	0.6	0.6	12.8
	range	2	8	8	2	0.3	0.8	0.4
15	av	19	55	23	5	0.8	0.7	12.7
	range	6	9	5	8	0.4	0.8	0.4
30	av	23	59	8	2	0.7	1.2	12.8
	ange	9	31	15	7	0.7	1	0.3
80	av	28	57	7	0	0.8	1.1	13
	range	13	9	7	0	0.4	0.5	0.5

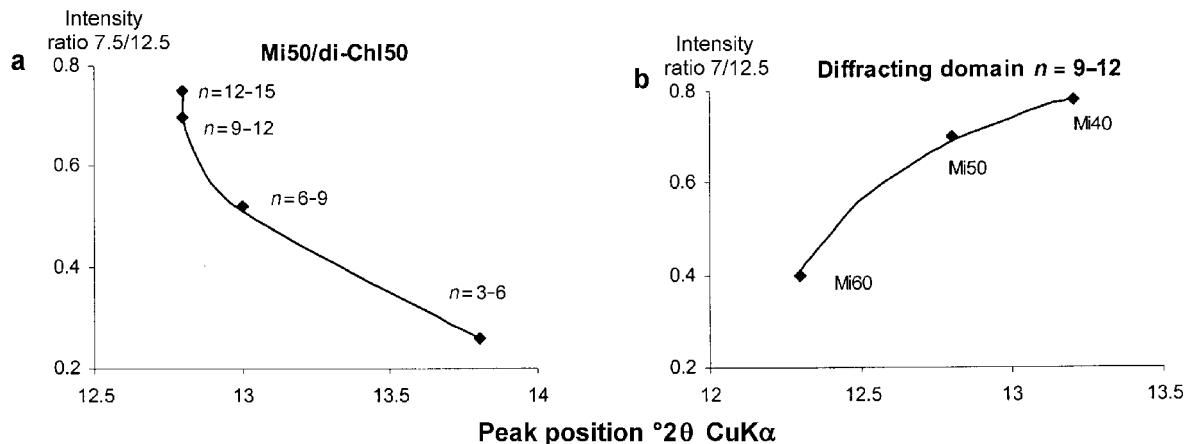


Figure 6. Peak position and relative intensity for simulated patterns of mica-di-dioctahedral chlorite mixed-layer minerals as a function (a) of average diffracting domain size (n) at constant composition (50% mica) and (b) of varying mixed-layer composition (proportion of mica and di, dioctahedral chlorite) at constant diffracting domain size (9–12).

is virtually impossible to assign a given composition to a phase using the limited variation of an XRD pattern (1 dimension). Nevertheless, some relations can be pointed out. Initially, the Fe content must be low in the hydroxide sheet of the chlorite to produce a wide 11–13 Å peak of roughly the same intensity as that found at near 7.5 Å. Reducing the Fe content increases the intensity of the 11–13 Å peak. Also, the hydroxide sheet must be filled in order to produce a reasonably low intensity 11–13 Å peak.

Some compositional effects on the XRD patterns calculated can be modeled, however, and compared with the experimental data. These are shown in Figure 6. The position of the 12.5 Å peak and the intensity ratio of the 7.5–12.5 Å peak can be changed by either changing the coherent diffracting domain size (n) or the proportion of mica compared to di-dioctahedral chlorite. In general, the 7.5 Å peak is the least sensitive to variation in diffracting domain size or composition (mica-di-dioctahedral chlorite). The larger the coherent diffracting domain, the lower the relative intensity of the 12.5 Å peak and the lower its d spacing. The higher the mica content (10 Å layer) the lower the relative intensity of the 12.5 Å peak and its lower d spacing. The changes of intensity ratio and peak position due to change in mixed-layer composition or diffracting domain size are the inverse as shown in Figure 6.

In the paddy soil samples; the peak position at near 12.5 Å shifts to slightly higher spacings in the plots cultivated for a longer time and the relative intensity of the 12.5 Å peak decreases compared to that of the 7.5 Å peak (Table 2 columns 7 and 5). This observed change in peak positions and relative intensity of the 12.5 Å peak can best be explained by a decrease in mica content of the mixed-layer mineral (Figure 6b) at roughly constant coherent diffracting domain size (n).

From the above we deduce that the composition (proportions of chlorite and mica components) changes

with cultivation time, the mixed-layer mineral losing mica content.

OBSERVATIONS

The primary observations in our study are the changes in XRD patterns of the clay-sized fraction. One should remember that the clay fraction decreases with time of cultivation. Triplicate analyses were made for each age or time span of cultivation and two depths were investigated, 0–10 cm and 10–20 cm for each plot. Relative intensity values for the major phases are plotted in Figure 7 using the peaks in the range 14–7 Å (Table 2). The mica, illite, chlorite (14 Å peak) and mixed-layer mica-dioctahedral chlorite (12 Å) peaks are used in this comparison.

It is clear that the intensities of the mica peak are reduced to near 0% of the total in the 30 and 80 y cultivation plots. The illite peak is drastically reduced also so that the total of the micaceous mineral fraction is near 10% relative intensity. In Figure 7 both illite and mica are plotted to give an idea of the change in the abundance of potassic minerals present. The 14 Å peak for magnesian, trioctahedral chlorite increases in relative intensity. However, the fact that the ratio of 7–14 Å peaks increases with age indicates that the apparent increase in chlorite content would be underestimated. The mixed-layer mineral with wide peaks at 12.5 and 7.5 Å maintains roughly the same area percent of the XRD patterns. However, the average ratio of 7 to 12 Å peak intensity changes to higher values in the plots cultivated for a longer time indicating that this mineral would be underestimated somewhat by using the first order peak intensities.

Thus, the loss of micaceous material (K-rich) is compensated by a relatively larger amount of a more ferrous trioctahedral chlorite. The mixed-layer mica-dioctahedral chlorite phase becomes less mica-rich at

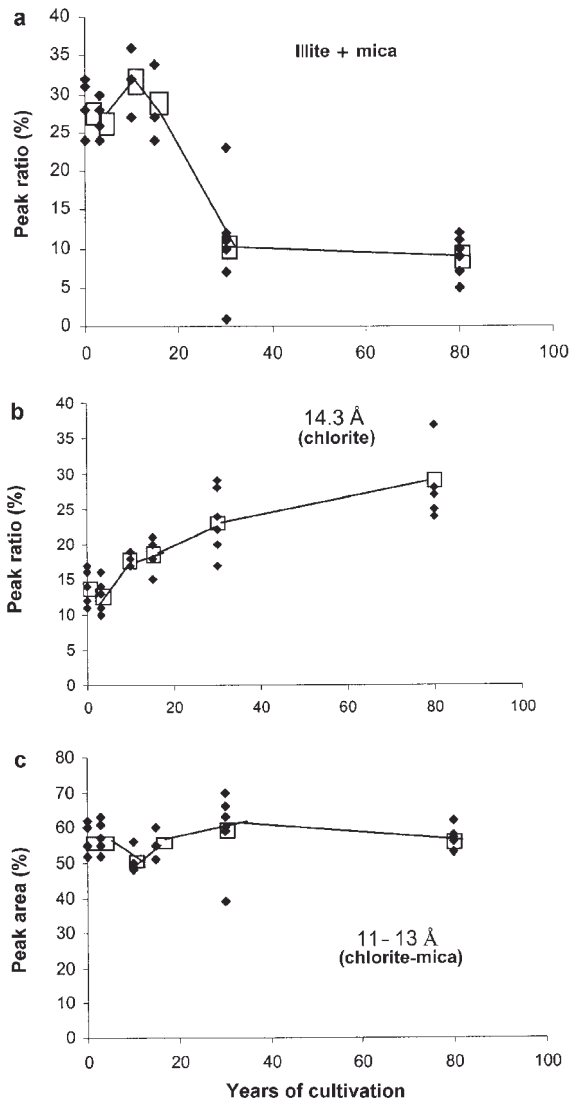


Figure 7. Peak area percentages expressed as percent (a) of illite+mica, (b) 14 Å chlorite and (c) 12 Å mica-chlorite mixed-layer minerals, related to years of cultivation.

about constant relative abundance in the clay fraction. Both of the remaining clay minerals change composition.

DISCUSSION

The observations on clay mineral change accompanied by the whole-soil chemical data suggest that the cultivation methods employed during the last 80 y in the Jiangxi rice paddies effect significant chemical changes which are reflected by changes in the clay mineralogy. Two observations are striking: the loss of Fe (total and free Fe) and the loss of K from the soils. At the same time there is a loss of mica-illite potassic phases and an increase in a more ferrous chlorite. A plot of K_2O against illite+mica content indicates that there is a strong correlation but it is not linear (Figure 8). Initially the

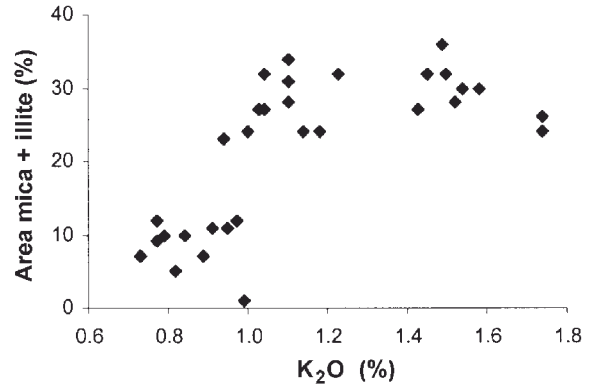


Figure 8. Peak area percent of mica + illite 10 Å vs. K_2O content.

loss of K is not reflected in a relative decrease in illite+mica peak surface. This indicates that the K in the chlorite-mica mixed-layer mineral is the first to be released during mineral change.

The change in clay mineralogy is accompanied by a decrease in the clay fraction of the soils. Thus, some or all of the different clay minerals are lost during the cultivation time. The mineral which is almost totally lost is mica, supposed generally to be a detrital mineral which would be found in the coarse part of the clay fraction. The mineral most likely to be of soil origin is the mixed-layer mica-di-octahedral chlorite whose relative abundance seems to be about constant. Chlorite appears to increase in relative abundance as it became more ferrous. Chlorite is also generally considered to be in the larger size fraction of the clays, and its relatively sharp peaks indicate larger diffracting domain sizes. Since illite-mica is in the coarse clay fraction and chlorite is of larger average grain size, one could not expect them to be illuviated before other, finer-grained clays such as the soil-clay mixed-layer mica-chlorite mineral. We assume then that the micas are destroyed by chemical means. The change in mica content of the mixed-layer mineral suggests some chemical influence also. New, more Fe-rich chlorite is formed in the clay fraction present after longer periods of cultivation.

The decrease in Fe in the soils can be explained by the reduction of Fe due to an increase in organic matter. Such a change is classic in soils where bacteria transforming organic matter mobilize Fe in the ferrous state (Dassonville and Renault, 2002) which would probably render this element more soluble in aqueous solution, if other chemical factors do not interfere. The increase in organic carbon is effected by the practice of allowing residues of farming (manure) to be re-incorporated into the soils in one of the twice-yearly rice-crop cycles.

As is the case for desert soils and flood-irrigated Indian soils where surface evaporation is important and silica-poor magnesian silicates such as sepiolite and palygorskite form, the Chinese flood-irrigated rice-

paddy soils studied here also form silica-poor, ferromagnesian clay minerals (chlorites) at the expense of more siliceous minerals, the micas (Chen and Liu, 1994; Pharande *et al.*, 2000). Thus it seems possible that the effect of flood irrigation upon clay minerals may be similar to that classically known in desert soils, although it is appreciated that at this stage more work is necessary before this can be substantiated for chlorites.

The loss of K from the Chinese rice paddy soils is all the more striking in that the cultivation protocol uses KCl fertilizer. Even though abundant K is available in aqueous solution, the principal K phase diminishes in the clay assemblage of the cultivated zone as the time of cultivation increases.

CONCLUSIONS

It is apparent that the flood irrigation agriculture process alters the clay mineralogy in the soils of the Chinese rice paddies investigated here by eliminating the potassic minerals. The use of K fertilizer will become more necessary with time given that the amount of natural K-bearing reservoir minerals decreases with cultivation time. In the Chinese soils investigated here, irrigation makes the system more dependent on a supplement of K which cannot be regenerated from the clay minerals which have lost their potassic component.

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REFERENCES

- Bertsch, P.M. and Bloom P.R. (1996) Aluminum. Pp 516–550 in: *Methods of Soil Analysis* (A. Klute, editor). SSSA Book Series 5, Soil Science Society America, Madison Wisconsin.
- Chen, M. and Liu, G.L. (1994) Clay mineral compositions, soil fertility and surface chemistry characteristics of Quaternary red soils of southern Hunan province. *Scientia Agricultura Sinica*, **27**, 24–30.
- Dassonville, F. and Renault, P. (2002) Interactions between microbial processes and geochemical transformations under anaerobic conditions: a review. *Agronomie*, **22**, 1–18.
- Deng, S.Q. and Xu, M.X. (1990) Studies on soil particles in China. III Physical and chemical properties of different particle size fractions of red earth in hilly lands of central Jiangxi Province. *Acta Pedologica Sinica*, **27**, 368–376.
- Gharrabi, M., Velde, B. and Sagon J.-P. (1998) The transformation of illite to muscovite in pelitic rocks: Constraints from X-ray diffraction. *Clays and Clay Minerals*, **46**, 79–88.
- Ionue, K., Yoshida, M., Kaneko, K. and Nakano, K. (1977) Chloritization of paddy soils caused by acidic irrigation-water. *Journal of Science of Soil Manure Japan*, **48**, 193–200.
- Jiang, M.Y., Yang, D.Y. and Hseung, Y. (1982) Soil colloid researches, VIII. Mineralogical composition of the colloids of five important soils of China. *Acta Pedologica Sinica*, **19**, 62–70.
- Lanson, B. (1997) Decomposition of experimental X-ray diffraction patterns (profile fitting): A convenient way to study clay minerals. *Clays and Clay Minerals*, **40**, 40–52.
- Loeppert, R.L. and Inskeep, W.P. (1996) Iron. Pp. 639–664 in: *Methods of Soil Analysis* (A. Klute, editor). SSSA Book Series, 5, Soil Science Society of America, Madison Wisconsin.
- Moore, D.E. and Reynolds, R.C. (1997) *X-ray Diffraction and the Identification of Clay Minerals*, 2nd edition, Oxford University Press, New York, 378 pp.
- Pharande, A., Hillier, S., Cotter-Howells, J. and Roe, M. (2000) Possible effects of irrigation on the clay mineralogy of Vertisols from Maharashtra, India. *Abstracts of the 37th Annual Meeting of the Clay Minerals Society, Loyola University, Chicago*.
- Prikhod'ko, V.E., Dronova, T.Y. and Sokolova, T.A. (2000) Clay minerals in soils of the Solonchic complex and their alteration upon irrigation in the northern part of the Caspian Lowland. *Eurasian Soil Science*, **33**, 1295–1302.
- Reynolds, R.C., Jr. (1985) *NEWMOD a computer program for the calculation of one dimensional diffraction patterns of mixed layer clays*. R.C. Reynolds, 8 Brook Rd, Hanover, New Hampshire, USA
- Shanmei, W., Shuau, Y. and Ruicai, H. (1988) Clay minerals of Vertisols and vertic Fluvents in relation to soil classification in China. *Journal of Nanjing Agricultural University*, **11**, 60–66.
- Velde, B. (2001) Clay minerals in the agricultural surface soils in the Central United States. *Clay Minerals*, **39**, 277–294.
- Velde, B. (1985) *Clay minerals: A Physico-chemical Explanation of their Occurrence*. Elsevier, Amsterdam, 427 pp.
- Zhang-Ming, K. and He-Zhen, X. (1998) Clay mineralogy of major soils in mountain and hilly areas in Zhejiang Province, China. *Acta Agriculturae Zhejiangensis*, **10**, 201–205.

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