



Potassium supply capacity response to K-bearing mineral changes in Chinese purple paddy soil chronosequences

Guang-Zhong Han¹ · Lai-Ming Huang^{2,3} · Xian-Gan Tang⁴

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Abstract

Purpose Purple paddy soils are important for food production. Their potassium (K) supply capacity affects rice yields through its effect on nutrient availability. We hypothesize that changes in soil mineralogy can influence the K supply capacity and the efficiency of K fertilizer. Designing management practices that optimize crop yield while minimizing environmental impacts is a major challenge in agriculture. For this, it is necessary to understand the evolution of, and interaction of, minerals and different chemical forms of K in the soil system.

Materials and methods Taking advantage of the long-term paddy cultivation history in China, two purple paddy soil chronosequences, one in Guang'an, Sichuan Province (P sequence) and the other in Longsheng, Guangxi Autonomous Region (PS sequence) in Southwest China, were investigated.

Results and discussion Depotassification is prevalent in both paddy soil chronosequences, which is consistent with the decrease of illite and K-feldspar in the P sequence and with the decrease of muscovite in the PS sequence. K-bearing primary minerals are the long-term stable source of non-exchangeable K (interlayer K) in both chronosequences. Illite in clay fractions acts as the main sources of non-exchangeable K in the P sequence. In contrast, clay minerals derived from muscovite are the main sources of non-exchangeable K in the PS sequence. Clay mineral authigenesis is an important process in the purple paddy soils rich in K-bearing minerals.

Conclusions The changes in mineralogy of purple paddy soils do not conform to the usual sequence found in the well-drained natural soils. Artificial submergence promotes the conversion of mineral K (lattice-bound K) to non-exchangeable K and enhances the availability of mineral K. The disintegration of K-bearing primary minerals thus controls the K supply capacity in purple paddy soils.

Keywords Chronosequence · Illite · Muscovite · Potassium supply capacity · Purple paddy soils

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✉ Lai-Ming Huang
huanglm@igsnr.ac.cn

¹ Laboratory of Simulation on Soil Process, School of Geography and Resources Science, Neijiang Normal University, Neijiang 641112, Sichuan, China

² Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

³ College of Resource and Environment, University of the Chinese Academy of Sciences, Beijing 100049, China

⁴ National Engineering and Technology Research Center for Red Soil Improvement, Jiangxi Academy of Agricultural Sciences, Nanchang 330200, China

1 Introduction

Purple paddy soils are widely distributed in Southwest China. They cover about 66% of the paddy soils in Sichuan Basin and have a history of rice cultivation of over 1000 years. This popular name is due to their origin from upland purple soils (classified as Rhodi-Calcaric, Rhodi-Dystric, or Rhodi-Eutric Cambisols according to WRB (FAO 2014)), which are characterized by a weak degree of weathering, low content of SOM and high content of mineral nutrients. Some features of the original soils have been retained when they were converted to paddy soils. These soils are important for food production, and their potassium (K) supply capacity affects rice yields through its effect on nutrient availability. These soils in the hilly regions are an example of successively expanding cultivated lands in a sustainable system due to increasing

population pressure. They have been expanding upslope by conversion of upland purple soils, so that soil properties related to soil fertility after conversion show a chronosequence.

The interaction between minerals and different chemical forms of K is complex. Water soluble K (K_{water}) and exchangeable K (K_{ex}) are traditionally believed to form a reserve that is available for uptake by plants in the short term. Under certain circumstances, interlayer K may also significantly contribute to the supply of K for plant uptake (Tabatabai and Hanway 1969). It is well-recognized that crops can extract K from non-exchangeable sources (interlayer K) on a time scale of only a few years (e.g., Gholston and Dale Hoover 1948). The ability of soil minerals to release K varies substantially and depends on the reactivity of soil minerals (Sparks and Huang 1985; Fanning et al. 1989; Huang 2005). The types and contents of K-bearing minerals present in a soil may give some indication of the potential source of K for plants. For paddy soils abundant in K-bearing minerals, depotassiation is strong and the resulting change in clay minerals is comparatively substantial (Chang 1961; Han et al. 2015). Complex interactions complicate the effect of long-term paddy management on K release from K-bearing minerals, and it remains unclear that how this affects the K supply capacity in these paddy soils. We hypothesize that the changing clay mineralogy can influence the K supply capacity and the efficiency of K fertilizer. In order to determine correct management methods, it is necessary to understand the evolution of, and interaction of, minerals and different chemical forms of K. Therefore, we designed this study to characterize two chronosequences, in particular their change in soil minerals related to K supply capacity.

2 Materials and methods

2.1 Sample selection

One purple paddy soil chronosequence (P sequence) was selected in Guang'an prefecture-level city ($30^{\circ} 01' - 30^{\circ} 52' \text{ N}$ and $105^{\circ} 56' - 107^{\circ} 19' \text{ E}$), Sichuan Province, Southwest China. Mean annual temperature is 16°C , and mean annual rainfall is 1200 mm. In common with other purple paddy soils in the area, prior to the 1980s, manure and plant ash were the main fertilizer inputs. Then, organic fertilizers were gradually replaced by chemical fertilizers. For the last 5 years, recommended local fertilization technology was $85 - 105\text{-kg ha}^{-1} \text{ N}$, $80 - 110\text{-kg ha}^{-1} \text{ P}_2\text{O}_5$, and $65 - 115\text{-kg ha}^{-1} \text{ K}_2\text{O}$ in base fertilizer; $35 - 40\text{-kg ha}^{-1} \text{ N}$ and $30 - 50\text{-kg ha}^{-1} \text{ K}_2\text{O}$ at the tillering stage; and $15 - 20\text{-kg ha}^{-1} \text{ N}$ and $30 - 50\text{-kg ha}^{-1} \text{ K}_2\text{O}$ as panicle fertilizer. This survey found that the actual amounts of N fertilizer applied were generally far higher than the above amounts. Local farmers often enhance the N fertilizer ratio of top dressing based on the plant growth to increase the rice

yield. The other chronosequence (PS sequence) was selected in Longsheng ($109^{\circ} 43' - 110^{\circ} 21' \text{ N}$ and $25^{\circ} 29' - 26^{\circ} 12' \text{ E}$), Guangxi Autonomous Region, South China. Mean annual temperature is 18°C , and mean annual rainfall is 1557 mm. Prior to the 1990s, manure and plant ash were the main fertilizer inputs. Then, chemical fertilizers became the main fertilizers. Due to scattered paddy terraces and historical reasons, local farmers generally estimated the area sown to rice based on rice yield and not on actual measurements, so that the per-area fertilizer amount cannot be accurately determined.

The history of paddy cultivation in the older profiles at the bottom of the slopes was determined by reviewing local historical literature from when the nearby villages were settled. For newer profiles at the top of the slope, this information was obtained through questioning local farmers. This type of chronosequence was first constructed by Han and Zhang (2013), who compared pedogenic changes in magnetic properties. Within the P sequence from Guang'an, four representative paddy profiles and three natural profiles were chosen for soil sampling based on the soil landscape and morphological characteristics (Fig. 1). In 2003, plantation forests were established on the upland purple soils (not paddy); soils under these plantations at the same slope position were considered as the original soil, i.e., time zero, with respect to paddy cultivation. Within the PS sequence from Longsheng, three representative paddy profiles and one natural profile were chosen for

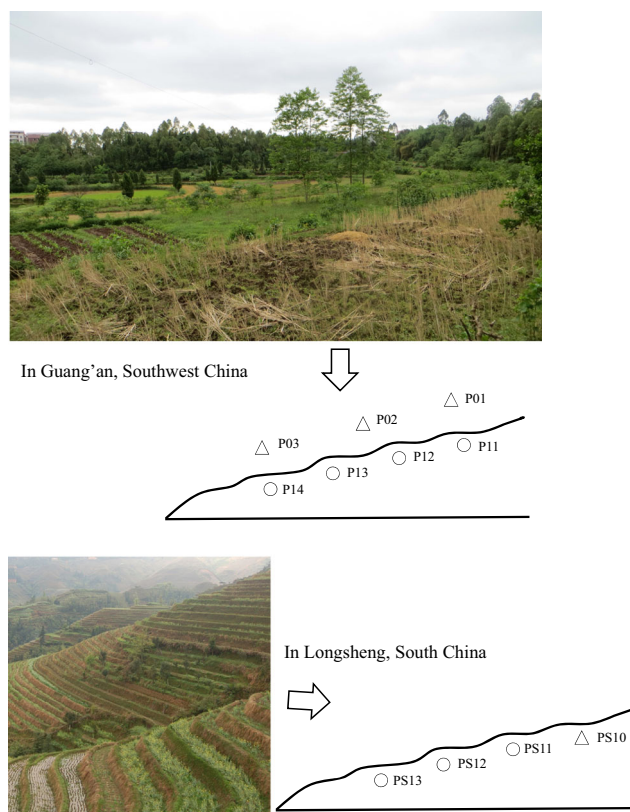


Fig. 1 Sampling design for the purple paddy soil chronosequences

soil sampling. The uncultivated soil profile at the highest slope position was treated as the original soil.

All soil profiles were described and sampled after the rice harvest, when the fields were drained to avoid possible direct influences of fertilization. Descriptions were based on genetic horizons following standard field description guidelines (Schoeneberger et al. 2002) (see Table 1 for descriptions and Fig. 2 for images). The effect of climate was not considered in this study because its influence on pedogenesis decreases during periods of artificial submergence (Gong et al. 1999). However, these chronosequences are also toposequences, which complicate the interpretation of the results (Zhang and Gong 2003). For the P sequence, compared to the non-paddy soils with a similar topographic position, the paddy soils required the construction of terraces. This greatly reduced run off and soil erosion. For that reason the influence of topography on pedogenesis, has been substantially weakened. Sites were on geomorphically stable topographic positions with low slope gradients (< 6°), minimizing the effect of local erosion and deposition. The timing of cultivation plays a more significant role, since it is temporally aligned with the maintenance of paddy soils' moisture regimes. Thus, the role of topography is not separately addressed in this research, and we ascribe any observed differences between paddy and their corresponding non-paddy soils to the effect of paddy cultivation over time. For PS sequence, different elevation and slope are disturbances of time, and the result is still uncertain in some extent. However, their results can provide reference for the P sequence, as we ascribed the differential pedogenesis to the difference in time available for pedogenesis.

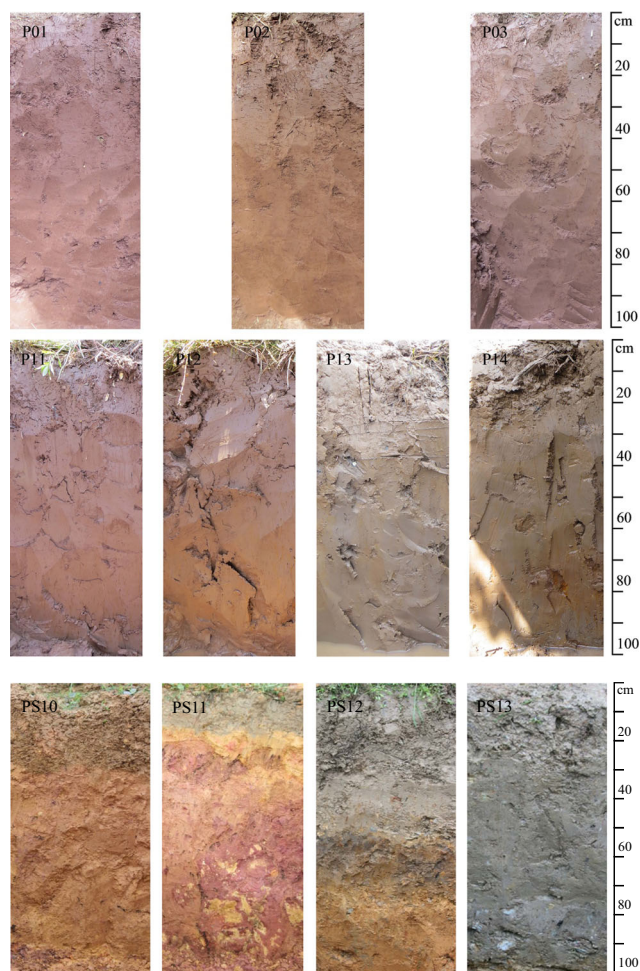


Fig. 2 The studied pedons of the purple paddy soil chronosequences

Table 1 Description of the studied chronosequence profiles

ID	Location	Layer depth (cm)	Landscape position	Land use/vegetation	Paddy cultivation age (a)	Slope (°)	SOC (g/kg)	Clay (g/kg)	TK (g/kg)	TK ^b (g/kg)	TK ^c (g/kg)	CEC (cmol(+)kg ⁻¹)
P01	Guang'an	0–18	Top	Plantation forest ^a	0	<6	9.31	249.0	24.60	32.73	21.90	12.22
P02	Guang'an	0–20	Middle	Plantation forest ^a	0	<6	8.22	261.6	23.27	32.35	20.05	11.78
P03	Guang'an	0–20	Bottom	Plantation forest ^a	0	<6	9.45	225.6	22.34	32.63	19.34	19.44
P11	Guang'an	0–21	Top	Farmland/rice	20	<6	5.27	261.1	22.37	30.76	19.41	21.11
P12	Guang'an	0–18	Middle	Farmland/rice	60–100	<6	9.21	362.0	22.18	31.13	17.10	23.55
P13	Guang'an	0–23	Middle	Farmland/rice	100–300	<6	13.98	366.6	21.59	30.12	16.65	23.44
P14	Guang'an	0–20	Bottom	Farmland/rice	300	<6	15.70	394.8	22.32	30.18	17.19	16.89
PS10	Longsheng		Top	Waste upland	0	23	9.35	131.7	32.52	13.71	35.37	10.55
PS11	Longsheng		Top	Farmland/rice	30	23	13.02	130.2	30.84	15.51	33.14	11.70
PS12	Longsheng		Middle	Farmland/rice	100–300	36	23.05	141.7	22.70	17.47	23.65	12.78
PS13	Longsheng		Bottom	Farmland/rice	300	28	25.43	153.5	22.82	19.44	23.38	12.81

^a The plantation forests were converted from dry farmlands in 2003; most common tree species are *Platyclusus orientalis* and *Eucalyptus grandis*

^b Total K of clay minerals

^c Total K of silt minerals

2.2 Basic soil property analyses

Soil samples were dried at room temperature and gently crushed with a wooden mortar and pestle before being passed through a 2-mm nylon sieve. The Walkley-Black wet oxidation method (Nelson and Sommers 1982) was used to determine the soil organic carbon (SOC) content of samples passed through a 0.18-mm nylon sieve. The pipette method was used to determine the particle size distribution, and the soil pH was determined in a 1:2.5 soil:water ratio. Cation exchange capacity (CEC) was determined by saturating 5-g soil with 1-mol L⁻¹ ammonium acetate at pH 7 and replacing ammonium by subsequent washing with ethanol according to Zhang and Gong (2012). K_{water} was extracted in a 1:10 soil:water ratio. K_{ex} and 2-mol L⁻¹ HCl-extractable K (K_{HCl}, non-exchangeable K) were extracted following the procedures of Egnér et al. (1960). The method for K_{ex} involves extraction in 0.1-mol L⁻¹ ammonium lactate + 0.4-mol L⁻¹ acetic acid (pH 3.75) at room temperature (20–25 °C). For K_{HCl}, the soil is extracted by 2-mol L⁻¹ HCl in a boiling water-bath (100 °C) for 2 h. Total K was extracted with the acid digestion (HF, HClO₄, and HCl) (Zhang and Gong 2012). Extracts of K were analyzed by flame atomic emission spectrophotometry (flame-AES).

2.3 Soil mineral analysis

Soil samples were oxidized with H₂O₂ to remove the SOM and dispersed ultrasonically with a 0.5-mol L⁻¹ NaOH solution. The sand (> 50 μm) fraction was separated by wet sieving. The clay (< 2 μm) and silt (50–2 μm) fractions were separated by the pipette method (Lanson and Besson 1992; Velde and Peck 2002). X-ray diffraction (XRD) analysis was performed on both the silt and clay fractions using a D8 ADVANCE X-ray diffractometer (Bruker AXS, Madison, WI). Silt samples were prepared by filling holders for step scanning from 3° to 60°. The diffractometer was operated at 40 kV and 40 mA using Cu-Kα Ni-filtered X-rays. Clay samples were prepared by wiping slides for step scanning. Duplicate 50-mg subsamples were taken from each clay sample. One group of samples, whose Fe_d was removed by dithionite-citrate-bicarbonate, was saturated with a 1-mol L⁻¹ MgCl₂ solution and then saturated with a 1:9 glycerol:water solution. The other group of samples was saturated with a 1-mol L⁻¹ KCl solution. The Mg²⁺- and K⁺-saturated clays were analyzed by XRD. The K⁺-treated slides were subsequently heated to 300 and 550 °C and rescanned (Moore and Reynolds 1997). Each slide was scanned between 3° and 30° (2θ). The Jade software (Materials Data Inc., Livermore, CA) was used for calibration and analysis by comparing the given X-ray pattern with known minerals to identify the mineral composition. The relative amounts of the major silicate clay families were based on the differences in

diffractogram patterns from the Mg²⁺-saturated samples. Minerals were identified based on their diagnostic XRD spacings (Brown and Brindley 1980; Whittig and Allardice 1986).

3 Results

3.1 Evolution of basic soil properties

Figure 2 shows the soil morphology within each chronosequence. In contrast to their corresponding original soil profiles, the paddy soil profiles generally showed complicated patterns, in which pedogenic horizons were more evident with depth. The soil horizons in the paddy soils mainly consisted of an anthrostatic epipedon, including (in order of increasing depth) the cultivated horizon (Ap1, surface layer), the plow pan (Ap2), and a hydragic horizon (Br). The Ap1 horizons were characterized by abundant rice roots, a lower value, and chroma than underlying horizons and loose structure (bulk density range was 0.85–1.28 g cm⁻³). The Ap2 horizons were characterized by a compact and angular blocky structure (bulk density range was 1.01–1.44 g cm⁻³). The Br horizons were characterized by a distinctive pattern of redoximorphic features, including yellowish brown or orange cutans, mottles, and concretions. The morphological differences in the Br horizons between the younger pedons (P11 and PS11) and the older ones (P14 and PS13) in each chronosequence could be clearly identified in the field (Fig. 2). Observable differences mainly included soil color, structure, and redoximorphic features (i.e., cutans, mottles, concretions, or nodules). For example, with increasing length of paddy cultivation, the hue of soil colors gradually changed to yellow (munsell hues) and the chroma decreased.

Basic soil properties showed increasingly observable changes with the increasing length of cultivation in the purple paddy soils (Table 1). SOC in the cultivation horizon (Ap1) of the P and PS chronosequences increased from 5.27 and 9.35 g kg⁻¹, respectively, in the youngest paddy soils to 15.70 and 25.43 g kg⁻¹, respectively, in the oldest paddy soils. The average SOC of the P and PS paddy soils (11.04 and 20.5 g kg⁻¹, respectively) was greater than the average of their corresponding original soils (8.99 and 9.35 g kg⁻¹, respectively). Clay contents of the P and PS chronosequences increased from 261.1 and 130.2 g kg⁻¹, respectively, in the youngest paddy soils to 394.8 and 153.5 g kg⁻¹, respectively, in the oldest paddy soils. The average clay content of the P and PS paddy soils (346.1 and 141.8 g kg⁻¹, respectively) was greater than the average value of their corresponding original soils (245.4 and 131.7 g kg⁻¹, respectively). Our results demonstrated that SOC and clay accumulation occurred under flooded cultivation in the purple paddy soils, and the degree of enrichment was affected by the time span of cultivation history. The average CEC value of the P and PS paddy soils (21.25 and

12.43 cmol(+) kg⁻¹, respectively) was much higher than the corresponding original soils (14.48 and 10.55 cmol(+) kg⁻¹, respectively). CEC values of the P paddy soils increased initially in the younger paddy soil (0–100 years) and then decreased in the oldest paddy soil (> 100 years) (Table 1). This indicated that the initial paddy cultivation (0–100 years) favored the enhancement of CEC value in the purple paddy soils from Guang'an, but longer paddy cultivation (> 100 years) showed the opposite effect. In contrast, CEC values of the PS paddy soils increased from 11.70 cmol kg⁻¹ in the youngest paddy soil to 12.81 cmol kg⁻¹ in the oldest paddy soil, which indicated that paddy cultivation (0–300 years) favored the enhancement of CEC values in the purple paddy soils from Longsheng.

3.2 Temporal changes in K contents with paddy management

The average total K concentration of the P and PS paddy soils (22.12 and 25.45 g kg⁻¹, respectively) was much higher than the average total K concentration of Chinese paddy soils (17.08 g kg⁻¹, $n = 1527$, data from the Second National Soil Survey of China) (Soil Survey Office of China 1995), but the concentration was lower than that of their corresponding original soils (23.40 and 32.52 g kg⁻¹, respectively). This indicated that depotassification occurred during long-term paddy cultivation when the original soils were rich in K-bearing minerals.

The average K_{water} and K_{ex} of the studied paddy soils (61.5 and 44.4 mg kg⁻¹, respectively, for P sequence; 52.3 and 30.1 mg kg⁻¹, respectively, for PS sequence) were much lower than that of their corresponding original soils (106.5 and 56.7, respectively, for P sequence and 98.6 and 53.8 mg kg⁻¹, respectively, for PS sequence). The K_{water} and K_{ex} values of the P and PS paddy soils decreased simultaneously in the cultivated horizon during the initial cultivation stage and were reduced to relatively small values within 20–30 years of rice cultivation (Fig. 3). Thereafter, no further decreases were observed with increasing paddy cultivation age. In contrast, the average K_{HCl} of the P and PS paddy soils (675.6 and 680.3 mg kg⁻¹, respectively) was greater than the average value of their corresponding original soils (650.6 and 636.5 mg kg⁻¹, respectively). Specifically, K_{HCl} was higher in the youngest paddy soils than those in the oldest paddy soils. This indicated that paddy cultivation in the purple paddy soils did not enhance the available K concentrations but led to the increase of K_{HCl} , especially in the early stage of paddy cultivation.

The K supplying potential of the studied purple paddy soils is middle-high (non-exchangeable K range between 500 and 750 mg kg⁻¹) based on the criteria described by Xie et al. (1983). In contrast, their available K supplying ability is medium (available K range between 50 and 100 mg kg⁻¹) based on the criteria described by Soil Survey Office of China (1998). Overall, the total amount of K_{water} , K_{ex} , and K_{HCl}

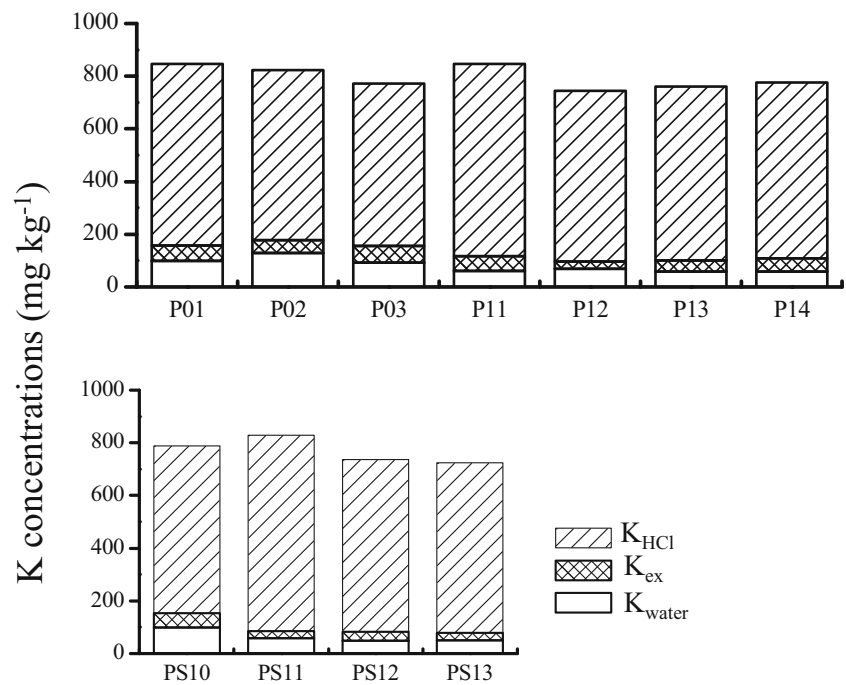
decreases slightly and their proportion change significantly under long-term paddy cultivation.

3.3 Response of soil minerals to paddy cultivation time

Mineralogical assemblages in the clay-size fractions and the differences among the cultivated horizon (Ap1) of paddy soils and the eluvial horizon (A) of their original uncultivated soils are shown in Figs. 4 and 5. The XRD patterns showed reflections at 1.0, 0.5, and 0.33 nm before and after the various chemical and heat treatments, which are indicative of illite (Fig. 4) (P and PS sequences). Kaolinite, which is characterized by 0.7- and 0.35-nm peaks in Mg²⁺-saturated and K⁺-saturated specimens, was lost when K⁺-saturated clays were heated at 550 °C (P and PS sequences). The XRD patterns indicated that smectite (1.8-nm peak with Mg²⁺-glycerol solvation, with a tailing toward the 1.0-nm peak in K⁺-saturated clays) (P sequence) and quartz (0.43- and 0.33-nm peaks after the various chemical and heat treatments) were present (P and PS sequence). There was a 1.42-nm peak in Mg²⁺-saturated specimens, with a tailing toward the 1.0-nm peak when K⁺-saturated clays were heated at 300 °C, indicating the presence of 1.4-nm interlayer mineral (PS sequences). Bayerite shows a narrow peak at 0.48 nm in Mg²⁺-saturated specimens; this peak was also present when K⁺-saturated clays were heated at 300 °C (PS sequence). For PS older paddy soils, there was an extra peak at 0.34 nm in Mg²⁺-saturated and K⁺-saturated specimens, which was lost when K⁺-saturated clays were heated at 550 °C. Considering that the wider component was at 0.7 nm, this indicates the presence of halloysite or possibly low crystallite kaolinite as interlayered species. Similarly, one more wide peak, centered at 1.2 nm from the Mg²⁺-saturated, and K⁺-saturated clays, suggests one of the components should be expanded illite or illite-smectite interlayer. The peak tailing toward the low-angle at positions between 1.0 and 1.4 nm in K⁺-saturated clays, or when K⁺-saturated clays were heated at 300 °C, suggests that the other component is degraded chlorite or secondary chlorite (PS sequence). The XRD primary basal peak reflections for the clay fractions of the P sequence soils were higher for smectite than for illite, chlorite, kaolinite, and quartz. Similarly, kaolinite was higher than 1.4-nm interlayer minerals, secondary chlorite, illite, halloysite, and quartz for the clay fractions of the PS sequence soils.

Clay mineral changes for PS sequence were reported previously by Han et al. (2015). The average percentage content of secondary chlorite (which dominated the total peak area of clay fractions) (11%), bayerite (21%), and halloysite (3%) was greater than the original soils (3, 8, and < 1%, respectively). Considering the increase of clay content, this result suggested that secondary chlorite, bayerite, and halloysite were accumulated through flooded cultivation in the PS sequence paddy soils. In contrast, the average content of kaolinite (58%) in

Fig. 3 K_{water} , K_{ex} , and K_{HCl} changes in purple paddy soil chronosequences



Ap1 paddy soils was less than in original soils (76%). This result indicated that the relative content of kaolinite decreased in the PS sequence paddy soils due to long-term paddy cultivation. For P sequence, the average relative content of smectite (39%) in Ap1 of paddy soils was greater than in original soils (27%). Similarly, this indicated that smectite was accumulated through flooded cultivation in the P sequence paddy soils. Smectite increased gradually within 100 years of rice cultivation, and it had sharper peaks in the paddy soils than in the original soils (Figs. 4 and 5). Then, no further increase in smectite was observed, even decreasing with increasing paddy cultivation age (> 100 years) (particularly in P14). In contrast, the average relative content of illite (16%) and chlorite (19%) were less than the original soils (19 and 22%, respectively). Considering that the average increase of clay content is faster than the decrease of relative illite and chlorite content, the total illite and chlorite in clay fractions seem to be increased. For P sequence, the CEC changes mainly coincide with smectite changes instead of SOM. In contrast, the CEC changes mainly coincide with both SOM and clay minerals in the PS sequence. This indicates that the effects of paddy cultivation on CEC changes were complex.

Mineralogical assemblages in the silt fractions are shown in Figs. 6 and 7. For the P sequence, the XRD patterns showed reflections at 1.0, 0.5, and 0.33 nm, which are indicative of the amount of illite (Fig. 6). Similarly, chlorite (characterized by 1.4-, 0.7-, 0.47-, 0.35-, and 0.256-nm peaks), quartz (with 0.43-, 0.33-, 0.198-, and 0.181-nm peaks), plagioclase (with 0.40 and 0.31 nm peaks), and K-feldspar (with 0.32-, 0.216-, and 0.181-nm peaks) were present. Illite and chlorite are preserved in silt fractions and they may directly originate from

their parent rocks, which are mainly Mesozoic Jurassic, and Cretaceous purple sandstones and shales. The XRD primary basal peak reflections for the silt fractions of the P sequence soils were higher for quartz than for illite, chlorite, plagioclase, and K-feldspar. The average percentage content of quartz (49%) and plagioclase (28%) in Ap1 of paddy soils was greater than in original soils (44 and 21%, respectively). This result indicates that the relative content of quartz and plagioclase increased via flooded cultivation in silt fractions. In contrast, the average contents of illite (12%) and K-feldspar (4%) were less than in the original soils (19 and 9%, respectively). Considering the decrease of silt content, this result suggested that illite and K-feldspar could not be preserved in silt minerals due to long-term paddy cultivation. For PS sequence, the XRD patterns showed reflections at 1.0, 0.5, 0.33, 0.30, 0.286, and 0.256 nm, which are indicative of the amount of muscovite (Fig. 6). Similarly, kaolinite (characterized by 0.7-, 0.47-, 0.35-, and 0.256-nm peaks), quartz (with 0.43-, 0.33-, 0.198-, and 0.181-nm peaks), plagioclase (with 0.40- and 0.31-nm peaks), and bayerite (with 0.48-nm peaks) were present in the studied soils. The XRD primary basal peak reflections for the silt fractions of PS sequence were higher for quartz than for muscovite, kaolinite, plagioclase, and bayerite. The average content of quartz (79%) in Ap1 of paddy soils was greater than in original soils (65%). This result indicated that the relative content of quartz in silt fractions increased through flooded cultivation. In contrast, the average content of muscovite (16%) was less than in the original soils (26%). Similarly, this result suggested that muscovite could not be preserved in silt minerals due to long-term paddy cultivation. It should be noted that the degree of crystallinity of muscovite

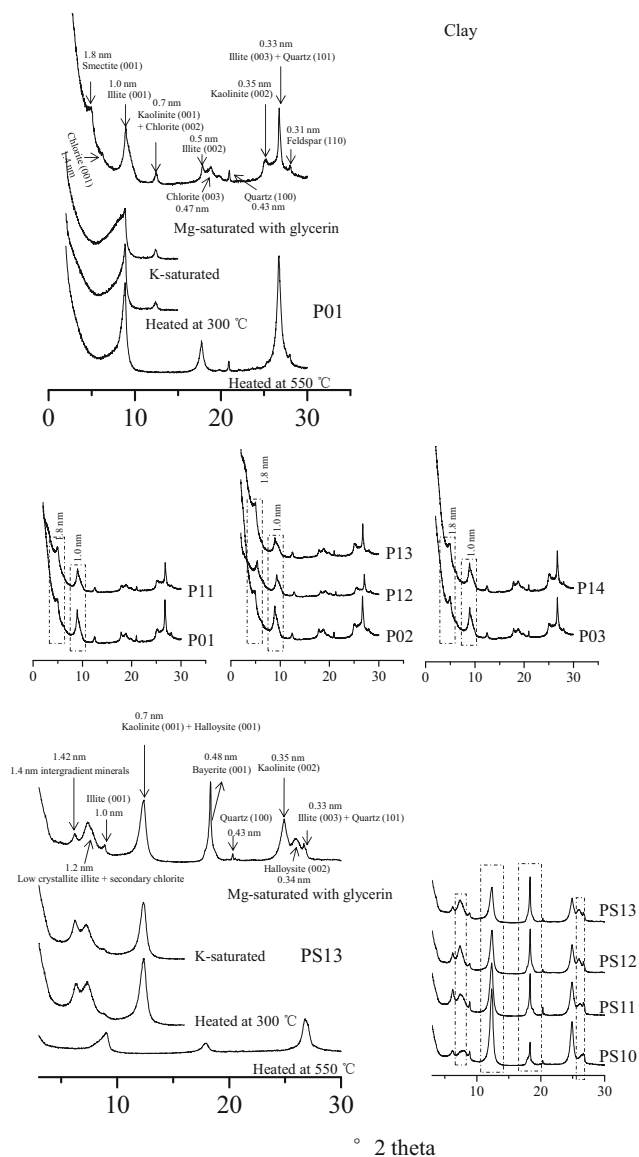


Fig. 4 The XRD characteristics of clay minerals in purple paddy soil chronosequences

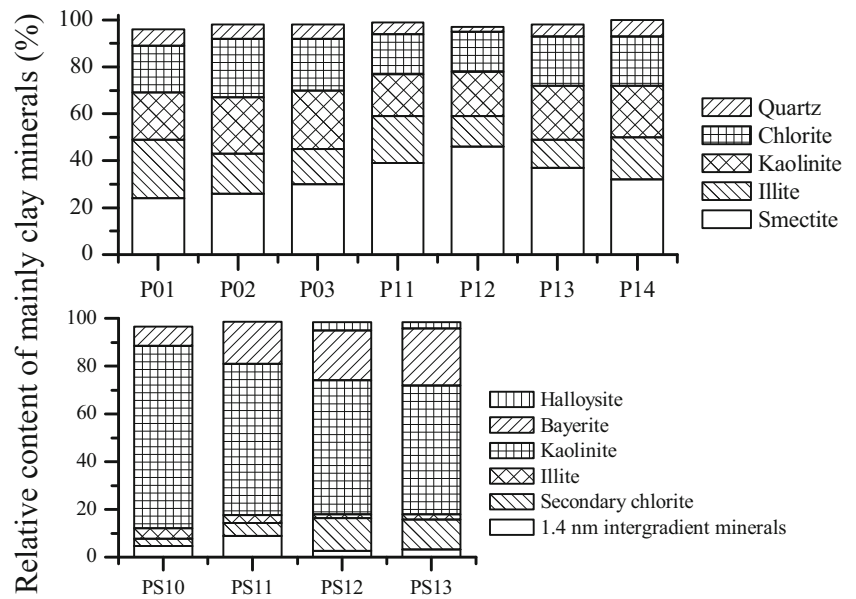
(silt fractions) and illite (silt and clay fractions) in the paddy soils was generally lower than in the original soils, as indicated by the shorter and broader peaks at 1.0 nm in the paddy soils of both sequences (Figs. 4 and 6).

4 Discussion

SOC accumulated with cultivation age in the studied paddy soil chronosequences. The accumulation of SOC is common in paddy soils, and this phenomenon is elaborated in published literature (Li 1992; Gong et al. 1999; Huang et al. 2014). K release from natural sources is prevalent in both the P and PS sequences (Table 1), which was consistent with the decrease of illite and K-feldspar in the P sequence and with

the decrease of muscovite in the PS sequences (Fig. 7). In general, the pool of exchangeable K in soils corresponds to crop demand during only a few years of intense cropping and the release of K from weathering of K-feldspar and phyllosilicates is the long-term natural source of K (e.g., Bertsch and Thomas 1985; Malavolta 1985; McLean and Watson 1985). The release of fixed or structural K from phyllosilicates is the dominant mechanism of K release in moderately weathered agricultural soils (Sparks and Huang 1985). The reaction may proceed via a slow dissolution of the entire mineral structure and via selective exchange of interlayer K (Huang 2005). The latter occurs when the K concentration in the soil solution is inferior to a mineral-specific critical value (Scott and Smith 1966; Fanning et al. 1989). In paddy soils, alternating reduction and oxidation cycles occur corresponding to wetting and drying periods. In wetting periods, the exchange reaction of Fe^{2+} and Mn^{2+} for exchangeable K might enhance the K concentrations of soil solutions (Islam and Ullah 1973; Huang et al. 1985; Tandon and Sekhon 1988). Because of the deep groundwater table in our observations, one characteristic of the paddy soil formation process in the hilly region was related to strong mechanical eluviation and/or lateral leaching, the latter of which was associated with large nutrient loss. In this condition, the K_{water} and K_{ex} in the purple paddy soils were generally low (Fig. 3). Under the conditions of artificial submergence and soil K depletion, the K in the interlayer of muscovite and illite can also be exchanged by hydrated cations, although K was less readily removed from illite than from biotite and phlogopite (Rausell-Colom et al. 1965; Scott and Smith 1966; Scott 1968). The interlayer K release also helps explain the generally lower degree of crystallinity of muscovite and illite in the paddy soils than in the original soils. The decrease of K-feldspar in silt fractions indicated that K could be released from K-feldspar under paddy cultivations. Xie et al. (2016) reported similar results in which the weather of illite and K-feldspar can be accelerated under long-term K deficient input through a 22-year continuous study. They also supported that it is difficult to prevent the weathering of K-bearing minerals, even excessively applied K fertilizer in purple paddy soils. However, other studies reported that K-feldspar is likely to persist in the soil, while K is lost from illitic components in the clay (Andrist-Rangel et al. 2013; Simonsson et al. 2016). Thus, the release of K from K-feldspar is still controversial when the soil contains far more reactive minerals than K-feldspar, so that further research is required to clarify the activity of K-feldspar under paddy submergence. During drying periods, the oxidation of Fe^{2+} to Fe^{3+} is the most important process for determining specific soil profile morphology. The oxidation process also favors to the release of interlayer K (Farmer and Wilson 1970; Mengel and Kirkby 1980). Therefore, it appears that depotassification can be accelerated by strong mechanical eluviations, lateral leaching, plant

Fig. 5 Relative content of main clay minerals in purple paddy chronosequences



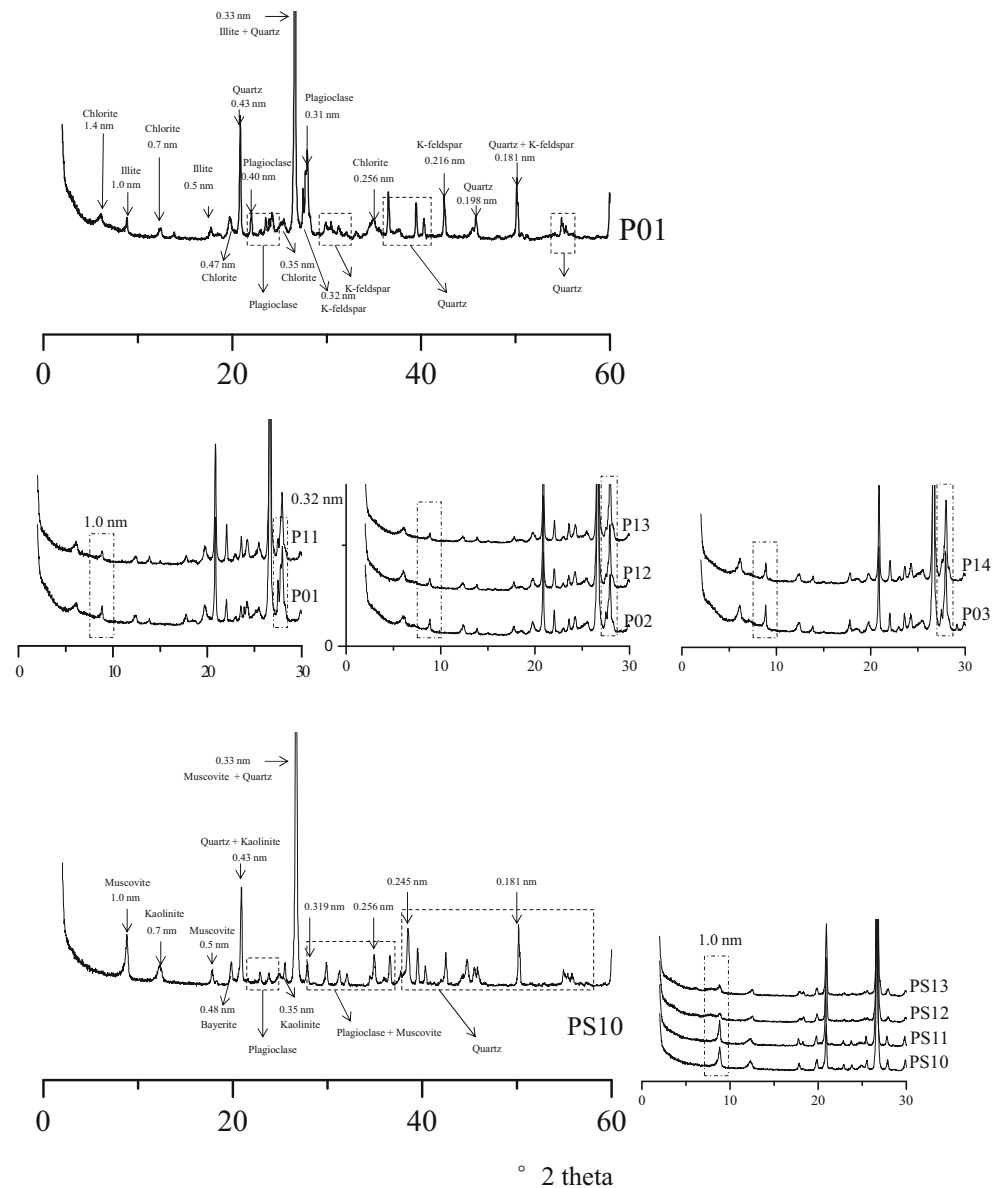
uptake, and erosion and sedimentation during paddy submergence in the hilly region.

It is important to note that the mineral changes did not follow the usual sequence found in the well-drained natural soils. The rate of depotassification was high, and depotassification products were rapidly produced during the early stage of paddy cultivation. For the P sequence, the increase of clay fractions is consistent with the disintegration of K-bearing primary minerals (e.g., illite and K-feldspar). It is possible that smectite was a product of the depotassification of illite as well as of the removal of magnesium from chlorite. The newly formed clay fraction from primary minerals may have prevented some clay loss of illite and chlorite and even increased their total contents in clay fractions. Similarly, for the PS sequence, it is possible that expanded illite (or illite-smectite interlayer) or secondary chlorite might be an intermediate product of the depotassification of muscovite. Halloysite might be derived from the surface leaching of muscovite by two possible mechanisms: dissolution-precipitation or local dissolution-rearrangement of residue structure (Lu et al. 2016). In contrast, kaolinite is generally a very stable mineral, especially under moist conditions. Their decreases might be caused by leaching and/or other clay fraction increases. Bayerite might be an end product of silicate minerals under the alternating reduction and oxidation cycles.

Various processes contribute to the loss of clay in paddy soils, including eluviation, reduction and dissolution chelation and ferrolysis due to anthropogenic flooding (Gong et al. 1999). However, Han et al. (2015) reported that paddy soils had higher clay content than their corresponding predecessor in the PS sequence. They attributed the increase to clay authigenesis during the process of depotassification of the primary minerals, although there is a lack of silt mineral evidence. Similar result was also found in the P sequence. Based

on the silt mineral changes, we propose that clay authigenesis is an important and up till now neglected process in the paddy soils abundant in K-bearing minerals. The disintegration of K-bearing primary minerals could support the generation of new clay. In contrast, existing clay also could be destroyed by various processes due to anthropogenic flooding. These results suggest that the changes in clay mineral content were mainly caused by the equilibrium between the formation and loss of clay minerals. If the newly formed clay minerals were dominant, they became enhanced; otherwise, they declined. This explains why smectite increased initially and then decreased with increasing paddy cultivation age. Considering that paddy cultivation has lasted for only several hundred years in this region, the rate of depotassication and the generation of clay fractions is expected to be much faster than that in natural soils. From the Table 1, it seems that there is more obvious increase of clay in the P sequence but more obvious decrease of total K in the PS sequence. Direct empirical evidence for the formation and transformation of clay minerals is still sparse. Certainly a better understanding is required of the transformation of minerals as opposed to the K release under alternating reduction and oxidation. The disintegration of K-bearing primary minerals should be more complex than anything found in statistical results and might control the K supply capacity in purple paddy soils. 2:1 phyllosilicate clay minerals were often the main sources of the non-exchangeable K in the soils. This may be explained by the fact that compensated K⁺ are generally in the interlayer of 2:1 phyllosilicates and can be more easily extracted by HCl. Thus, illite in clay fractions are likely the main sources of non-exchangeable K in the P sequence. In contrast, the clay minerals derived from muscovite are likely the main sources of non-exchangeable K in the PS sequence. Huang et al. (1985) reported that the amount of non-exchangeable K absorbed by early rice and late

Fig. 6 The XRD characteristics of silt minerals in purple paddy soil chronosequences

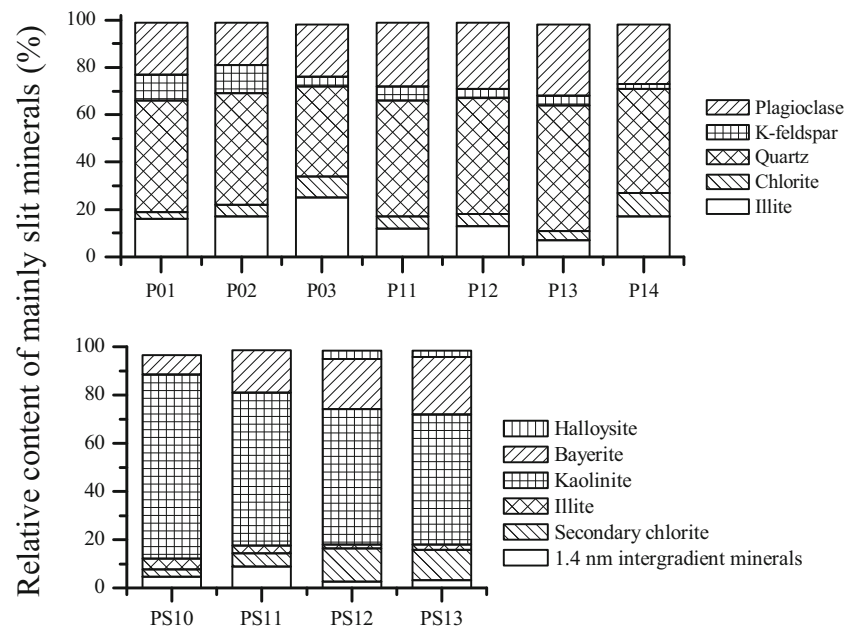


rice are about 28–45% and 33–56% of the total K absorbed by rice. Liao et al. (1983) supported that plants have higher capacity of K uptake in the late stages of rice growth and about 35–84% of K is supplied by non-exchangeable K. These results indicate that non-exchangeable K plays a very important role in rice plant nutrition even if there might be a complex transformation before it was absorbed by rice plant. Artificial submergence should promote the conversion of mineral K (lattice-bound K) to non-exchangeable K, which enhanced the availability of mineral K. The comparison is based on Ap1 horizons, so that of subsurface horizons may differ from these results, which is not involved in this study.

The use of K fertilizer has a long history in China. Prior to the 1980s, manure and plant ash were the main K fertilizer inputs in purple paddy soils according to local and historical sources. It has become evident that negative K balances (harvest > plant

ash + manure) may be a concern in the purple paddy soils which commonly are used for two crops a year due to pressure for food production. In this study, older paddy soils (P13, P14, PS12, and PS13) at a cultivation age of more than 100 years still had higher non-exchangeable K contents and a large amount of the K-bearing minerals. This implies that the K from soil minerals chronically compensate for nutrient removals and losses in purple paddy soils. Therefore, non-exchangeable K and K-bearing primary minerals could be a stable source of K for rice plant in the purple paddy soils. The size of non-exchangeable K is more than 1000 kg ha^{-1} at 0–20-cm depths alone and the fact should not be ignored in modern agricultural management. Unfortunately, because of the strong leaching in paddy terraces in the hilly region, large nutrient loss is unavoidable, especially for water soluble and exchangeable nutrients. This can be confirmed by the lower contents of K_{water} and K_{ex} and the loss of

Fig. 7 Relative content of main silt minerals in purple paddy chronosequences



total K in the purple paddy soils. Some tillage measures may be used to prevent the loss of K as well as other nutrients. One option is to reduce the flood depth and thus decrease leaching. Considering the lower contents of available K, management-induced K release from K-bearing minerals might not fully compensate K uptake by plants under condition of modern intensive agriculture or K loss by leaching. Suitable K fertilizer is thus required to ensure that the required K is able to quickly be absorbed by plants. The other option is to reduce the concentration of K in soil solution. Consequently, K fertilizer applications should be split, with suitable amounts applied several times during different stages of paddy growth. However, in the past 10 years, chemical fertilizers were the main fertilizers on purple paddy soils. The scarcity of organic fertilizers and large chemical fertilizer applications may also have an impact on the depotassification of K-bearing minerals in paddy soils, but the degree of these impacts is still unclear. It was difficult to determine the availability of K newly released from soil minerals. More work is needed to yield a precise understanding of the kinetics of K release and how its measurement might be used to predict the availability of K in the purple paddy soils.

5 Conclusions

Depotassification is prevalent in both paddy soil chronosequences, which is consistent with the decrease of illite and K-feldspar in the P sequence and with the decrease of muscovite in the PS sequence. Artificial submergence promotes the conversion of mineral K to non-exchangeable K and enhances the availability of mineral K. The disintegration of K-bearing primary minerals thus controls the K supply capacity in purple paddy soils and K-bearing primary minerals are the

long-term stable source of non-exchangeable K. Illite in clay fractions act as the main sources of non-exchangeable K in the P sequence. In contrast, clay minerals derived from muscovite are the main sources of non-exchangeable K in the PS sequence. The changes in mineralogy of purple paddy soils do not conform to the usual sequence found in the well-drained natural soils, and clay mineral authigenesis is an important process in the purple paddy soils rich in K-bearing minerals. Some tillage measures may be used to prevent the loss of K as well as other nutrients.

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