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Evolution and significance of soil magnetism of basalt-derived chronosequence soils in tropical southern China

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ABSTRACT

Soil samples were collected from eight basalt-derived chronosequence soils with the ages of 0.01, 0.58, 0.92, 1.33, 2.04, 3.04, 3.76 and 6.12 Ma respectively from Leizhou Peninsula and northern Hainan Island of tropical southern China. Magnetic parameters of magnetic susceptibility (MS), percentage of frequency-dependent magnetic susceptibility (FDS%), anhysteretic remanent magnetization (ARM), saturation isothermal remanent magnetization (SIRM), soft and hard isothermal remanent magnetization (IRM_s and IRM_h) of the collected samples were measured to study the evolution and the significance of the magnetism with soil age. The results show that the magnetic parameters changed fast from Primosols to Ferrosols (0.01 - 0.92 Ma) but slowly at Ferralosols stage (1.33 Ma~), it suggests a stable phase occurred for soil magnetism at Ferralosols, the existence of this phase could be supported by the little changes in the contents of clay, Fe_t and Fe_d. Obvious differences existed in the values of magnetic parameters between Ferralosols and other soil types (Primosols and Ferrosols), FDS%: Ferralosols > 10%, Primosols and Ferrosols < 10%; ARM, Ferralosols < 7000 × 10^{-8} $SIm^3 \cdot kg^{-1}$, Primosols and Ferrosols > 8000 × 10^{-8} $SIm^3 \cdot kg^{-1}$, thus, it is possible to differentiate Ferralosols from other soil types in tropical region by using magnetic indices.

Keywords: Magnetic Parameters; Basalt-Derived Chronosequence Soil; Iron Oxides; Tropical Southern China

1. INTRODUCTION

Soil chronosequences, given that the other soil-forming factors are similar, are often used to demonstrate the relative degree of soil development under varying duration of soil formation [1]. Studies have proved that different soil types may be formed from the same parent material in a region with the continuation of the weathering process, for examples, the systematical studies of soil development in Hawaii by Kennedy *et al.* [2], Chadwick *et al.* [3,4], Kurtz *et al.* [5] and Derry *et al.* [6] and in northern Hainan Island by Huang and Gong [7], Huang *et al.* [8,9] and Zhang *et al.* [10].

Magnetic measurement is a simple, quick and non-destructive technique for characterizing soils and sediments. Soil taxonomy has got remarkable achievements in the world, for examples, USDA-NRCS, 2010; IUSS-ISRIC-FAO, 2007; CRGCST, 2001. Although some researchers attempted to use magnetic susceptibility as a tool for soil classification to separate Oxisols, Ultisols and Entisols at a low taxonomic level [11-14], no quantitative diagnostic information of magnetism available in current soil taxonomy.

As Huang *et al.* [9] disclosed that basalt-derived soils in the tropical Leizhou Peninsula and Hainan Island of south China can develop gradually from Primosols into ferralic-horizon characterized Ferralosols [15], so here we collected chronosequence samples of basalt-derived soils in this region in 2007 to explore the possible significance of magnetic parameters in identifying soil types by studying the evolution of soil magnetism.

2. MATERIALS AND METHODS

2.1. Chronosequence Red Soil Samples

The studied soils are from located in the tropical Leizhou Peninsula and northern Hainan island of southern China, where with a present tropical monsoon climate of a mean annual rainfall of 1400 - 1800 mm and a mean temperature of 23˚C - 24˚C. The change of climate during the Quaternary is negligible, which remains in a warm subtropical climate and no more than 2.5˚C change of temperature [16]. The studied eight basalt-derived chronosequence soils (see **Table 1**) were located at uplands Soils, all sampled sites have udic soil moisture regimes and hyperthermic soil temperature regimes and under secondary shrub or forest vegetation. The ages of the parent basalt-rocks of the eight soil profiles were dated by using K-Ar methods [17-19], which could be taken roughly as the proxies of the time-spans of soil formation due to the general lack of well-dated soil real age [20].

Fe_d/Fe_t usually can be used to validate the chronosequence reliability because it is a good indicator of the wearthering degree of soils [10,21-25], The increase of Fe_d/Fe_t in B horizons with soil age proved the reliability of the studied chronosequence soils (**Figure 1**).

2.2. Measurements of Soil Samples

Soil magnetic parameters of all horizons of the sampled profiles were measured in the State Key Lab of Estuary and Coast of East China Normal University. Magnetic susceptibility (MS) was measured at low frequency (0.47 kHz, MS_{lf}) and high frequency (4.7 kHz, MS_{hf}) using a Bartington MS2 meter with dual frequency sensor. Frequency-dependent magnetic susceptibility (FDS%) was calculated as: FDS (%) = 100 × $[(MS_{lf} - MS_{hf})/MS_{lf}]$. Anhysteretic remanent magnetization (ARM) was measured in the Molspin magnetometer after magnetization with a Molspin AF demagnetizer. The peak AF field used was 100 mT and the DC bias was 0.04 mT. Isothermal remanent magnetization (IRM) was produced in progressively increasing magnetic fields up to 1000 mT with a Molspin pulse magnetizer. $IRM_{1000\ mT}$ was defined as the saturation isothermal remanent magnetization (SIRM). $IRM_{20\ mT}$ was defined as soft IRM (IRM_s), and ($SIRM-IRM_{300\ mT}$) was defined as hard IRM (IRM_h). $DC_{-100\ mT}$ was defined as demagnetizing factor in 100 mT.

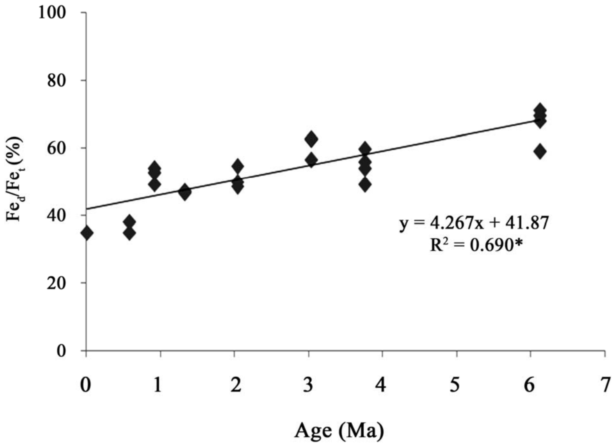


Figure 1. The temporal change of Fe_d/Fe_t in B horizons of basalt-derived chronosequence soils.

Table 1. Basic information of basalt-derived chronosequence soils.

Profile	Sampling site	Location	Soil age (Ma)	Soil type$^{(CRGCST, 2001)}$	Vegetation	Horizon (cm)
HN01	Shizilu town, Northern Hainan	19˚51.488'N 110˚21.327'E	0.01	Primosols	Pineapple, loquat, azedarach	A 0 - 16 B 16 - 40 BC 40 - 100 C > 100
LZ01	Yinli town Leizhou Peninsula	20˚36.361'N 110˚10.147'E	0.58	Ferrosols	Sparse grass, shrub	A 0 - 20 B 20 - 90 BC 90 - 150 C > 150
LZ04	Chenbei town Leizhou Peninsula	20˚20.367'N 110˚07.051'E	0.92	Ferrosols	Eucalyptus, sparse grass	A 0 - 23 B 23 - 105 BC > 105
HN03	Yongfa town Northern Hainan	19˚46.346'N 110˚12.887'E	1.33	Ferralosols	Azedarach, eucalyptus,	A 0 - 15 B 15 - 118 BC > 118
LZ07	Nanshan town Leizhou Peninsula	20˚15.947'N 110˚09.583'E	2.04	Ferralosols	Eucalyptus, sparse grass	A 0 - 20 B 20 - 120 BC > 120
LZ05	Haian town Leizhou Peninsula	20˚16.609'N 110˚15.218'E	3.04	Ferralosols	Eucalyptus, sparse grass	A 0 - 18 B 18 - 120 BC > 120
HN04	Bailian town, Northern Hainan	19˚53.998'N 110˚07.438'E	3.76	Ferralosols	Eucalyptus, sparse grass	A 0 - 30 B 30 - 120 BC > 120
LZ08	Hainan town Leizhou Peninsula	20˚17.662'N 110˚11.441'E	6.12	Ferralosols	Eucalyptus, sparse grass	A 0 - 20 B 20 - 150 BC > 150

Soil other properties were measured in the Soil and Environmental Analysis Center of the Institute of Soil Science, Chinese Academy of Sciences (ISSCAS) according to the standard methods outlined by the Chinese Society of Soil Science [26] (CSSS, 1984). The sand, silt and clay fractions were extracted by the pipette method. For the fine earths (<2 mm), the content of total iron (Fe_t) was measured by ICP-AES method after hydrofluoric acid digestion and the content of free iron oxide (Fe_d) was determined by the phenanthroline-colorimetry method after being extracted by the dithionitecitrate-bicarbonate solution (DCB) [27].

Particle size distribution (PSD) of clay fraction obtained by the pipette method was measured by laser diffraction (LD) method: soil samples were sieved by 2 mm mesh size after air-dried at room temperature, the organic matter was removed with 6% H_2O_2, carbonate removed with 0.2 $mol·L^{-1}$ HCl, Ca^{2+} and chlorides removed with 0.05 $mol·L^{-1}$ dilute HCl and distilled H_2O. Then soil samples were put into 0.5 $mol·L^{-1}$ NaOH for a night after being shaken for several minutes and were dispersed with the supersonic method (160 w, 10 - 15 min), then PSD data were obtained by using Beckman Coulter LS230 (He-Ne laser, 5 mw power, 750 nm wavelength, 0.04 - 2000 μm measuring range, about 0.1 g soil for each sample).

3. RESULTS AND DISCUSSION

3.1. Temporal Changes of Magnetic Parameters

The data of mesured magnetic parameters of 0.01 Ma (Primosols), 0.58 Ma (Ferrosols), 1.33 Ma (young Ferrosols) and 6.12 Ma (old Ferralosols) were compared here to disclose the evolution of magntism with time (see **Figure 2**).

MS gives an approximate indicator of concentration of the ferrimagnetic minerals in the soil. From the irregular change of MS with soil age, we fails to find the decline tendency of magnetic susceptibility of basalt-derived soils with pedogenic development or soil age as proposed by Lu *et al.* [25]. Most studies found that MS hardly can be used solely to indicate the pedogenic development becauese that fatcors which can affect MS are complicated [7].

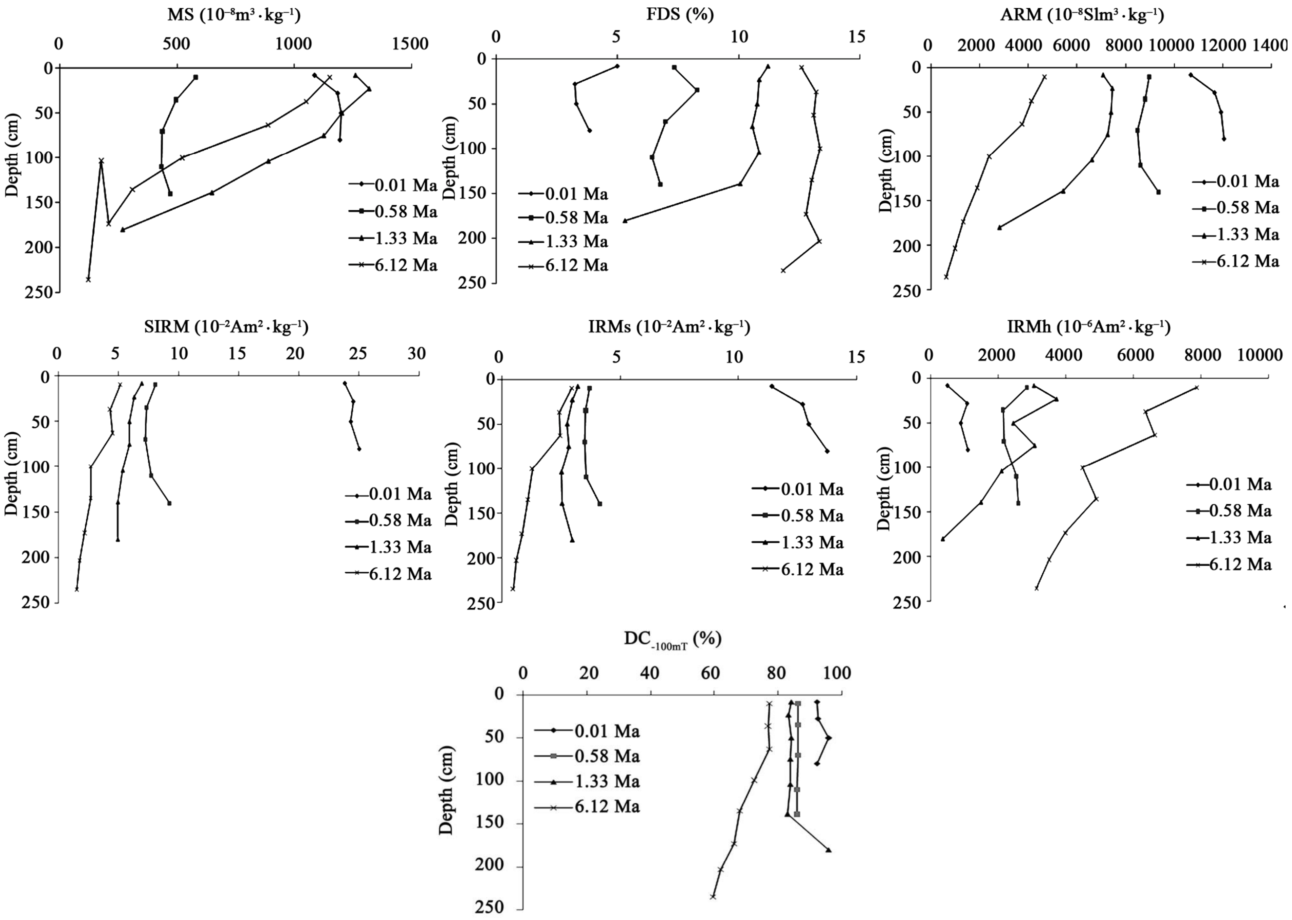


Figure 2. The temporal change of magentic parameters of basalt-derived chronosequence soils.

From MS change from C to BC to B to A horizons it can be found that pedogenic process can enhance MS of basalt-derived soils as others have found it (for example, [7]). No significant correlation exitsed between MS and Fe_t, Fe_d, Fe_o, Fe_d/Fe_t and Fe_o/Fe_t,which prove that MS is determined by the concentration of ferrimagentic minerals but not of iron iorn oxdies.

FDS indicates the presence of grains lying at the stable single domain (SSD)-superparamagnetic (SP) boundary, around 0.02 μm for isodiametric grains [28,29], while ARM is generally more sensitively proportional to the concentration of SSD grains of ferrimagnetic minerals. According to Dearing's model [29], FDS of 0.01 Ma profile is lower than 5%, indicating little SP grains in the soil. FDS% of 0.58 Ma profile ranges from 5% to 10%, indicating significant amount of SP grains existed in the soil [11,28]. FDS of 1.33 Ma profile and 6.12 Ma profile both are higher than 10%, suggesting more than 75% frequency-dependent ultra-fine SP grains appeared in the soils. The origin of the magnetic susceptibility in 0.01 Ma is believed to be inherited coarsed MD grains, while SP particles are assumed to be autogenic and suggest enhanced pedogenic development [30,31], thus, from the decrease of ARM and the increase of FDS with soil age, it may be concluded that SSD grains were weathered further into SP grains.

SIRM is a concentration-dependent magnetic parameter, while IRM_s is more sensitively proportional to the concentration of coarsegrained (MD or PSD grains) ferrimagnetic minerals. The significantly positive liner correlation between SIRM and IRMs ($R = 0.991^{**}$, $n = 24$) proves that SIRM is dominantly contributed by IRM_s. SIRM and IRM_s decreased with soil age means MD and PSD grains decrased grudally. SIRM and IRM_s of 0.01 Ma profile is higher than those of other three profiles, which means higher concentrations of coarsed-ferrimagnetic phases (e.g. magnetite and maghemite) in young profile due to the input of parent material. The rapid decrease of SIRM and IRM_s after 0.01 Ma shows the quick reduce of ferrimagnetic phases with soil age in soils, howere, the reduce becomes slowly from 0.58 Ma to 6.12 Ma, which means a slow decrease of MD or PSD grains of ferrimagnetic phases in the older soils.

IRM_h can reflect the concentrations of antiferromagnetic minarals (e.g., hematite and goethite). $DC_{-100\ mT}$ reflect the ratio of antiferromagnetic minerals to ferrimagentic minerals (e.g., magnetite and maghemite). The increase of IRM_h and the decrease of $DC_{-100\ mT}$ with soil age means the more and more antiferromagnetic minerals appeared in the soils due to the transformatiuon of ferrimagentic minerals to antiferromagentic minerals. From the values of IRM_h, it may be concluded that the magnetic minerals in 0.01Ma proflie is dominated by the little amount of ferrimagnetic minerals, but 0.58 Ma and 1.33 Ma profiles contain ferrimagnetic minerals and antiferromagentic minerals, while in the 6.12 Ma the magnetic minerals are dominated by antiferromagentic minerals.

3.2. Evolution Mechanism of Magnetic Parameters

Soil magnetism is dominated by magnetic minerals, particularly by ferrimagentic minerals. It has been proved well that the evolution mechanism of soil magnetism are mainly on the following two underlying hypotheses: with pedogenic development, firstly, the lithogenic ferromagnetic minerals, in subtropical and tropical basalts mainly magnetite and titanomagnetite, were weathered gradually and partly transformed into maghemite, hematite; secondly, at the same time nano-sized pedogenic grains (mainly SP grains) of ferromagnetic minerals were being progressively formed [9,14,25,32-34,].

X-ray diffraction results of iron oxides from Huang *et al.* [9] (see **Table 2**) in the similar basalt-derived chronosequence soils in northern Hainan Island were cited here to show the transform of ferromagnetic minerals, from **Table 2** it can be found with the increase in soil forming age magnetite descended while hematite and maghemite ascended in fine earth fraction and clay fraction. Although now it is impossible to differentiate between magnetite and maghemite using X-ray diffraction

Table 2. Iron oxides in soils at different developing and weathering age (cited from [9]).

Age	Iron oxides in clay fraction (<2 μm)	Iron oxides in fine earth (<2 mm)
0.01 Ma	He (+)	He (+), magnetite (+)
0.58 Ma	He (+), Tm (+)	Tm (+)
1.33 Ma	He (+++), Go (+++), Mh (+)	He (+++), Go (+++)
6.12 Ma	He (+++), Mh (++)	He (+++), Mh (++), Go (++)

He, hematite; Mn, magnetite; Tm, Titanomagnetite; Go, gothite; Mh, maghemite; +, small amount; ++, certain amount; +++, larger amount.

because their peaks are very close and practically indistinguishable, studies found that the corresponding magnetic phase in the superparamagnetic (SP) and single domain (SD) particles is maghemite rather than magnetite because pedogenic ferrimagnetic mineral particles with high surface to volume ratios are eventually oxidized into maghemite regardless of their initial states (magnetite or maghemite). To prove the maghemite is the main controbutor to the mangetism of studied soil profiles, DCB solution is used to treated the soil samples, it found that FDS after DCB solution treatment decreased by 58.0% ~ 95.7% with a mean of 81.6%, which indicates the high content and the significant contribution of maghemite to soil magnetism in the studied soils because DCB solution can dissolve nanosized (<100 nm) magnetite but not maghemite [7,35-37].

The grain sizes of magentic minerals in soils are usually less than 2 μm (clay fractions), LD techniques can provide the information of PSD distributions of clays [38,39]. **Figure 3** showed that Primosls is domintaed by the particles of 0.4 - 2 μm (PSD grains, 0.05 - 1 μm; MD grains, 1 - 2 μm), and then from Ferrosols to Ferralosols the particles of ≤ 0.4 μm increased obvisouly, means more finer particles formed. Due to the detect limit (usually is 0.04 or 0.05 μm) of LD instrument, it can’t give PSD informatoion of particle fractions of ≤ 0.04 or 0.05 μm, however, the uniform PSD distribution patterns in clay fractions in Ferrosols and Ferralosols may indicate that PSD similarity of magnetic iorn oxides in Ferrosols and Ferralosols.

3.3. Potential Significance of Magnetic Parameters in Identifying Soil Types?

The data of the less disturbed B horizons of the studied soils were used here to explore the potential significance of magnetic parameters in identifying soil types (**Figure 4**). Significant correlations existed between FDS, ARM, SIRM, IRM_s and soil age, among of which, a positive exponential correlation for FDS, while negative logarithmic correlations for ARM, SIRM and IRM_s, which proved that these magnetic parameters of B can indicate the soil age or soil development degree, which were already disclosed well by other studies (for examples, [7,25]).

It could be also found from **Figure 4** that in the period of Ferrolosols (1.33 Ma~), FDS, ARM, SIRM and IRM_s changed slowly, suggesting a relative stable phase occurred at 1.33 Ma for soil magnetic parameters, which may be regarded as a stable phase to be added into Lu et al.’s new conceptal model of soil magentism evolution [25], the lack of this new stable phase in Lu *et al.*’s model is attributed to no Ferrolosols in subtropical Zhejiang province.

The existence of the stable phase may be proved from one aspect by the temporal changes of clay content and Fe_t and Fe_d. Soil magnetism is mainly dominated by the contents, components and grain sizes of magnetic iron oxides. Iron oxides are concentrated mainly in the fine fractions of soils in subtropical and tropical regions, particularly in clay fractions. **Figure 5** shows Ferralosols was dominated by clay fractions and Fe_t and Fe_d changed little in Ferralosols stage.

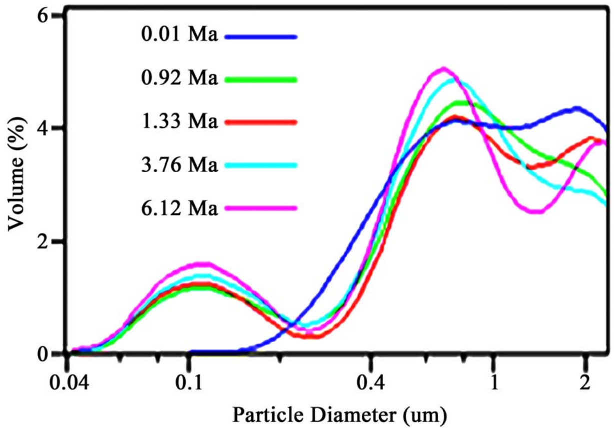
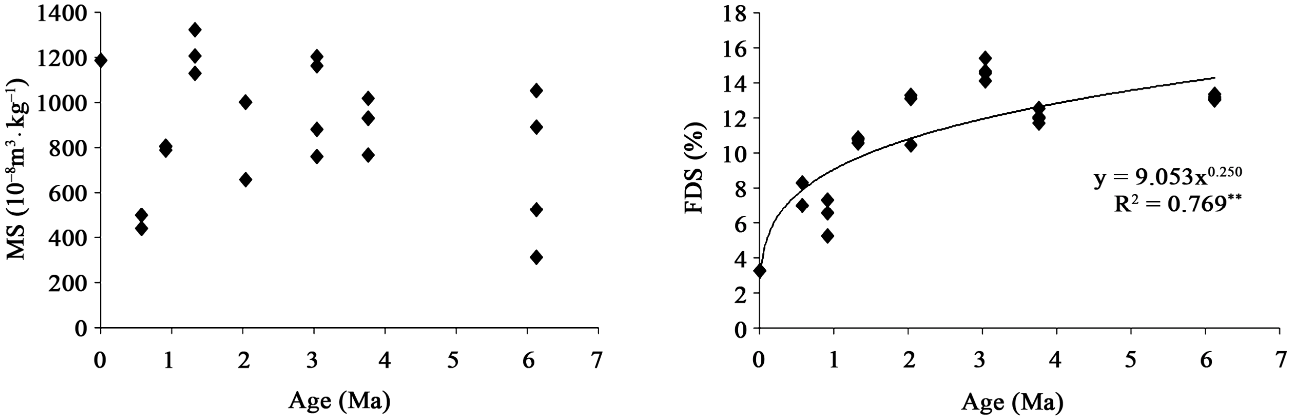


Figure 3. The temporal changes of clay fractions of basalt-derived chronosequence soils.



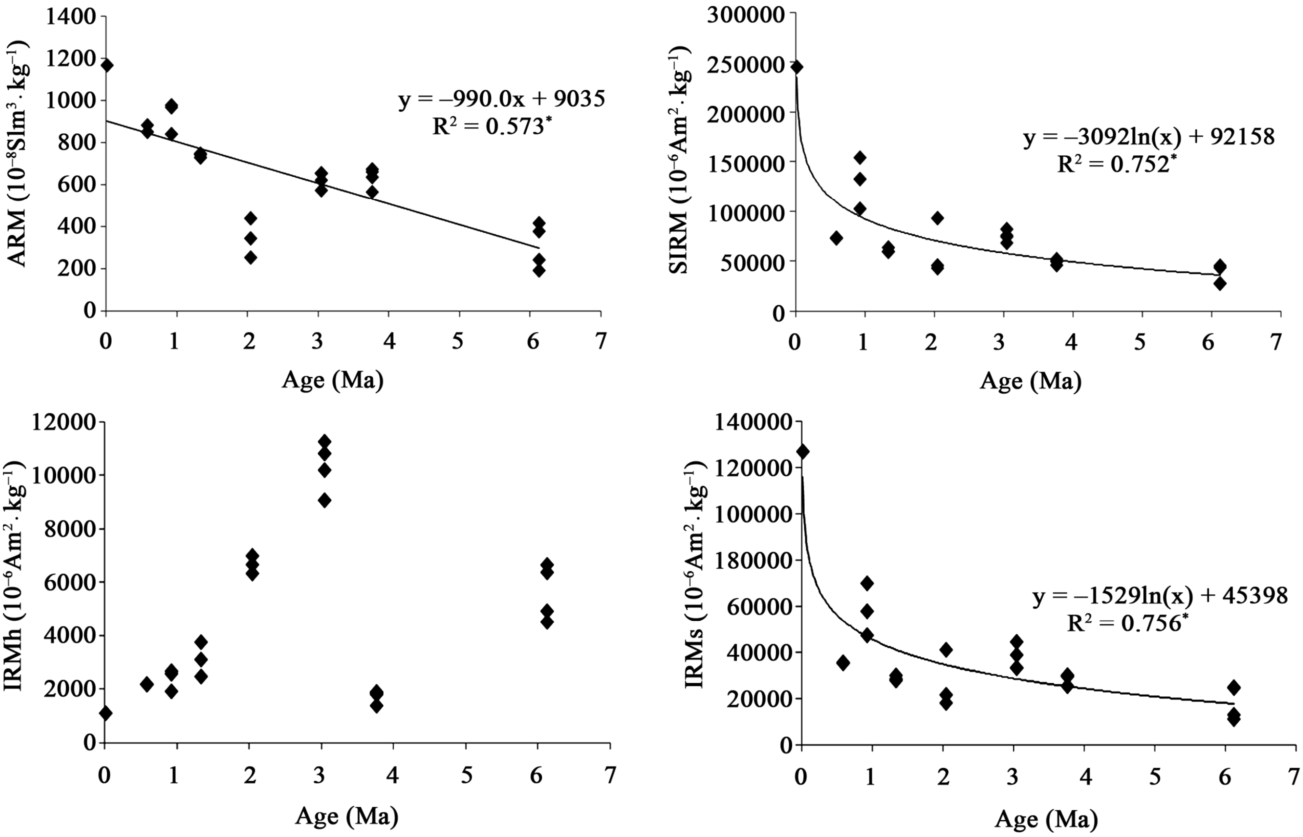


Figure 4. The temporal changes of magnetic parameters of B horizons of basalt-derived chronosequence soils. R^{2*} significant at $P < 0.05$ level, R^{2**} significant at $P < 0.01$ level.

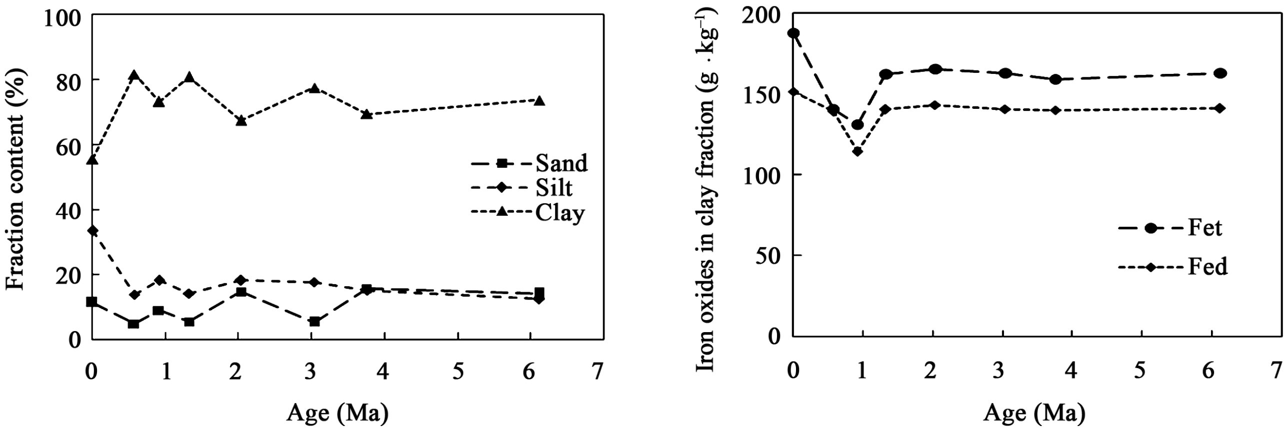


Figure 5. The temporal changes of clay content, Fe_t and Fe_d of B horizons of basalt-derived soils.

The above stable phase is significant in Ferraloslos identification with soil magnetism. From **Figure 4** it can be found that obvious differences in the values of FD and ARM between Ferralosols and other soils, *i.e.*, Primosols or Ferrosols: FDS, Ferralosols > 10%, Primosols and Ferrosols < 10%; ARM, Ferralosols < 7000 × 10^{-8} $SIm^3 \cdot kg^{-1}$, Primosols and Ferrosols > 8000 × 10^{-8} $SIm^3 \cdot kg^{-1}$.

With the consideration of the measured values of magnetic parameters in other studies on basalt-derived soils [7,25,40], for examples, FDS of Ferralosols B horizons in Huang and Gong [7] were also > 10%, while < 10% in other soil types; in the five soil profiles of Lu *et al.* [25], B horizons FDS% of four profiles were < 10%, therefore, it is possible to use magnetic indices to identify Ferralosols in tropical region. To establish the magnetic diagnostic indices of soils, one way more reliable is by the systematical collection and analysis of enough soil samples, but it is costly in time and fund; the other way more conveniently may be by studying the chronosequence soils as we did here. However, we advise here that more studies need to validate the above-mentioned magnetic indices and they should be used simultaneously with the existing other indices of profile morphological, physical and chemical properties.

4. CONCLUSIONS

Our study disclosed further that evolution of soil magnetic parameters with soil age, and they changed fast from Primosols to Ferrosols but slowly during Ferralosols, which suggested a relative stable phase occurred in Ferrolosols phase, it proves the possibility to use establish magnetic diagnostic indices for Ferralosols identification in the tropical regions.

5. ACKNOWLEDGEMENTS

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