Investigation on Phosphorus Speciation of Soil in Tibet of China Using XRD, SEM and EDS: The Case of Hydrothermal Treatment

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Abstract: Limited information is available on the changes of phosphorus speciation of soil in Tibet of China. A soil sample was collected from Tibet of China. Phosphorus availability from soil is influenced by its chemical speciation. The major objective of this study was to investigate the P speciation in the soil of Tibet of China treated by a Hydrothermal Method in the solution of distilled water, $NaHCO_3$ (0.5 M), NaOH (0.1M) and HCl (0.1 M) at 180°C for 12 h. The obtained samples were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Results show that the obtained samples were high crystallinity with decreasing particle size after hydrothermal treatment compared with that treated by Traditional Sequential Extractable Method. A possible reaction mechanism was proposed and discussed.

Key words: Soil, Tibet, China, hydrothermal treatment, phosphorous speciation

INTRODUCTION

Information on the chemical forms of phosphorous is significant to understand phosphorous dynamics and its interactions in soil that is necessary for management of P. Soil P chemistry is complex with numerous forms and possible transformations. Soil P occurs in organic forms as well as in inorganic compounds with Calcium (Ca), Aluminum (Al) and iron (Fe) with a consequent effect on its availability to plants (Jalali and Ranjbar, 2010). Consequently, during the past decades many efforts have devoted to the methods of P speciation and to quantify their contribution to plant P nutrition (Shen et al., 2004; Yu et al., 2006; Jiang et al., 2010). The alkali and acid solutions used in these sequential fractions or single extractions of soil P vary in efficiency and may alter the P forms (Cade-Menum and Preston, 1996). However, until now due to the different P speciation in different soils and no existing uniform criteria to soil sample preparation a common standard of P fraction is still not established.

Recently, microscopic and spectroscopic techniques have been used to the analysis of inorganic P solid phase in animal manure. For example, struvite has been identified in pig, cattle, sheep manure and poultry litter using qualitative Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS). X-Ray powder Diffraction (XRD), X-Ray Absorption Near-Edge Structure spectroscopy (XANES) and solid-state ^{31}P NMR techniques (Shand et al., 2005; Toor et al., 2005; Seiter et al., 2008; Castaldi et al., 2008). However, few reports have studied the P speciation in soil using the above-mentioned instruments.

Considering the complex hydrothermal reaction during the formation of soil in the geographical movement on earth for the first time, the hydrothermal treatment was introduced to the soil sample preparation. Actually, the hydrothermal treatment is a common method to prepare many kinds of nano- and micro- materials (Wu et al., 2008; Zhang et al., 2010a). Under the high temperature and pressure the materials with special nano and micro structures were formed. Furthermore, compared with the traditional method under normal temperature and pressure the precursor materials can react more completely during the hydrothermal treatment.

In this study, researchers chose the soil sample from Tibet, China as precursor followed by a hydrothermal process. The precipitate was collected to analysis the P fraction by XRD, SEM and EDS. To the best of the knowledge this was the first report related P fraction of soil to prepare soil sample by hydrothermal treatment.

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Followed by the idea it will open a new way to deal with the soil sample and to create a new method to analysis the P fractions.

MATERIALS AND METHODS

Soil sample preparation: The soil sample used in the current experiment was collected from the top soil (0-20 cm) in Winter wheat crop field at the Lhasa Plateau cosystems Research Station, a member of the Chinese Ecosystem Research Network (CERN). The station is located in the lower reaches of the Lhasa River valley (latitudes 29°40'-40"N, longitudes 91°20'-37"E, altitude 3688 m) on the Tibetan Plateau and characterized by a continental temperature climate with annual mean, maximum and minimum air temperature of 7.5, 27.4 and -11.8°C, respectively. Annual precipitation is 425.4 mm with 94% concentrated from June through September. Annual atmospheric pressure is 650.3 mbar (Comprehensive scientific expedition to the Qinghai-Xizang (Tibet) plateau, Chinese Academy of Sciences, 1984). Soil sample was randomly collected with a hand auger from a depth of 0-5 cm at 15 locations, mixed and air-dried at room temperature to constant weight passed through a 2 mm sieve before laboratory ananlysis.

Soil physical-chemical properties: The sandy loam soil was classified as Typic Fluvaquents Entisols. The physical-chemical properties of the soil used in this study were: pH 7.25 (soil: water = 1:2), H_2SO_4-$K_2Cr_2O_7$ digested organic water content 11.68 g kg^{-1}, NH_4Cl-NH_4OAc extractable CEC 9.28 cmol kg^{-1}, total N 0.76 g kg^{-1}, total P 1.22 g kg^{-1}, total K 1.84 g kg^{-1}, total Ca 28.8 mg kg^{-1}, total Mg 0.07 mg kg^{-1}, total Al 28.8 mg kg^{-1}, total Fe 0.07 mg kg^{-1} and 2 M KCl extractable N 68.48 mg kg^{-1}, 0.5 M $NaHCO_3$ extractable P 15.39 mg kg^{-1}, NH_4OAc extractable K 66.64 mg kg^{-1}, 2 M KCl extractable Ca 78.31 mg kg^{-1}, 0.5 M $NaHCO_3$ extractable Mg 11.95 mg kg^{-1}, NH_4OAc extractable Al 103.5 mg kg^{-1}, NH_4OAc extractable Fe 103.5 mg kg^{-1}. Content of textural fractions was: 66.3% (2-0.05 mm), 23.8% (0.05-0.002 mm), 9.9% (<0.002 mm). The standard methods described in the handbook Methods of Soil and Agrochemistry Conventional Ananlysis (Agrochemistry Committee of Soil Science of China, 1983) were used to determine the basic properties of soils in triplicate. Soil total P was determined by H_2SO_4-$HClO_4$ digestion and molybdenum antimony-ascorbic acid Colorimetric Method. Soil texture was determined by mechanical analysis (Pipette Method).

Soil hydrothermal treatments: All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and were used without further purification. In a typical procedure, 0.5 g soil samples were

Fig. 1: Digital photo of the hydrothermal reactor

poured into 80 mL distilled water $NaHCO_3$ (0.5 M), NaOH (0.1 M) and HCl (0.1 M) under fierce stirring which marked sample A-D, respectively. The soil suspensions were then transferred into four Teflon-lined stainless autoclave of 100 mL capacity as shown in Fig. 1. The autoclave was sealed and heated at 180°C for 12 h then cooled to room temperature naturally. The precipitates were taken out into a tube for centrifugal separation. The products were then dried at 80°C in a vacuum oven for 4 h. As a comparison, the soil samples were sequentially extracted by H_2O, $NaHCO_3$ (0.5 M), NaOH (0.1 M) and HCl (0.1 M) as well.

Soil samples characterizations: The crystal structure of the products were determined by XRD (type: Bruker D8 advance) meter with a Ni monochromator using Cu Ka radiation (λ = 1.5418 Å) in the range of 20-70°C at room temperature while the tube voltage and electric current were held at 40 kV and 40 mA. Morphology of the prepared soil samples were studied by SEM, (type: Zeiss EVO LS-15) with n accelerating voltage of 15 kV equipped with an EDS.

RESULTS AND DISCUSSION

A typical XRD pattern of the resultant soil samples treated by sequential extracted by H_2O, $NaHCO_3$ (0.5 M), NaOH (0.1M) and HCl (0.1 M) is shown in Fig. 2. It is evident that strongest diffraction peak can be indexed to the $Ca_2P_2O_7$ and $AlPO_4$ corresponding to the JCPDS card 1-667 and 3-445. The other diffraction peaks can be fitted to MgP_2O_7, $CaHPO_4.2H_2O$ (Brushite) and $Fe_4(P_2O_4)_3$ except for the $Ca_2P_2O_7$ and $AlPO_4$ which is corresponding to the the JCPDS card 5-579, 1-395 and 3-124, respectively. In particular the relative intensity of the peaks in sample B is
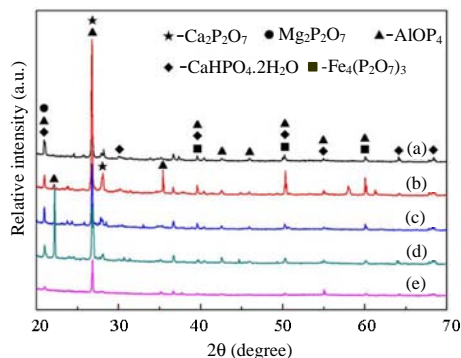
Fig. 2: XRD pattern of the soil samples sequentially extracted by a) distilled water; b) $NaHCO_3$ (0.5 M); c) NaOH (0.1 M); d) HCl (0.1 M) and e) original soil sample
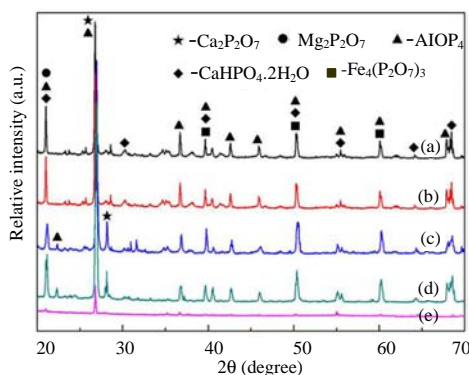

Fig. 3: XRD pattern of the soil samples hydrothermally treated by a) distilled water; b) NaHCO3 (0.5 M); c) NaOH (0.1 M); d) HCl (0.1 M) and e) original soil sample

obviously increased indicating that a proper amount of $NaHCO_3$ (0.5 M) can enhance the crystallinity of phosphate in soil. Also, the intensity of the peak at the diffraction angle of 22.04° in sample D is higher than that in other samples which illustrates that the $AlPO_4$ dominate the phosphate phase after extracted by HCl (0.1 M). Figure 3 shows the XRD pattern of the soil samples hydrothermally treated by distilled water $NaHCO_3$ (0.5 M), NaOH (0.1 M) and HCl (0.1 M) original soil sample. Different from the XRD pattern obtained by traditional Sequential Method all the diffraction peaks obtained by Hydrothermal Method is greatly enhanced compared with the peaks of the original soil sample indicating that the crystallinity of the soil sample was greatly enhanced after the hydrothermal reaction due to the high temperature and pressure. Sei *et al.* (2006) reported that the main peak at

22.04° was described to the kaolinite phase (JCPDS card 1-527). Probably, the kaolinite ($Al_2Si_2O_5(OH)_4$ should not exist after the extraction by alkali and acid solutions. The kaolinite will be dissolved by NaOH solution as follow: $Al_2Si_2O_5(OH)_4 + NaOH \rightarrow Na_2SiO_3 + Na_2AlO_2 + H_2O$. Also, no peaks of $Ca_5 (PO_4)_3$ (OH) (hydroxylapatite, JCPDS card 9-432) was found which is different to the previous report (Shaltout *et al.*, 2011). No SiO_2 peaks were appeared as well due to the amorphous structure of silica. Most of earlier research on P fraction was mainly focused on the extractable solution not the sediment soil sample. From the XRD data in Fig. 3, the diffraction intensity of P forms are still very strong indicating that most of the P forms can not be extracted by alkali and acid solutions even by a hydrothermal process. Compared with the diffraction intensity of the original soil sample all the intensity of the samples with hydrothermal treatment was greatly enhanced therefore, the amounts of the P forms such as Ca-P, Al-P, Mg-P and Fe-P and so on could be obtained which is equal to the integral area of the corresponding peaks. Furthermore, the size of the nanocrystals (D) was calculated on the basis of the Scherrer equation (Zhang *et al.*, 2010b):

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where:

k = 0.9 D is the shape factor
λ = The X-ray wavelength of Cu Kα radiation (1.5418 Å)
θ = The Bragg diffraction angle
β = The Full Width at Half Maximum (FWHM) of the peak

In a sense, hydrothermal treatment provides a significant and effective way to study the P forms in soil.

Figure 4 and 5 show the SEM morphologies of the original soil samples treated by traditional sequential extraction and hydrothermal reaction, respectively. The average size of the samples in Fig. 4 is about 50 μm. However, most of the soil particles decrease to no more than less 10 μm after hydrothermal treatment which is probably ascribed to the well-known ostwald ripen effect during the hydrothermal process. Usually, the soil sample was dispersed in the solution to form an unstable suspension which is not a really meaningful soil colloid solution. However, with a hydrothermal treatment under high temperature and pressure the soil particles will diffuse to the solvent to form a Stable Colloidal System. Then, under the Ostwald ripen effect, the soil colloidal
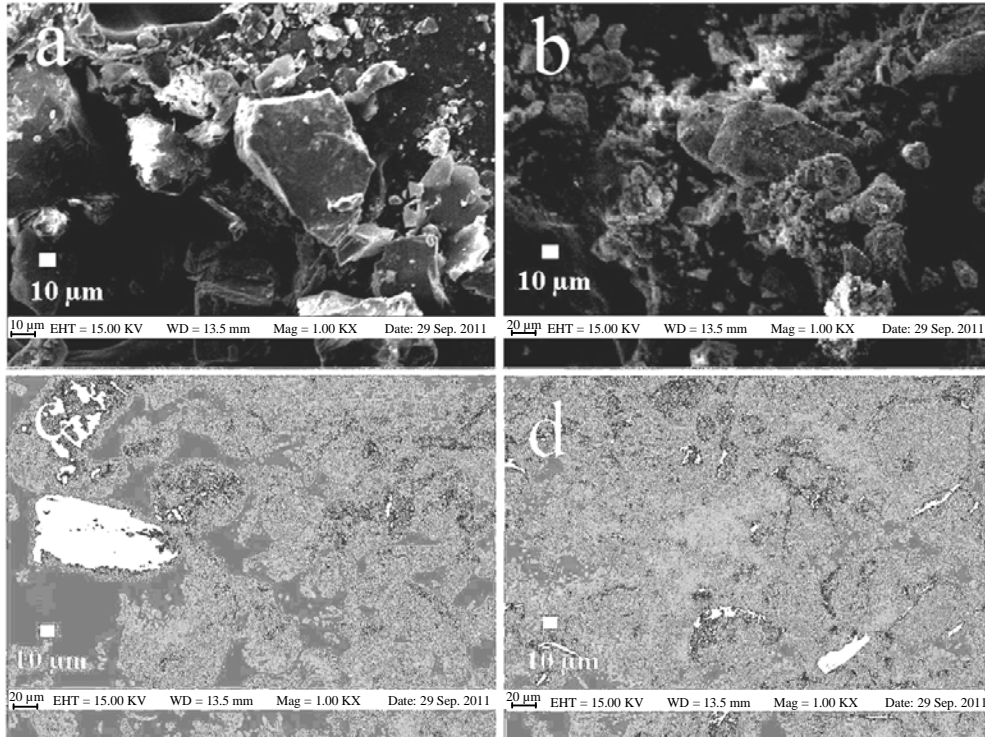
Fig. 4: SEM images of the soil samples sequentially extracted by a) distilled water; b) NaHCO$_3$ (0.5 M); c) NaOH (0.1 M); d) HCl (0.1 M) and e) original soil sample
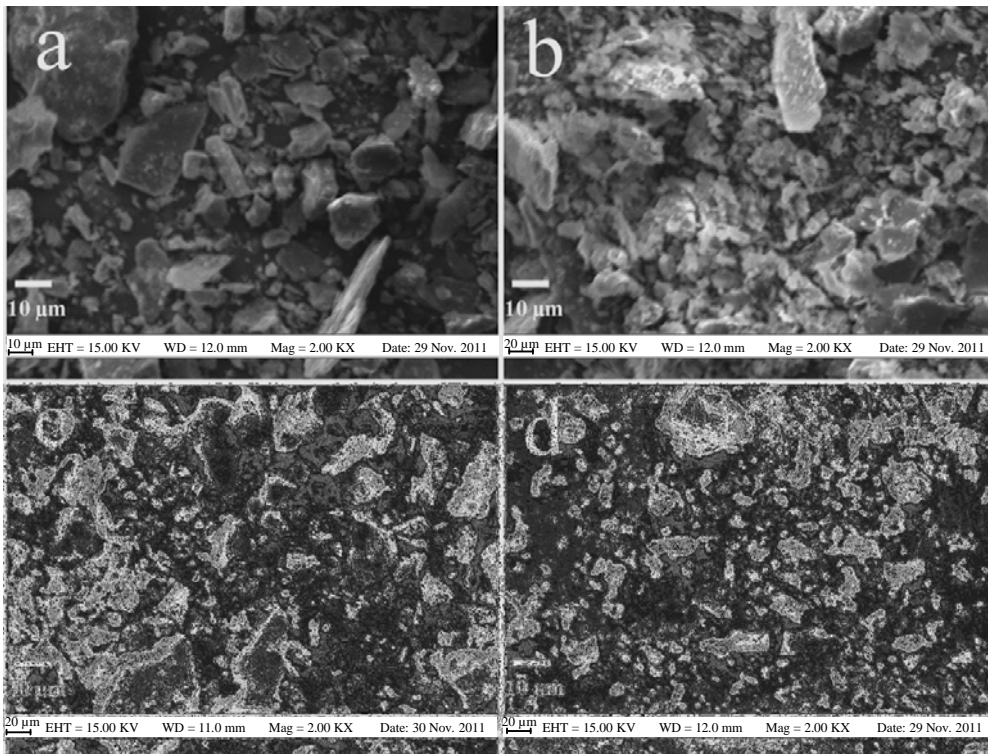

Fig. 5: SEM images of the soil samples hydrothermally treated by a) distilled water; b) NaHCO$_3$ (0.5 M); c) NaOH (0.1 M); d) HCl (0.1 M) and e) original soil sample
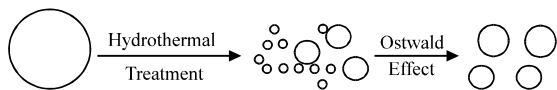
Fig. 6: Schematic diagram of the soil sample reaction by a hydrothermal treatment

particles were aggregated to form clusters as shown in Fig. 6. Actually, the hydrothermal reaction is a very complex process including many dissolving, hydrolysis and crystallization steps, i.e., $Ca_2P_2O_7 + H^+ \rightarrow H_3PO_4 + Ca^{2+}$, $CaHPO_4.2H_2O + H^+ \rightarrow H_3PO_4 + Ca^{2+}$, $AlPO_4 + H^+ \rightarrow H_3PO_4 + Al^{3+}$, $Fe_4(P_2O_7)_3 + H^+ \rightarrow H_3PO_4 + Fe^{3+}$, $H_3PO_4 = H_2PO_4^- + H^+ = HPO_4^{2-} + 2H^+ = PO_4^{3-} + 3H^+$, $Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$, $Mg^{2+} + 2H_2O = Mg(OH)_2 + 2H^+$, $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$, $Ca^{2+} + HPO_4^{2-} = CaHPO_4$ and $Al^{3+} + PO_4^{3-} = AlPO_4$. The soil samples were mainly composed of many dense clusters and interconnected blocks. Especially, in sample B in Fig. 5 there exist many loosenanoparticles on the surface of the clusters and blocks which are probably originated from the CO_2 bubbles by hydrolyzed $NaHCO_3$ during the hydrothermal reaction, i.e., $NaHCO_3 + H^+ = CO_2 + H_2O + Na^+$. The CO_2 bubbles maybe play a soft template role during the formation the loose nanoparticles (Zhang *et al.*, 2011). In addition, some organic components in the soil sample such as humic acid, fulvic acid and organic P forms maybe discompose to inorganic ingredients under the special hydrothermal conditions. Earlier some novel inorganic materials with special architecture have been synthesized by hydrothermal reaction. For example, Ag-carbon core-shell structures can be fabricated by a simple hydrothermal reaction using glucose as template (Sun and Li, 2004). The novel In_2O_3 hollow microspheres can be easily obtained by a hydrothermal process only using glucose and In $(NO_3)_3.6H_2O$ as precursors (Zhang *et al.*, 2010c). Here, the glucose plays a template role during the formation the Ag and In_2O_3 microspheres. Followed by this idea some modifiers and extractable agent can be used to change the morphology, the P forms and improve crystallinity of soil due to the synergistic effect between the soil and the proper modifier. Consequently, it will open a new visual angle and provide a new method to investigate the soil properties including morphology, component and P forms.

The composition of the obtained soil samples hydrothermally treated by distilled water $NaHCO_3$ (0.5 M) NaOH (0.1 M) and HCl (0.1 M) is shown in Fig. 7 by the EDS analysis which reveals the relative weight percent of the main elements related the P forms. Actually, it is just a relative value of a sample due to the different reaction in different solutions. Obviously, the silicon amount decreased and increased sharply in NaOH and HCl solutions, respectively. In NaOH solution, the silica in the soil will be dissolved to Na_2SiO_3 to be transferred to the
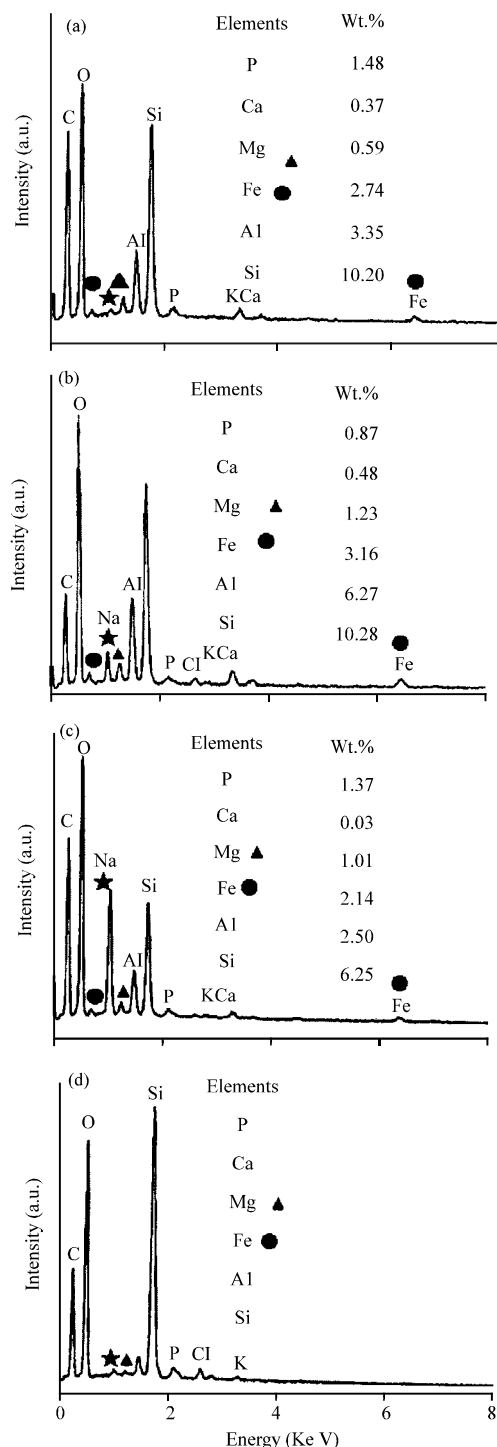

Fig. 7: EDS spectrums of the soil samples hydrothermally treated by a) distilled water; b) $NaHCO_3$ (0.5 M); c) NaOH (0.1 M) and d) HCl (0.1 M)

solution, i.e. $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$. Some Al_2O_3 will be transferred to the solution as well i.e., $Al_2O_3 +$

$2NaOH = 2NaAlO_2 + H_2O$ for Al_2O_3 is a kind of amphoteric oxide, i.e., it can be dissolved by both alkali and acid. On the contrary in sample D the silica can not be dissolved by HCl solution however the other metal oxide and some P forms can be dissolved as a result, the relative amount of silicon increased greatly. Compared with the distilled water, the $NaHCO_3$ solution will extractable more Olsen-P, i.e., the relative amount of P in sample B is lower than that of sample A as a result other metal amount will be relative higher compared with sample A.

CONCLUSION

The hydrothermal reaction was firstly applied to treat with the soil sample from Tibet of China. The obtained samples were high crystallinity with decreasing particle size compared with that treated by traditional Sequential Extractable Method. The hydrothermal reactions of soil samples were composed of many dissolving, hydrolysis and crystallization processes. The ingredient of the hydrothermal treated soil samples was influenced by the properties of solution. It will open a new approach and provide a new method to study the soil properties of morphology, components and P forms.

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