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Research paper

How the unique properties of soil kaolin affect the fertility of tropical soils

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ABSTRACT

The kaolin (*s.l.*) in many tropical soils is distinctly different from most specimen and industrial kaolins. Crystal structure is highly disordered and crystal sizes are much smaller than for specimen and industrial kaolins. The crystal habit of soil kaolins is diverse ranging through euhedral hexagonal and anhedral platy, spheroidal and tubular. The specific surface of soil kaolins is higher than for most industrial kaolins. Consequently, cation and anion retention capacities are higher although there is no compelling evidence that the high structural disorder of soil kaolin is associated with a greater specific reactivity of the kaolin surface. A small amount of ferric iron substitutes for octahedral Al but there is generally little or no substitution of other cations. Soil kaolin commonly contains minor amounts of potassium but this is present in mica layers within, attached or associated with kaolin crystals so that potassium is not within the kaolin structure. Due to its considerable chemical reactivity soil kaolin helps provide an effective substrate to support agriculture and other land uses in the tropics.

1. Introduction

Should a paper on the significance of soil kaolin (*s.l.*) be included in a publication that is mostly concerned with commercial clay minerals? Our response is simply that kaolin dominated soils are abundant in the wet tropics and as a high proportion of the world's population relies on these soils for the agriculture that produces food and fiber (Fig. 1) we should be aware of these kaolins. Kaolin enables these soils to provide clean water and buffer the environment against diverse contaminants. To the many people in this region the unique properties of soil kaolin are of critical importance so that the mineral deserves the research attention that it has received in recent decades. We have chosen to use the term kaolin rather than kaolinite as soil kaolins may include minerals that might be classified as variously ordered kaolinites, halloysite, nacrite and dickite but are not readily distinguished by routine examination. We are therefore considering the kaolin group of minerals as discussed by Guggenheim et al. (1997) but also include halloysite in its variously hydrated conditions.

Soil kaolins are as diverse as those used in industry but they may differ from industrial kaolins in several important respects. The kaolin present in the solum (the uppermost "living" part of the soil) is commonly different from kaolin in the underlying saprolite or sediment where the kaolin may resemble many industrial kaolins; consisting of large, structurally ordered, euhedral crystals (Varajão et al., 2001; Hughes et al., 2009). The specimen kaolins described in many publications commonly consist of large, euhedral and highly ordered crystals (Hart et al., 2002; Hughes et al., 2009). Soil kaolin crystals are mostly very small with habits ranging from euhedral hexagonal plates through anhedral plates to tubular and spherical forms. Consequently, specific surface area (SSA) is high resulting in substantial cation and anion retention capacities which are of great benefit to agriculture as cationic and anionic forms of plant nutrient elements are retained against leaching under the high rainfall condition of the wet tropics. Similarly soil kaolin can reduce the mobility of toxic ions and harmful synthetic organic molecules in soils thereby moderating contamination of food crops and water resources. An important and desirable property of soil is its capacity to retain the water received from rainfall or irrigation and then release this water to plants in response to the demands of the growing plant transmitted through the root system. What is required is a stable, porous soil structure with an abundance of connected pores in the 0.1–10 μm size range. Many tropical soils with kaolin as the dominant clay mineral have exactly this characteristic and consequently they are less sensitive to drought conditions and water is used efficiently. The low bulk density and structural stability of some kaolin-rich tropical soils, notably oxisols, are thought to be a consequence of their stable low-density, porous "card house" structure where kaolin plates are secured in place by iron oxide crystals attached to kaolin crystals through electrostatic attraction (Tawornpruek et al., 2006). Kaolin has a negative surface charge and iron oxides have a positive surface charge at the acid pH conditions prevalent in tropical soils (Khawmee et al., 2013).

A commonly held view of the mineralogical basis of chemical soil fertility is that the clay fraction contains micrometric grain of mica, vermiculite, chlorite, feldspar, pyroxene, and other primary minerals (Retallack, 1990). These minerals contain several plant nutrient elements that are released to plants by dissolution and exchange reactions in the soil. This is certainly the situation in mid-latitudes where many soils have formed on glacial residuum which includes alluvium and

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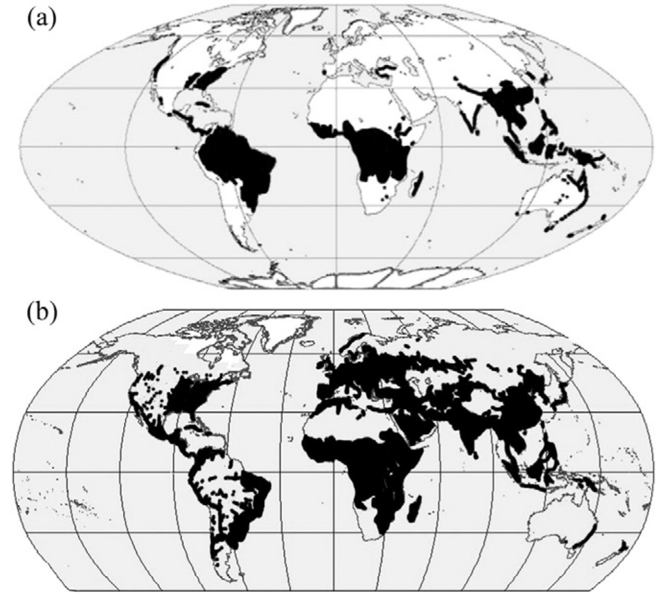

Fig. 1. (a) The global distribution of kaolinitic soils (based on ISSS, 1998) and (b) The global distribution of medium to high population density showing that the highly populated tropical region commonly has kaolin-rich soils (based on CIESIN-Columbia University, 2014).

loess transported for long distances by wind and water from regions of former glacial activity. Indeed some tropical soils have also been derived from rock debris resulting from tectonic activity and vulcanicity and these soils are consequently fertile. Large active river systems in the tropics deposit mineral rich alluvium in flood plains and deltas which support fertile productive soils (Young, 1976). However, much of the tropical and subtropical zone is occupied by ancient upland landscapes mantled by deep, highly weathered regolith with kaolin and iron oxides dominating the clay fraction of the solum. Quartz and a few resistant primary minerals comprise the silt and sand fractions which do not contribute significant amounts of nutrients to plants (Darunsontaya et al., 2012). Under these circumstances, it might be anticipated that the chemical fertility of the prevalent kaolinitic soils will be poor and this is usually the case. Soil organic matter may provide a reserve of some plant nutrients and is of particular value in highly weathered kaolinitic soils but the soils generally remain infertile. There is evidence for potassium and other plant nutrient elements being present in minor concentrations in soil kaolin and these elements may be at least partly available to plants (Singh, 1991).

It is evident from this overview that the properties of soil kaolins are rather different from specimen kaolinite and those kaolins utilized by industry and also that the properties of kaolin that are of particular interest to soil scientists may not coincide with those of researchers into the properties and performance of industrial and specimen clays. In this paper, we review the present state of knowledge of soil kaolin and attempt to identify relationships between chemical, morphological and structural properties of soil kaolins. We restrict our review to those papers that have used the same analytical procedures and we have been alert to data having been reproduced in several papers thus avoiding duplication of data in our summaries of experimental results.

2. Preparing soil kaolin for analysis

It is impossible to separate pure kaolin samples from soils as the clay fraction of all soils contains micrometric crystals of diverse accessory minerals. Consequently, measurements are made on clay separates including clays that have been chemically treated to remove Fe/Mn oxides, carbonate minerals and organic matter, but these separates are still not pure kaolin. This is a particular problem for measurements of surface properties of soil kaolin (SSA—specific surface area, ion exchange and retention, surface charge density) and bulk chemical composition where results are invariably confounded to some extent by the presence and properties of impurities. Crystallographic properties of kaolin such as basal spacing, peak shape and crystallinity indices are not very sensitive to the presence of small amounts of impurities. Transmission electron micrographs need to be interpreted with caution as micrometric particles may be impurities rather than being kaolin crystals. This problem can be avoided if individual particles are analyzed by X-ray spectrometry in the TEM (EDS) to confirm that they are kaolin although this is a time consuming process (Singh and Gilkes, 1995).

The common pretreatments of soil clay samples consist of (i) digestion in hydrogen peroxide solution at near neutral pH to remove organic matter although this treatment might oxidize structural ferrous ion in clay minerals (ii) removal of free Fe/Mn oxides by repeated digestion in DCB (dithionite–citrate–bicarbonate) solution which reduces and dissolves these oxides. The structural Fe in clay minerals can be reduced by this treatment which will then affect the layer charge of the minerals (Stucki, 2006). It is usual to check the purity of separated soil kaolins using XRD but this technique has limited sensitivity especially for highly disordered layer silicates and amorphous alumino-silicates such as allophane. The use of synchrotron XRD can provide greater sensitivity for the recognition of quartz, anatase, rutile, crandallite and other common crystalline impurities in kaolin samples but is not equally effective for determining poorly ordered silicate minerals. Other analytical techniques such as IR spectrometry and thermal analysis may be used to detect impurities in kaolin concentrates but these techniques are too insensitive to distinguish minor amounts of most mineral species.

Thus, it may not be possible to quantitatively determine the amounts of impurity minerals in kaolin concentrates consequently accurate corrections of chemical analyses can not be made. The use of Rietveld XRD analysis (Hillier, 2000) in recent years has greatly improved the quantification of minerals in clay concentrates so that reliable correction for some crystalline impurity minerals is now possible; however the sensitivity of XRD techniques for minor and disordered constituents remains poor. This is a particular limitation when attempts are made to allocate minor elements (e.g. Cr, Zn, Pb) in kaolin concentrates to mineral species. Thus, for example it may not be possible to conclude whether $\mu g\ g^{-1}$ amounts of Cr are in the structure of kaolin (Singh and Gilkes, 1991) or are in minor amounts of associated chromite. Unfortunately, EDS combined with TEM lacks sufficient sensitivity to determine trace levels of metals in single crystals of kaolin. With these reservations in mind, we will now turn our attention to what is known of the properties of soil kaolin.

3. Properties of soil kaolin

As mentioned in the introduction some mature leached tropical soils may contain large, euhedral kaolin crystals with a high degree of structural order. This kaolin has generally been inherited from deep regolith or sedimentary rocks and does not have a pedogenic origin (Varajão et al., 2001). More commonly kaolin in the solum consists of small crystals with a low degree of structural order (Brindley and Brown, 1980). Typical random powder XRD patterns of deferrated kaolin clay from tropical soils are shown in Fig. 2 where only basal (001) and two dimensional order (hk) diffraction peaks of kaolin are present. The prism (hkl) reflections that are characteristic of well ordered kaolin are absent due to the high extent of b-axis disorder in soil kaolins. The great width of the basal (001, 002) reflections is predominantly due to the small crystal size in the c-axis direction which can be estimated from diffraction line broadening using the Scherrer equation (coherently diffracting domain size CSD) (Brindley and Brown, 1980).

The basal spacing (d (001)) of kaolin appears to increase from 0.715 nm to about 0.730 nm as CSD decreases from 40 to 6 nm