# ALLOPHANE RICH CLAY
# A SPECIAL CLAY FROM SANTO DOMINGO DE LOS COLORADOS (ECUADOR)
# CHARACTERISATION AND POTENTIAL APPLICATION

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## INTRODUCTION

In late 1980s DINAGE and BGR explorated for brick raw material in the area of Santo Domingo de los Colorados. Instead of good brick materials a deposit of allophane-rich clay was found. This material covers an area of more than 4000 $km^2$ with a thickness of generally more than 5 m. The allophane content ranges from 50 to 60 wt.-%, locally up to 80 wt.-%. This allophane-rich clay occurrence seems to be unique in its distribution and quality.
Allophane is known as a short range order mineral, which has developed mainly from volcanic ashes, and consists of silica, alumina and water. Due to its unique morphology consisting of microporous hollow spheres it can be referred to as ‘special clay’. The particle size of allophane ranges from 3 to 5 nm (1 nm = $1*10^{-9}$ m) and it has a large specific surface area (SSA).
Since 2003 there is an investigation program on potential applications of this allophanic ‘special clay’ from Santo Domingo in the Federal Institute for Geosciences and Natural Resources (BGR, Hanover, Germany) in cooperation with the Institute for Soil Science and Plant Nutrition (Martin-Luther-University, Halle-Wittenberg, Germany).

## MATERIAL AND METHODS

The investigation concentrates on a profile with a thickness of 16 meters NW’ Santo Domingo de los Colorados. Each meter was sampled. To characterise this clay material, X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), differential thermal analysis (DTA), Fourier-Transform infrared spectroscopy (FTIR), cation exchange capacity (CEC) selective dissolution treatments, and phosphate retention experiments have been carried out.

## CHARACTERISATION

The XRD analysis proved that the mineralogical composition of this clay material is dependent on the depth (Table 1). Particularly two different facies were identified.
The *allophane facies* (PM 4-1 to PM 4-9) contains mainly allophane, imogolite and Fe oxides may be present as minor components or traces). Vermiculite and hornblende are specific minor components of this facies.
The *halloysite facies* (PM 4-10 to PM 4-16) contains mainly halloysite. Goethite is present as minor component, vermiculite and hornblende are absent.

**Table 1: Results of the qualitative X-ray diffractometry of the two facies.**

| | specimen | X-ray amorphous (allophane, imogolite and Fe oxides) | halloysite | gibbsite | quartz | cristobalite | vermiculite | hornblende | feldspar | goethite | dolomite |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **identified minerals** | | | | | | | | | |
| *allophane facies* | **PM 4-1** | +- | | | +- | - | -- | + | + | | -- |
| | **PM 4-2** | + | | | +- | +- | - | +- | - | | - |
| | **PM 4-3** | + | | | +- | - | - | +- | +- | | |
| | **PM 4-4** | + | | | -- | -- | - | - | +- | | |
| | **PM 4-5** | + | | | - | - | | - | -- | | |
| | **PM 4-6** | + | | | - | | -- | - | | | |
| | **PM 4-7** | + | | - | +- | +- | - | +- | - | | |
| | **PM 4-8** | + | -- | - | - | - | -- | -- | | | |
| | **PM 4-9** | + | - | -- | - | - | | -- | | | |
| *halloysite facies* | **PM 4-10** | | + | +- | - | - | | - | | - | |
| | **PM 4-11** | | + | +- | | +- | | | | | |
| | **PM 4-12** | | + | -- | - | - | | | | - | |
| | **PM 4-13** | | + | | - | -- | | | | +- | |
| | **PM 4-14** | | + | | - | - | | | | + | |
| | **PM 4-15** | | + | | +- | - | | | | +- | |
| | **PM 4-16** | | + | | +- | - | | | | +- | |

**+** = main comopnent, **+-** = minor component,
**-** = minor component/trace, **--** = trace

The XRF results support the XRD findings. The MgO content likely can be correlated with the occurrence of minor amounts of vermiculite. In addition to the XRD results some specific horizons within the both facies are identified. Within the first facies the specimen PM 4-7 (at a depth of 6 to 7 m), which has a higher content of $SiO_2$ and is consistent with the XRD results (cristobalite and quartz occurrence). Specimens PM 4-13 and PM 4-14 of the second facies have a high $Fe_2O_3$ content, which is also consistent with the XRD finding of goethite. These two samples represent the horizons from 12 to 14 m. Possibly, these two horizons can be used for the correlation of different allophane profiles.

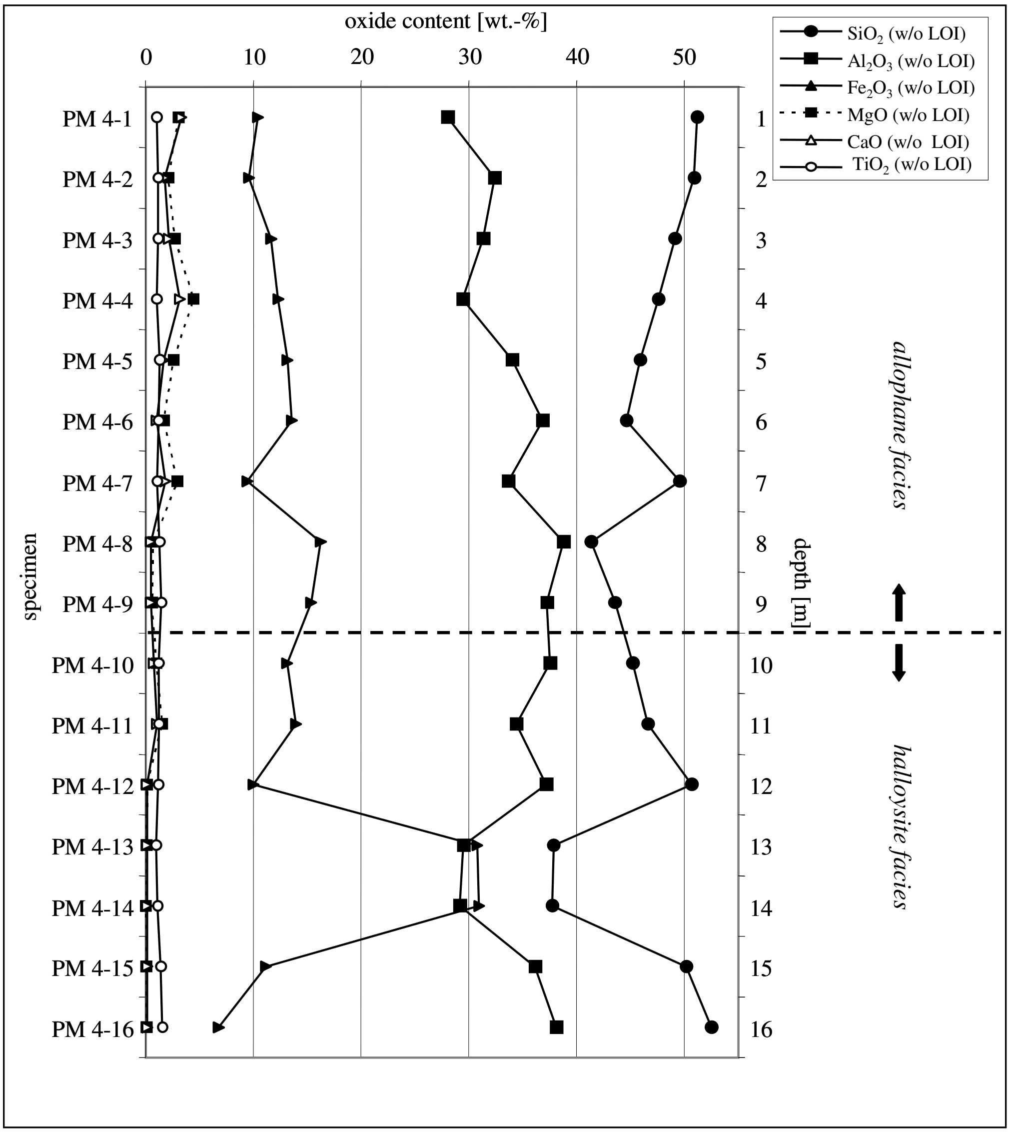


**Figure 1: Profile PM 4 and its quantitative chemical distribution.**

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DTA was carried out to characterise the X-ray amorphous phases, particularly to distinguish allophane from imogolite. The investigated specimens of the allophane facies all show a large endothermic peak between 50 and 300 °C (desorption of water) and a characteristic exothermic peak between 900 and 1000 °C (recrystallisation of mullite). The typical peak for imogolite between 390 and 420 °C is missing, which means that imogolite is not identified in both facies. This will be checked by means of transmission electron microscopy analysis.

Whereas XRD gives only limited information about allophane (short-range order), FTIR can be used for the investigation of structural features as well as isomorphic substitutions. This method is a useful tool to investigate the structural change of this material while using different pre-treatments (e.g. heating and grinding).

CEC was investigated to compare this clay material with presently technically used clays (e.g. bentonite). Three different methods were carried out: Na-acetate method (Bouwer et al., 1952), Cu-triene method (Kahr and Meier, 1996; Kaufhold and Dohrmann, 2003), and $BaCl_2$-method (Dohrmann, 1997)**.** The Cu-triene method and the $BaCl_2$ method provide comparable values of 3 to 9 meq/100 g. The Na-acetate method provides values between 17 to 103 meq/100 g. It is an open discussion whether the enormous differences in CEC are dependent on pH values (Na-acetate: pH 8.2, Cu-triene and $BaCl_2$: pH 5 to 6) and/or the accessibility of the various molecules to the inner hollow sphere of the allophane.

Further the retention of phosphate (Blakemore et al., 1987) was investigated. The allophane-rich specimen adsorbed 99 wt.-% of the utilised phosphate ($KH_2PO_4$; initial concentration: 1 mg P/ml). Reference material like iron hydroxide (goethite) and zeolite (clinoptilolite) adsorbed 50 and 83 wt.-% of the initial phosphate concentration, respectively.

## SPECIAL PROPERTIES AND POTENTIAL APPLICATION FIELDS

Allophane is known as a good adsorber for organic matter, some anions (e.g. phosphate, arsenate) and water. This natural 'special clay' has a high specific surface area (BET method, nitrogen) with a maximum of 320 $m^2/g$. Further investigations will concentrate on the enhancement of the SSA by different pre-treatments.

Another interesting property is the low content of total organic carbon (TOC) of less than 1.5 wt.-% and locally less than 0.4 wt.-%. This may be important for industrial applications.

The adsorption of water was investigated at different relative humidity. The allophane-rich specimens adsorbed high amounts of water. At a relative humidity of 20 % the specimens adsorbed 10 wt.-% of water and at a relative humidity of 90 % up to 30 wt.-% were adsorbed. The high water affinity causes problems during processing procedures like grinding. The result are smearing and sticky aggregates. For different applications special processing has to be employed

Due to the interesting properties of allophane-rich material, primarily the high specific surface area, it could be used in the following applications:

- The ability of allophane to adsorb high amounts of organic matter and some anions like phosphate and arsenate makes it a suitable candidate in the field of wastewater treatment, which focuses on the adsorption and flocculation of toxic substances and organic matter. In this respect the selective sorption of other toxic substances (e.g. chromate) by allophane-rich materials has to be investigated. Furthermore allophane has a variable surface charge which is depending on the pH value of the surrounding solution. Therefore the flocculation could be controlled by different pH values.
- The water affinity of allophane, which is comparable to zeolites, is a further characteristic. Allophane could be used as drying material and furthermore as a heat accumulator. Hence it is necessary to investigate the capacity of water uptake and the influence of different drying cycles.

There are a lot of possible applications for the 'special clay' allophane from Santo Domingo, especially in the field of environmental technology. The most important thing, from the technical point of view, is to optimise the processing with respect to the application. However, the decisive aspect for the worldwide competitiveness of allophane products is the final price.

## LITERATURE

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