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# AMORPHOUS MATTER IN KAOLINS AND ITS GEOLOGICAL IMPLICATIONS

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**Abstract:** Selective dissolution with ammonium oxalate was carried out to extract amorphous matter in some kaolins from China. Ammonium oxalate extraction is an effective method to extract amorphous constituents without destroying the kaolinite crystalline structure. The study showed that, absolute amounts of amorphous constituents in kaolins are in the order Al > Si > Fe, but that relative amounts are in the order Fe > Al > Si. The amorphous phases are probably mainly in the form of separate particles, or colloidal particles absorbed on the surface of kaolinite particles. Compared to older kaolins, younger kaolins contain much more amorphous iron content.

**Key words:** amorphous matter, kaolin, extraction
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## INTRODUCTION

There are many reports on using silicate gel and oxide gel to synthesize kaolinite, but few on the gels and amorphous material in natural kaolin. Clays can be regarded as consisting of both crystalline minerals and noncrystalline materials (Smith and Mitchell, 1987). The existence of amorphous material in the form of oxide and hydrous oxide gels, sometimes in the form of allophane, opal, *etc*. in clay was known long ago. Amorphous aluminosilicate, the soluble silicate and aluminate in certain alkaline solutions, affects clay dispersion. This work's selective dissolution method proved effective for extracting various kaolin amorphous phases in soils (Wilson, 1987) and plays a very important role in the characterization of kaolinite minerals. Quantitative measurement of extractable aluminium, iron and silicon can help much in getting better understanding of kaolin behavior and physical properties.

## MATERIALS AND METHODS

Relatively pure kaolinites from selected geological ages were used to extract amorphous materials from them. Kaolin's mineral composition, kaolinite crystallinity and geological sequences and origins were investigated in detail by Shen (1994, 1995, and 1996) and are summarized in Table 1. Chemical compositions of the major oxides were measured by XRF using the fusion method. The results for $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ are listed in Table 2.

Amorphous constituents were extracted by selective dissolution as described by Smith and Mitchell (1987). Ammonium oxalate solution was prepared by mixing 700 ml ammonium oxalate solution (28.3 g/l) with 535 ml 0.2 M oxalic acid (25.3 g/l) and after adjustment to pH = 3, was stored in a polyethylene bottle. Then, 200 mg kaolin clay ( < 100 mesh) and 80 ml 0.2 M ammonium oxalate at pH = 3 were put into a 100 ml polypropylene centrifuge tube. The mixture was shaken in the dark for four hours in a big black plastic container to ensure that only amorphous phases were dissolved (Smith and Mitchell 1987). The supernatant solution, obtained after centrifuging at 3000 r/min for 10 minutes, was siphoned into a 200 ml volumetric flask and diluted to the mark with distilled water. Duplicate samples were prepared for the amorphous phase analysis. With this procedure,

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Smith and Mitchell (1987) emphasized, only amorphous constituents will dissolve into the solution. The soluble elements were finally determined with an ARL 3580B ICP analyzer for Fe, Al and Si which were the most abundant amorphous phases.

**Table 1 Kaolins used for this study**

| Samples | Geological environments | Origin | Hinckley index | Mineral compositions(%) |
|---|---|---|---|---|
| Kao-1 | Altered acidic tuff in upper Jurassic Moshishan Formation, Zhejiang Province | Hydrothermal | 0.75 | Kaolinite: 98<br>Quartz: 1<br>Goyazite: 1 |
| Kao-2 | Kaolin from coal seam of upper Permian Longtan Formation, Zhejiang Province | Sedimental | 0.76 | Kaolinite: 96<br>Anatase: 2<br>Quartz: 1<br>Pyrite: 1 |
| Kao-3 | Kaolin from coal seam of middle Carboniferous Formation, Zhejiang Province | Sedimental | 0.92 | Kaolinite: 96<br>Illite: 2<br>Quartz: 1<br>Anatase: 1 |
| Kao-4 | Kaolin from coal seam of middle Carboniferous Benxi Formation, Liaoning Province | Sedimental | 1.30 | Kaolinite: 98<br>Geothite: 1<br>Anatase: 1 |
| Kao-5 | Kaolin from coal seam of middle Carboniferous Benxi Formation, Liaoning Province | Sedimental | 0.91 | Kaolinite: 40<br>Illite: 40<br>Geothite: 13<br>Quartz: 7 |

**Table 2 Extractable elements and their contents**

| Samples | Chemical composition (%) | | | Extractable elements ($\times 10^{-6}$) | | | Ratio of soluble matter | Percentages in the total elements (%) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | Fe | Al | Si | Si/Al | Fe | Al | Si |
| Kao-1 | | | | 180 | 4015 | 1235 | | | | |
| | | | | 125 | 4030 | 1320 | | | | |
| Average | 46.36 | 39.27 | 0.21 | 152 | 4023 | 1278 | 0.30 | 10.34 | 1.93 | 0.59 |
| Kao-2 | | | | 380 | 1600 | 805 | | | | |
| | | | | 380 | 1635 | 870 | | | | |
| Average | 44.82 | 37.87 | 0.75 | 380 | 1618 | 836 | 0.50 | 7.24 | 0.81 | 0.40 |
| Kao-3 | | | | 215 | 2800 | 1600 | | | | |
| | | | | 315 | 2820 | 1435 | | | | |
| Average | 44.59 | 39.28 | 0.93 | 265 | 2810 | 1518 | 0.52 | 4.08 | 1.35 | 0.73 |
| Kao-4 | | | | 415 | 5910 | 2000 | | | | |
| | | | | 395 | 5945 | 2060 | | | | |
| Average | 44.26 | 39.01 | 1.47 | 405 | 5928 | 2030 | 0.33 | 3.94 | 2.87 | 0.98 |
| Kao-5 | | | | 3105 | 2385 | 1645 | | | | |
| | | | | 3095 | 2345 | 1635 | | | | |
| Average | 44.35 | 24.24 | 12.38 | 3100 | 2365 | 1640 | 0.67 | 3.58 | 1.84 | 0.79 |

Note: $Fe_2O_3$ was measured as total iron; The average represents average value of two parallel experiments; Ratio of soluble matter = (amount of extractable Si/Si atomic weight) ÷ (amount of extractable Al/Al atomic weight); Percentage in the total element was calculated by dividing the extracted content by the total content of the element analyzed by XRF.

## RESULTS AND DISCUSSIONS

Selective extraction with ammonium oxalate solution was thought to be an effective method to dissolve amorphous phases in soils. It could dissolve amorphous Fe, Al and Si compounds, but had almost no affect on geothite and hematite, well-crystallized silicates and clay minerals. Only very poorly or not-crystallized aluminum silicate compounds with a high Al to Si ratio, colloid particles, amorphous Fe, Mn oxides and hydrous oxides could be dissolved. Two conditions ensuring dissolution of amorphous Al, Si and Fe compounds are pH value and dark environment.

Samples of the amorphous constituents were analyzed in parallel (Table 2). Ammonium oxalate dissolution technique indicated kaolin clays contained a certain amount of extractable or soluble elements. The present study showed that part of Si, Al and Fe exists presumably as amorphous materials.

## THE EXISTENCE FORMS OF AMORPHOUS Fe, Al AND Si

The extractable Si amount was $805 \times 10^{-6} - 2060 \times 10^{-6}$, being 0.35% – 0.85% in total Si; Al amount was $1600 \sim 5945 \times 10^{-6}$, being 0.70% – 2.63% in total Al; and Fe amount was $125 - 310 \times 10^{-6}$, being 3.46% – 11.69% in total content. The Si/Al values indicated that Al was more readily extracted, reflecting that Al forms amorphous material more easily than Si. However, Fe most readily formed amorphous material. Thus, the extraction showed that the amounts of amorphous material formed were in the order Fe > Al > Si. Figure 1 clearly illustrates these relations. The descending order from Fe to Al to Si, the amount of amorphous materials indicates possible relation with absorption of their colloids with various charges. Generally, clays and $SiO_2$ colloids have negative charges, Al and Fe hydroxides positive charges. To keep electrical neutrality, kaolinite preferably absorbs positive charges of Al and Fe hydroxides. In this process, $Fe^{3+}$ has an obviously larger ion diameter (0.064 nm) than that of Al (0.051 nm) and hence, is more easily absorbed. At least, part of these absorbed Al, Fe and Si colloids were formed during the formation of kaolinite from the ambient medium. However, it is possible that the surface bond of the kaolinite absorbed the colloid particles with positive charges (Dixon, 1989).

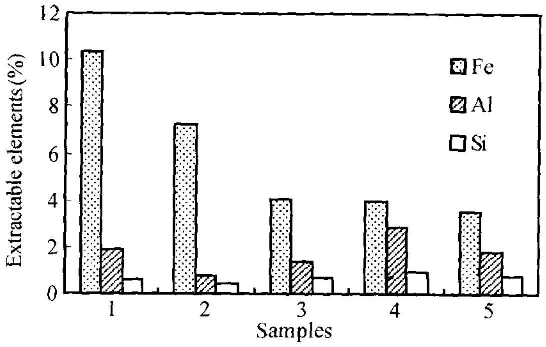

**Fig. 1** **Histogram showing the percentages of soluble Fe, Al and Si in their total contents**

On the other hand, the amounts of extractable elements do not follow the stoichiometry of kaolinite, indicating that the amorphous material occurs not in poorly disordered "kaolinite" but in the other phases such as pseudoboehmite. These extractable elements are therefore presumably present as amorphous oxides and hydroxides (Weaver and Pollard, 1973). The amounts of extractable Al are apparently roughly proportional to extractable Si, though they do not follow the stoichiometry of kaolinite, indicating a possible complex amorphous material, rather than simple silicon oxide or aluminia oxide gel. We used SEM with EDX accessory to examine the sample kaol-3 and found several micrometer size Si and Al particles, among which Al content was always greater than Si content by EDX, similar to the chemical compositions of extractable elements, suggesting existence of independent amorphous Al, Si compounds. Because amorphous silica and alumina exist in kaolins, it is clear that considerable care must be taken in determining and interpreting the significance of the Si/Al ratio of kaolinites.

Furthermore, when Robertson and Eggleton (1991) investigated weathering of granitic rocks to form kaolinite, they found that successive analyses by electron microprobe showed a steady drop in the intensity of the Al by X-ray emission with time, indicating mobilization of these elements under the electron beam. This loss of Al as well as Si, K and Fe may reflect that the extractable ions occur not only in the form of amorphous material but also in the rims of crystal flakes. It is reasonable to expect that in poorly crystallized kaolinite, the content of these extractable elements will be more than that in well-crystallized kaolinite.

Amorphous material in rims of crystals was always found under high resolution transmission electron microscopy. Because the continuity of the crystal lattice is destroyed at the crystal rim, the lattice fringes disappear and an amorphous phase around the crystal occurs as a blurred image. This may also explain at least in part the existence of amorphous and extractable phases in kaolin clays.

## CRYSTALLIZATION OF AMORPHOUS MATERIAL

Theoretically, amorphous phases are unstable and tend to crystallize. Hence, a natural amorphous material will gradually change into a crystalline material if there is enough time and proper ambient conditions. According to this, we can infer that geologically older kaolin has less amorphous Al, Si and Fe than a young one. Figure 2 shows the percentage of amorphous Fe in kaolin gradually decrease in the order Jurassic > Permian > Carboniferous. This means that amorphous Fe took longer time to crystallize and penetrate into the lattice of the main phases.

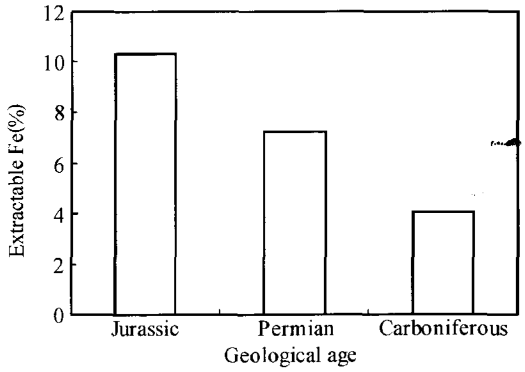

**Fig. 2 Histogram showing extractable Fe contents and geological ages**

$Fe^{3+}$ is recognized as an isomorphic substitution for $Al^{3+}$ at the octahedral site of kaolinite. However, a relatively big ion diameter difference between $Al^{3+}$ and $Fe^{3+}$ limits such a substitution. On the other hand, the $Fe^{3+}$ existing previous in the kaolinite octahedral site could be expelled during lattice ordering and substitution by $Al^{3+}$, which results in a self-purification process. Therefore, most $Fe^{3+}$ do not tend to penetrate into the kaolinite lattice but to form amorphous phase initially, thus forming geothite or limonite in oxidation environment and gregite in reduction environment (Wilkin and Barnes, 1997). In the studied samples, there was no obvious relation between geological ages and extractable Al and Si. This might indicate that amorphous Al and Si easily crystallize, most of them had already crystallized to kaolinite even in Jurassic. Comparison of our data with that of kaolinites from Cornwall, England, seemingly confirmed the above conclusion. Follett et al. (1965) found that kaolinites from Cornwall contained 3.1% – 4.9% of easily soluble $SiO_2$ and 1.5% – 5.9% of easily soluble $Al_2O_3$ which, he deduced, were positively charged hydrated ferric oxide colloids absorbed on kaolinite flakes. Similar experiments with Georgia kaolinite indicated that the amount of amorphous material varies as a function of particle size and preparation (Weaver and Pollard, 1973). Iron is the most frequently reported element substituted in kaolinite in these researches. Jefferson et al. (1975) noted that Fe-stained kaolinite could contain a maximum of 24.6 g/kg Fe extractable with concentrated HCl. Georgia kaolin also contains HCl soluble iron, comprising 5% to 15% of the total iron content (Brindley et al., 1986).

As to the absorption mechanism, a permanent negative charge on kaolinite from isomorphous substitution has been postulated (Dixon, 1989). The permanent negative charge attributed to kaolinite could also be a result of interstratification of kaolinite with smectite (Lee et al., 1975).

Such absorption occurs not only in natural process, but also in experiment. In an investigation of sodium amylobarbitone release by different crystallinity of kaolinite, Delgado et al. (1994) found that the higher the crystallinity of a kaolinite, the greater the release of the barbitone, the weaker the fixation of sodium amylobarbitone. This may be easily understood from the fact that kaolinite with lower Hinckley index has more amorphous content.

## AMORPHOUS MATERIAL AND KAOLINITE CRYSTALLINITY

The Hinckley index of kaolinite was calculated from the XRD pattern in 22° – 25°2$\theta$(CoK $\alpha$ radiation), which indicated the degree of b-axis ordering of a kaolinite. In a number of kaolinite samples measured, we found that even in the same geological location, the same stratigraphical layer, the kaolinites showed various crystallinities. For example, kaolinite widely distributed over the roof and floor of a coal seam of upper Permian Longtan formation in northern Zhejiang Province, China had various Hinckley indexes from 0.3 to 1.0. The reason for the variation in crystallinity is still not clear (Wilson, 1987). Synthetical kaolinite experiments proved that the crystallinity depends on the ambient pH value and time. Crystallinity is improved with longer time crystallization. However, the natural process is more complex. In general, kaolinite developed in relatively older environment shows better crystallinity. In this study, amorphous Fe content obviously decreased with Hinckley index increase, suggesting Fe's self-purification during kaolinite crystallization.

The difference of the enthalpy of kaolinite formation is insignificant (Deligny et al., 1999). Thus the geological occurrence of various crystallinities must be interpreted in terms of kinetics or as the result of a special process with amorphous effect rather than as resulting from changes in the thermodynamics.

## CONCLUSIONS

1. Ammonium oxalate selective dissolution technique is useful for characterization of amorphous phases in clays. Amorphous materials exist in kaolin clays. This study showed that the percentages of amorphous phases of Fe, Al and Si, compared to their total contents respectively, are in the order Fe > Al > Si.

2. The amorphous phases of kaolinite are possibly dominated by absorption by the kaolinite surface bond; a small part comes from the lattice rim that does not carry a neutral charge.

3. Among kaolins with various geological ages, the younger ones contain obviously more amorphous Fe; but it is not the same case with amorphous Si and Al.

4. Kaolinites with higher crystallinity have less amorphous Fe, while amorphous Al and Si are relatively unchanged.

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