

NACRITIC CLAY ASSOCIATED WITH THE JIANGSHAN-SHAOXING DEEP FAULT IN ZHEJIANG PROVINCE, CHINA

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Abstract—A kaolin clay occurring in Carboniferous mudstone near the Jiangshan-Shaoxing deep fault in Zhejiang Province, eastern China was characterized by XRD and IR. Although the dominant mineral appeared to be kaolinite, IR also suggested the possible occurrence of nacrite. This was confirmed by forming intercalation complexes with potassium acetate and with hydrazine hydrate, both water complexes having the same characteristic spacing at 8.35 Å. Different particle size fractions of the kaolin clay were studied and the results indicated that nacrite content increased with increasing particle size. This occurrence of nacrite is consistent with previous findings of the polytype in high temperature and pressure environments.

Key Words—Jiangshan-Shaoxing fault, Kaolin, Nacritic clay.

INTRODUCTION

The Jiangshan-Shaoxing deep fault is a major structural feature which traverses Zhejiang Province and divides it into two distinct geological zones (Figure 1). To the northwest is the Yangtze paraplatform, a relatively stable tectonic area dominantly composed of sedimentary rocks ranging from the Sinian (Pre-Cambrian) System to the Lower Triassic Series. To the southeast is the South China fold system which is commonly overlain by Yanshanian (Mesozoic to Cenozoic) volcanic and acid igneous rocks. The fault itself has been active since Proterozoic times when it was initiated (BGMZP 1982; Ren *et al* 1987).

Kaolin clay deposits are located on both sides of the fault, several hundred metres away from its centre. On the northwest side is the Yejiatang Formation of Lower Carboniferous age which consists of rhythmically deposited grey quartz conglomerate, sandstone, siltstone, claystone (mudrock) and carbonaceous claystone with unworkable coal beds. On the southwest side occurs the Lixiang Formation of Upper Permian age, which is also comprised of terrestrial coal-bearing clastic rocks. On both sides of the fault the rocks have suffered great compression and shear leading to an intensely twisted and fractured appearance. The kaolin deposits have a lenticular or bed-like form and extend about 1200 m along the strike. They have massive structure and are characterized by a very fine grained pelitic texture and conchoidal fracture. Because of rhythmic sedimentation there are 3–4 such kaolin beds in the Yejiatang Formation.

The different kaolin polytypes can be characteristic of certain types of environment. Thus kaolinite gen-

erally occurs in weathering, hydrothermal and sedimentary environments whereas dickite is usually associated with high temperatures. Nacrite is the rarest of the kaolin polytypes and is most often associated with high temperature and pressure conditions. However, Bühmann (1988) has recently recorded nacrite as occurring in a low temperature authigenic environment. Identification of the kaolin polytypes by X-ray powder diffraction (XRD) is not difficult when they are present in a relatively pure form but certainly dickite and nacrite can be easily overlooked if they are admixed with substantial quantities of kaolinite (Wilson 1987). In these circumstances definite confirmation requires the use of other techniques and supplementary methods. The complementary use of IR and XRD proved to be very useful in the identification of dickite in North Sea sandstones (Ehrenberg *et al* 1993) and the use of intercalation complexes with K-acetate (Wada 1961) or hydrazine (Range *et al* 1969) should, in principle, be effective in distinguishing small quantities of admixed nacrite. In the present study both IR and intercalation techniques have been used to characterize the kaolin clays of the Jiangshan-Shaoxing fault, where *a priori* nacrite might be expected to occur.

METHODS

The samples were studied by XRD using a Philips 1130 X-ray diffractometer with CoK α radiation and by IR using a Perkin Elmer 580B IR Spectrometer. Intercalation procedures were based on those described for K-acetate (Wada 1961) and for hydrazine (Range *et al* 1969).

The K-acetate method enables kaolin group minerals

to be distinguished from non-complex forming minerals such as antigorite, chrysotile, chlorite, etc. Further treatment with NH_4Cl and NaCl enables various members of the kaolin group to be distinguished. Thus dickite forms no water complex at all, whereas nacrite forms a well-defined water complex with a basal spacing at 8.35 Å. The method described by Wada (1965) to form water complexes A, B and C is as follows.

Step 1

(Preparation A) Two grams of clay sample were ground with 3.5 g of KCH_3COO in an agate mortar with hand pestle for 20 minutes, and then placed with 20 ml of a saturated KCH_3COO solution in a 100 ml centrifuge tube fitted with a plastic stopper. The tubes were shaken for several minutes, allowed to stand for two days and centrifuged. The supernatant liquid was discarded. The resulting KCH_3COO complex was washed 3–4 times with distilled water until dispersion. The various size fractions were separated by centrifugation.

Step 2

(Preparation B) The KCH_3COO complex was immersed in 4 N NH_4Cl for 15 days. After that it was divided into two portions. One was suspended in 70 ml of 2 N NaCl . After one hour, the suspensions were centrifuged, another 70 ml 2 N NaCl was added and kept for two days with occasional shaking. This was followed by centrifuging and washing with water three times, and various fractions were collected by centrifugation. Oriented aggregates were prepared for XRD by drying clay/water suspensions on glass slides.

Step 3

(Preparation C) Another portion was immersed in 70 ml 5 N KCH_3COO solution and allowed to stand for one hour. It was then centrifuged, the supernatant discarded, another 70 ml 5 N KCH_3COO added, and kept for two days with occasional shaking. The preparation was washed with water three times. Various size fractions were collected by centrifugation, and the final slurry was pipetted on glass slides for oriented samples and dried at room temperature.

The method used for hydrazine intercalation was that described by Range *et al* (1969) where they divided the kaolinite-halloysite minerals into four different types. The complex was formed by simply dispersing 2 g clay in 20 ml hydrazine monohydrate, sealing it in a test tube with a glass stopper and allowing to stand at 65°C for seven days with occasional shaking. This was followed by centrifugation and washing with distilled water three times. Two kinds of slides were prepared for each sample; firstly by pipetting the hydrazine slurry directly onto the glass slide and the second after the hydrazine had been replaced with water. Various particle sizes were separated by centrifugation in order

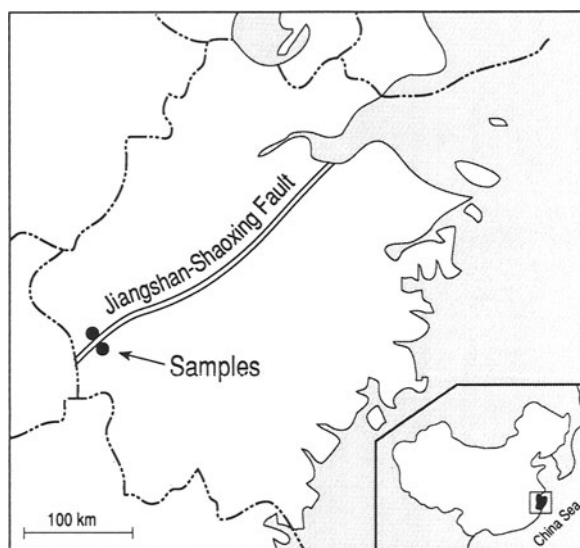


Figure 1. Location map showing Jiangshan-Shaoxing Fault in Zhejiang Province and sampling points.

to determine the relative abundance of kaolin polytypes in these fractions.

RESULTS AND DISCUSSION

General characterization

The XRD pattern of the clay is dominated by a kaolin mineral with strong basal reflections at 7.14 and 3.58 Å, with minor amounts of illite and chlorite. The complete diffraction pattern indicates that the kaolin mineral is mainly well-ordered kaolinite (Hinckley Index = 1.06), but weak reflections at 3.45, 3.09 and 2.41 Å indicate the possibility of a small amount of nacrite. IR spectroscopy tends to confirm this interpretation. The spectrum clearly shows OH-stretching bands at 3695, 3652 and 3620 cm^{-1} indicating a dominance of kaolinite, but careful observation shows an extra weak band at 3629 cm^{-1} (Figure 2) suggesting the possibility of nacrite (Farmer 1974; Russell 1987). This band has been attributed to the inner hydroxyl groups of the nacrite structure. According to Russell and Kirkpatrick (1992), IR is able to distinguish nacrite from other kaolin minerals down to a concentration of 10% weight or less. However, because the XRD reflections and the IR absorption band attributed to nacrite are exceedingly weak, it was essential to seek confirmatory evidence through the employment of intercalation techniques.

K-acetate and hydrazine intercalation

K-acetate intercalation of the bulk clay yields sharp but relatively weak reflections at 14.0 and 8.35 Å and a broad peak at 10.06 Å. Replacement of the K-acetate by NaCl or NH_4Cl followed by water washing yields a reflection at 8.35 Å which is characteristic of nacrite

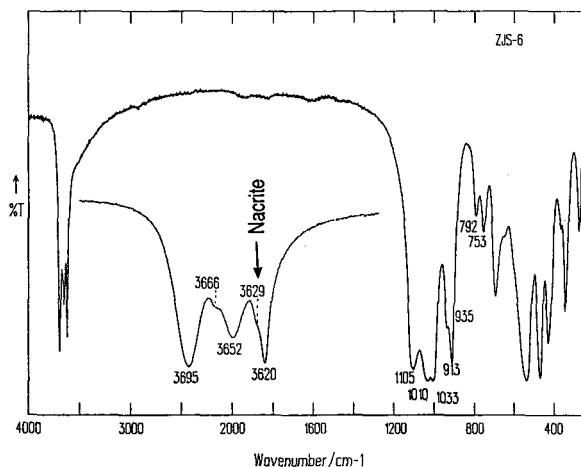


Figure 2. IR spectrum of bulk kaolin clay showing predominance of kaolinite with a weak band at 3629 cm^{-1} characteristic of nacrite.

(Wada 1965). Kaolinite itself yields a weak intercalated complex at 7.30 \AA . Similar results were obtained with the hydrazine intercalated samples. A broad weak peak at $10.3\text{--}10.4\text{ \AA}$ appeared which was replaced by a sharp reflection at 8.35 \AA after water washing. This result is not consistent with any of the four types of kaolinite described by Range *et al* (1969) but is consistent with the presence of nacrite, particularly when compared with the results of the K-acetate tests.

Particle size and nacrite content

Because scanning electron microscopy shows that the clay is made up of a range of particle sizes, from $<1\text{ }\mu\text{m}$ to $>5\text{ }\mu\text{m}$ in diameter, intercalation complexes were prepared for the fractions <1 , $1\text{--}2$, $2\text{--}5$ and $>5\text{ }\mu\text{m}$. Figures 3 and 4 show that there is a noticeable increase in the nacrite content of the coarser particles after treatment with both K-acetate and hydrazine. The 8.35 \AA reflection of the nacrite intercalate is sharp and strong in the $>2\text{ }\mu\text{m}$ fraction, but yields only a weak reflection in the $<1\text{ }\mu\text{m}$ fraction. Figure 5 shows the relationship between particle size and the ratio of the basal spacing intensities at 8.35 \AA and 7.16 \AA . It is clear that this ratio increases rapidly with increasing particle size, suggesting that nacrite occurs predominantly in thicker domains which might be expected to have more regular stacking than in the finer fractions.

Data were obtained from the XRD patterns of various preparations of a K-acetate intercalated clay (Table 1), where the peak widths at half maximum height for the 7.16 \AA reflection for kaolinite and the 8.35 \AA peak for nacrite hydrate were measured and the domain thickness calculated by the Scherrer equation. It can be seen that the total domain thickness of kaolinite plus nacrite decreases slightly with particle size but by no more than 10% which may not be statistically sig-

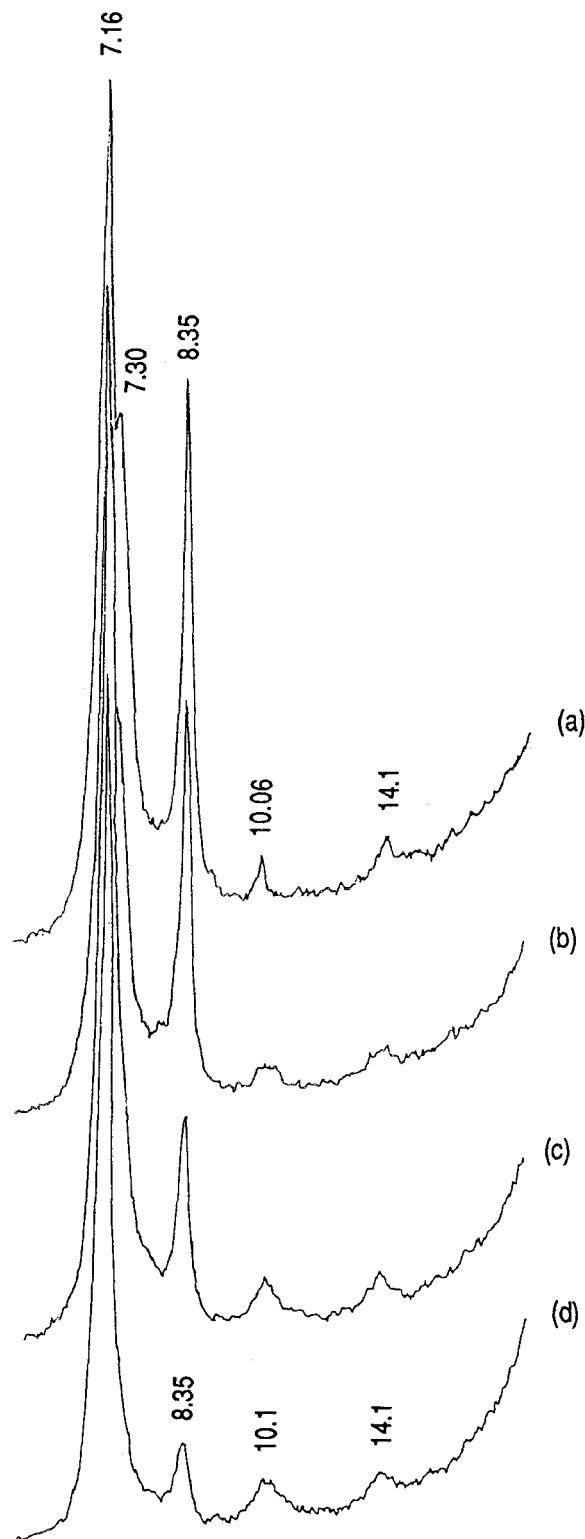


Figure 3. XRD patterns of K-acetate intercalations (Preparation B) for (a) $>5\text{ }\mu\text{m}$, (b) $2\text{--}5\text{ }\mu\text{m}$, (c) $1\text{--}2\text{ }\mu\text{m}$ and (d) $<1\text{ }\mu\text{m}$ fractions of kaolin clay.

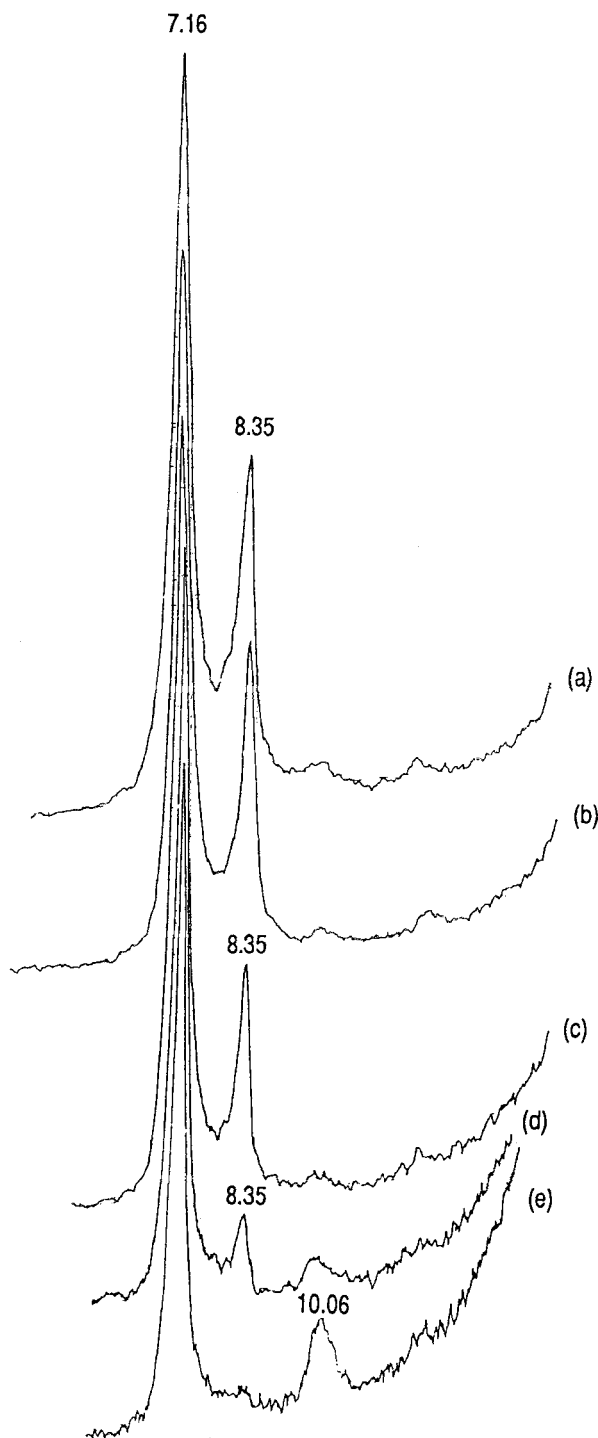


Figure 4. XRD patterns of hydrazine intercalations for (a) $> 5 \mu\text{m}$, (b) $2\text{--}5 \mu\text{m}$, (c) $1\text{--}2 \mu\text{m}$, (d) $0.5\text{--}1 \mu\text{m}$ and (e) $< 0.5 \mu\text{m}$ fractions of kaolin clay.

nificant considering the uncorrected nature of the peak width data. On the other hand, the thickness of the nacrite domains increases by about 30% as that of the kaolinite domains decreases by about 20%. This re-

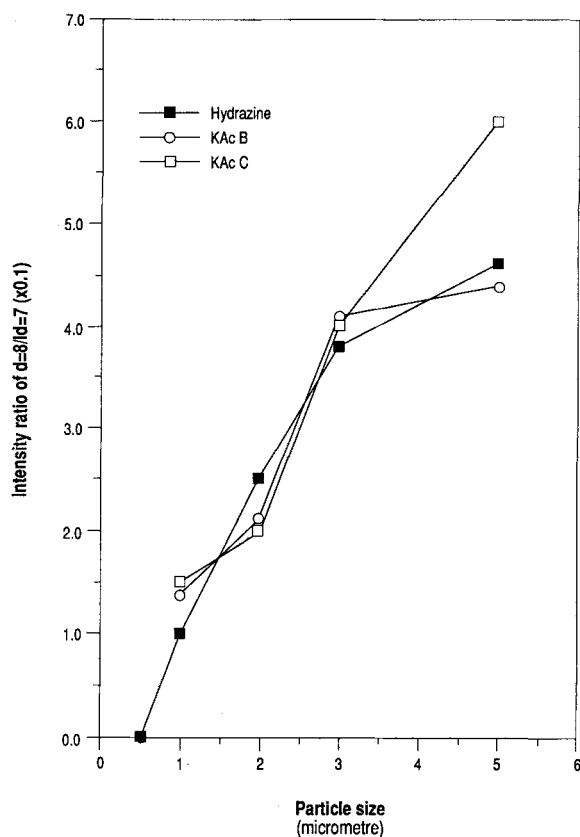


Figure 5. Relation between particle size and intensity ratio ($8.35 \text{ \AA}/7.16 \text{ \AA} \times 0.1$) for kaolin clay.

lationship suggests that in a given kaolin domain increasing numbers of nacrite layers may occur at the expense of kaolinite layers.

Particle size and kaolinite intercalation

Figure 3 shows that K-acetate treatment yields a peak at 7.30 \AA which is interpreted as indicating partial intercalation. This spacing is well-resolved in the $> 5 \mu\text{m}$ fraction and is represented by an inflection at about 7.40 \AA in the $2\text{--}5 \mu\text{m}$ and $1\text{--}2 \mu\text{m}$ fractions. In the finest $1 \mu\text{m}$ fraction, however, the basal reflection for kaolinite at 7.16 \AA becomes sharp suggesting that an intercalation complex is not formed in the finest particle sizes. This is consistent with the findings of Wie-

Table 1. Intensity (I) ratios, peak widths (Δ) and calculated domain thicknesses (DT) of particle size fractions of ZJS-6 sample after intercalation with K-acetate (Preparation C).

Particle size (μm)	I $8.35 \text{ \AA}/7.16 \text{ \AA}$	$\Delta 2\theta 7 \text{ \AA}$ (mm)	DT7 (\AA)	$\Delta 2\theta 8 \text{ \AA}$ (mm)	DT8 (\AA)	ΣDT (\AA)
> 5	0.60	4.3	218	3.9	241	459
$2\text{--}5$	0.40	3.8	247	3.8	247	494
$1\text{--}2$	0.20	3.5	268	4.3	218	486
< 1	0.15	3.4	276	6.0	156	432

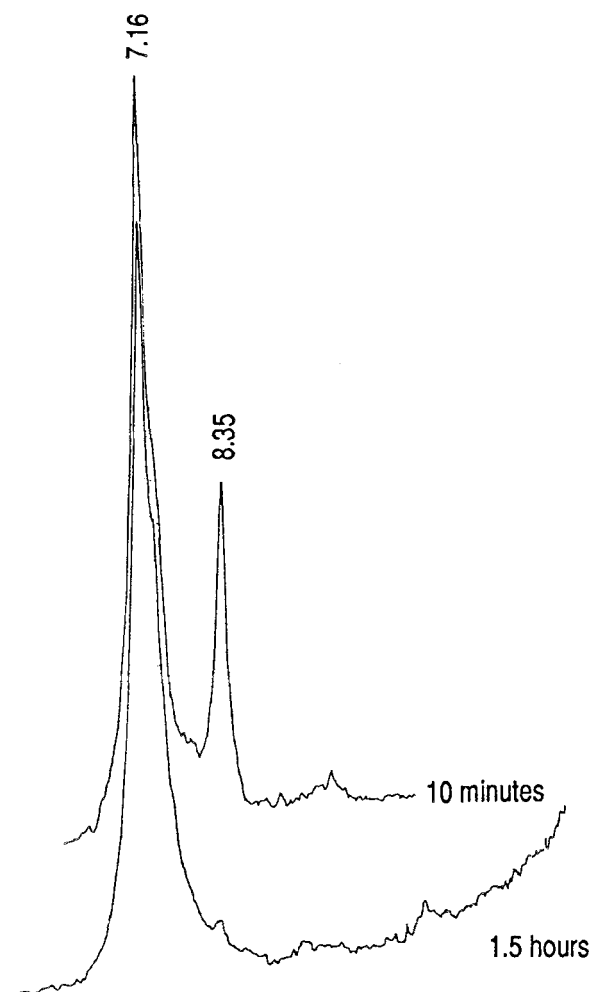


Figure 6. XRD patterns of K-acetate intercalation after ethylene glycol solvation showing disappearance of nacrite hydrate after 1.5 hours.

wiora and Brindley (1969) that kaolinite intercalation decreases as particle size becomes smaller.

Stability of nacrite hydrate

Wada (1965) proposed a structure for nacrite hydrate to account for the 8.35 Å spacing. The hydrate contains two water molecules per formula unit which lie flat in the hexagonal oxygen cavities with the oxygen of the water molecule being slightly tilted at one end so that the OH bond is directed downwards. This arrangement gave good agreement between observed and calculated intensities of the 001 reflections.

The 8.35 Å peak of the nacrite hydrate studied here is sharp and is accompanied by a higher order at 4.17 Å. The spacing was found to be stable at 65°C and at room temperature for 20 days, which is consistent with the observed dehydration peak for nacrite hydrate at about 100–120°C on the DTA curve (Wada 1965). However, when the nacrite hydrate was placed in a

desiccator with ethylene glycol vapour at 65°C for two hours, the intensity of the 8.35 Å reflection rapidly decreased, and after four hours it had almost completely disappeared (Figure 6). This phenomenon suggests that the polar water molecule in the hydrate is not stable in the presence of a non-polar molecule like ethylene glycol causing the structure to collapse. This response could be used as a further confirmation of the presence of nacrite.

Origin of the kaolin clays

There seems little doubt that the kaolin clay studied here was initially deposited in a deep swamp, terrestrial environment. This is indicated by proximity to coal seams and to the finding of abundant fossil plants in the sequence, including *Neuropteris gigantea*, *Sphenopteris* sp. and *Archaeocalamites* sp. (BGMZP 1982). The rhythmic sedimentation observed throughout the sequence is also compatible with a littoral swamp environment. The original source material for the kaolin clay is less certain. Using the method of Spears and Kanaris-Sotiriou (1976, 1979) the quartz content of the clays was plotted against the $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio. The plot obtained suggests that the source rocks were derived from both sedimentary and basic volcanic ash materials which, from the abundance of kaolinite, must have been deeply weathered in the source area. Kaolinite derived from weathered profiles and soils is typically poorly ordered, but as shown above the kaolinite in this deposit is rather well-ordered with a Hinckley Index of about 1.1. A change from poorly ordered to well-ordered kaolinite may therefore have occurred after sediment deposition and burial. In this connection it may be significant that according to the hydrazine intercalation technique of Range *et al* (1969) the bulk of the kaolinite in this deposit would be classed as fireclay-type kaolinite, a form which does not form intercalation complexes with hydrazine and is typically poorly ordered. It is speculated that the lack of hydrazine reactivity in this relatively well-ordered kaolinite may perhaps be related in some way to its previous history.

During Yanshanian times multiphased tectonic movements along the Jiangshan-Shaoxing deep fault brought about higher temperatures and pressures characteristic of green schist facies metamorphism. In the NE–SW trending linear fault basins there is evidence of widespread chloritization, hydrothermal activity, as well as the development of schistose and cataclastic structures. It seems likely that during compression and compressive shear movements along the fault the coarser grained kaolinite particles were either able to adjust their structure or recrystallized to form nacrite. It is relevant that nacrite associated with a major shear zone of the Southern Uplands Fault in Scotland has recently been recorded (Russell and Kirkpatrick 1992). This study reported here was part of a wider investi-

gation of Chinese kaolinitic clays (115 samples from a variety of geological environments) all of which were examined by XRD and IR. Nacrite was found only in the clay reported here. It is evident that the association of nacrite with a major fault must be of genetic significance but the precise P-T conditions for the formation of this mineral require more detailed study.

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