

## A COMPARISON BETWEEN THE CHINA CLAY DEPOSITS OF CHINA AND CORNWALL

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In the People's Republic of China kaolin deposits are found in a wide range of geological settings both in the coastal and the inland provinces of southern China. Major deposits, predominantly kaolinitic, were produced by alteration of arkosic sediments in the Tertiary Basin of Maoming in Guangdong Province, while extensive halloysitic-kaolinitic assemblages are located on acid intrusive and volcanic sequences formed during the Yanshanian magmatic cycle (Late Mesozoic) throughout southern China. A brief description of the chemistry and mineralogy is given and shows a great deal of variation often reflecting the differing host rocks. The morphology of the sedimentary Maoming kaolinites is platy in nature with a typical pseudo-hexagonal shape and is very similar to the morphology of kaolins from Devon and Cornwall. The morphology of the altered volcanics and granites is dominated by tubular halloysite and stacky to platy kaolinite. Halloysite is not found in deposits from Devon and Cornwall. A stable isotope study ( $\delta D$ ,  $\delta^{18}O$ ) from Chinese deposits shows that the sedimentary derived kaolinites with a platy morphology have isotopic compositions clustered along the "kaolinite line" but they show a considerable range. Samples from the other deposits with a mixed tubular and platy morphology have isotopic compositions that fall above this line. Previous isotopic work on kaolins with a platy morphology studied from Cornwall and the Czech Republic plot near the "kaolinite line". It is tentatively suggested that the occurrence of kaolinites and halloysites shows a close relationship with isotopic compositions and is governed by the origin and formation of the deposit in question.

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### INTRODUCTION

The term China Clay was given to kaolin discovered in Cornwall some 250 years ago and the mineral name kaolinite was derived from a hillside near the village of *Gaoling* in Jiangxi Province, China from where clay was traditionally mined to supply the nearby famous porcelain factories in Jingdezhen. The objective of the present study was to identify kaolin deposits in China and characterise them on the basis of their morphology, mineralogy, isotopic composition and potential commercial utilisation and to compare them with the kaolin deposits from Cornwall. The study was sponsored jointly by *ECC International Limited* and *NERC* as a project financed as part of the Extractive Industry Partnership Scheme (*EIPS*). The paper will consider the wide range of kaolins found in different geological environments in China and focus particularly on the shape and morphology of the clays and their relationship to their formation on the basis of isotopic studies.

### CHINESE KAOLIN DEPOSITS

Kaolin deposits in China have been formed from a wide variety of rocks but the largest primary resources have been derived from the alteration of granitic rocks and their extrusive equivalents. These rocks were emplaced during the major Mesozoic cycle of magmatism, named the Yanshanian, which affected a large area of the folded basement terrain of Southern China. The Yanshanian was also an epoch for mineralisation with tungsten, tin and rare earths of economic importance.

A classification of Chinese kaolin deposits has been proposed by Zhang *et al.* (1982) as follows:

- I. Hydrothermal alteration - Primary
- II. Weathering residual
- III. Weathering leaching
- IV. Sedimentary - Secondary

Some of the areas studied are shown in Figure 1 covering the location of kaolin deposits visited during the *NERC-EIPS* "Kaolins of South China Project" with more detail on the kaolin deposits of Guangdong Province shown in Figure 2. A brief description of some of the deposits studied based on the original host rock is now considered:

#### *Altered Granites:*

***Gaoling.*** This is the classic locality from where the name kaolin was derived. The alteration of the coarse-grained lithium-rich muscovitic albitic granite gave rise to an assemblage of halloysite and kaolinite. The presence of the lithium-rich mica Zinnwaldite has been recorded from the area. The original workings supplied clay for the production of porcelain in the Imperial kilns at Jingdezhen. The manufacture of fine porcelain continues at Jingdezhen although the original deposit of Gaoling was exhausted in the 1960's. Large quantities of clay of similar quality remain nearby at Dazhou and Xingsi.

***Longyan.*** The Donggongxia mine in the Longyan District is the largest deposit known in Fujian Province and was discovered as a result of exploration for Ta-Nb mineralisation in the albitemuscovite-zinnwaldite granite which forms the upper part of the biotite granite pluton. It has an age of 140-150 MY and is of early Yanshanian age.

The deposit is characterised by low iron and titanic levels which make it very suitable for ceramics, especially porcelain. The pluton shows vertical zoning from biotite granite at depth through albite-zinnwaldite granite to albite-muscovite granite in the upper levels. The clay is a mixture of halloysite and kaolinite with some illite present along quartz filled fractures.

**Zhanjiang.** There are a large number of deposits of kaolinised granite in the Zhanjiang area of Guangdong Province, some of which are exploited by the *Zhanjiang Kaolin Development Company*. The clay is again a mixture of halloysite and stacks of kaolinite and the kaolinised matrix often has a high yield of clay (up to 35% at -15 microns refining) and good brightness (up to 88-90 ISO). The clay has a poor viscosity which limits its use as a coating pigment but it shows good potential as a paper filler and for ceramics.

**Kaolinised Volcanics - Suzhou.** The kaolin deposits of the Suzhou area (Figure 1) are located in the Yangshan Hills and surrounding area about 20 km west of the city of Suzhou and 90 km due west of Shanghai. Several bodies of kaolinised ground have clearly originated by hypogene hydrothermal alteration of Yanshanian granite porphyry intrusives, there has also been some re-working of the argillic products in the karstic cavity system. The largest of the outcropping bodies of kaolinisation is at Guanshan. The zone of kaolinisation follows the unconformity between the Jurassic volcanic rocks which are acid tuffs and breccias cut by porphyry dykes. The kaolin body has been produced by intense hydrothermal alteration of the acid volcanic rocks and associated dykes. Sericitisation,

silicification and pyritisation accompany kaolinisation. The present workings are now underground and the blocks of clay-rock extracted show contorted lenticular and wavy laminations which could be the result of tectonic deformation. Alunite nodules up to 50 cm in diameter occur in the clay rock and fresh pyrite is also evident. There is a main set of north-north-east trending fault structures which have helped govern the location of the kaolinised zones. The *Suzhou Kaolin Company* produces a wide range of products for the paper, ceramic, paint and other industries. The morphology of the clay is dominantly halloysite with the presence of more kaolinite nearer to the surface.

**Sedimentary kaolin - Maoming.** The Maoming Basin in south-west Guangdong Province consists mainly of arkosic sediments which have been deposited and subsequently kaolinised. The main areas currently being mined are from the Shange, Xiachi and Shangtung sectors which are Pliocene to Miocene in age (Figure 3). Various kaolinitic sand layers are separated by oil-shales which are commercially exploited for their oil content. The morphology of the kaolin from all horizons of the basin are euhedral with no evidence of tubular halloysite. The kaolin shows a good brightness and viscosity and is suitable for paper coating, paper filling and ceramics (Yuan and Murray, 1993).

#### MORPHOLOGY OF KAOLIN

The morphology of some of the Chinese kaolinite-halloysite and kaolinite assemblages are shown in Figure 4 and compared to a

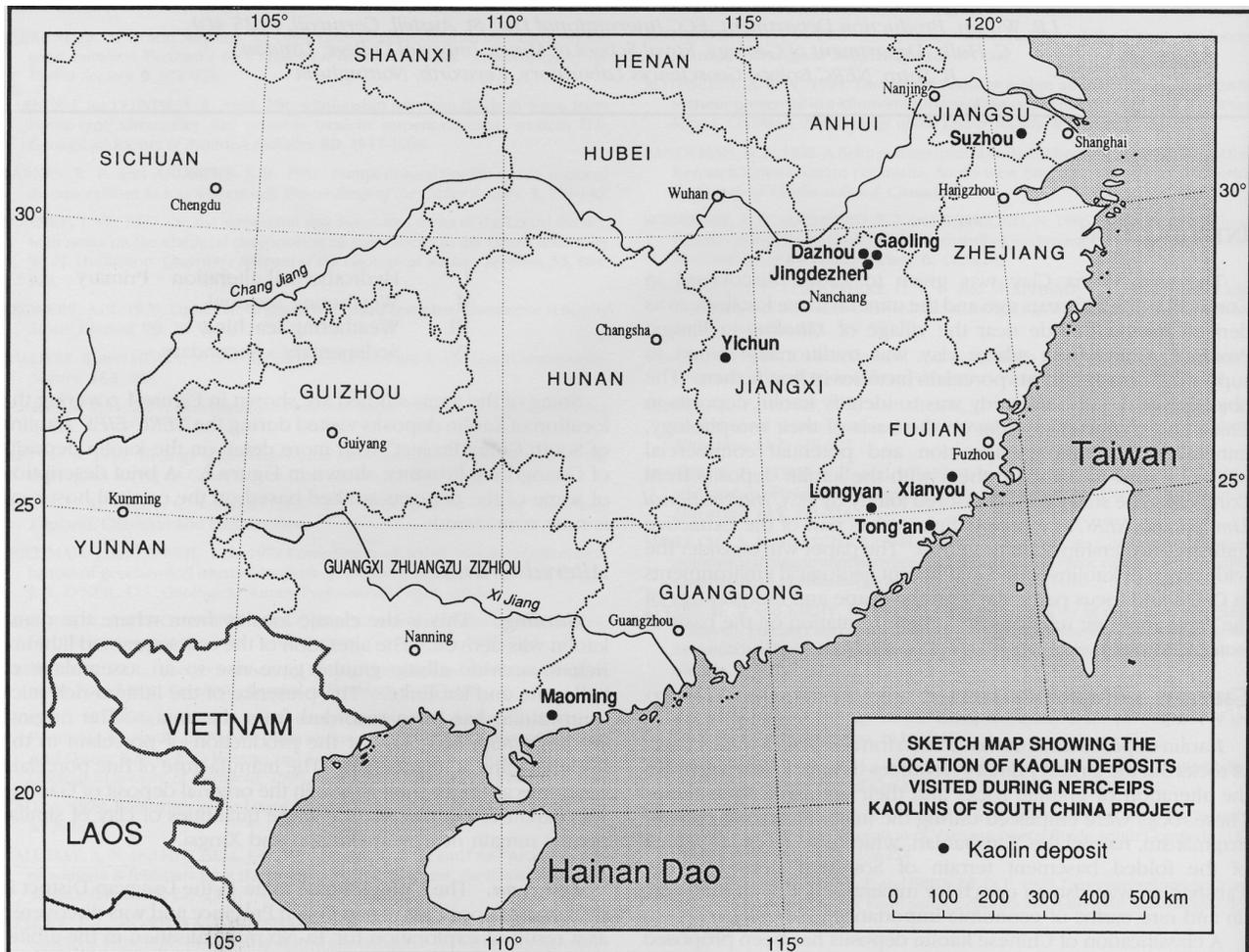


Figure 1. Map showing the location of some of the deposits studied during the NERC-EIPS kaolins of South China Project



Figure 2. Map showing the kaolin deposits of Guangdong Province, China (References - Wen (1991) and Zhou and Lin (1991) - personal communications)

sample of kaolinite from Cornwall. The only sample of purely kaolinitic clay identified in this study from China is the sedimentary kaolin from Maoming. All others shows a mixture of varying amounts of halloysite with stacky and platy kaolinite.

**CHEMISTRY AND MINERALOGICAL OF CHINESE KAOLINS**

Some chemical and mineralogical analyses of Chinese kaolins are shown in Table 1 and compared to an *ECC International Ltd* ceramic clay product, *SSP*. The halloysitic-kaolinitic assemblages from the kaolinised granites exhibit a range of iron and titania. The Longyan clay is dominantly halloysite and this shows low iron and titania levels which makes it very suitable for ceramic utilisation.. The volcanic-derived halloysite from Suzhou shows much higher levels of iron and titania which would limit its use as a high grade ceramic material for porcelain. It also shows the presence of 1% of alunite which is typically found in volcanic sequences. *Super Standard Porcelain (SSP)*, a kaolin produced from the Lee Moor (Dartmoor granite) area by *ECC International Limited*, shows low iron and titania levels (similar to Longyan) and is used in high quality ceramics. The *SSP* is a kaolinite whereas the Longyan clay is dominantly halloysite.

**ISOTOPIC COMPOSITIONS OF CHINESE KAOLINITES**

A stable isotope study ( $\delta D$ ,  $\delta^{18}O$ ) was carried out on several different deposits from different geological environments. It became clear in the early part of the investigation that a proper understanding of the particle size distribution and mineralogy was important. Most kaolin fractions generally contain some mica, quartz, feldspar and

	KAOLINISED GRANITES			VOLCANICS	SEDIMENTARY	ECC SSP
Deposit	Zhanjiang	Longyan	Dazhou	Suzhou	Maoming	Cornwall
Refining $\mu m$	-5	-15	-15	-15	-5	-5
%+10 $\mu$	0	11	11	6	0	1
%-2 $\mu$	78	43	22	74	80	85
Chemistry (wt.%)						
SiO <sub>2</sub>	47	47	49	47	47	46
Al <sub>2</sub> O <sub>3</sub>	38	38	36	38	38	38
Fe <sub>2</sub> O <sub>3</sub>	1.06	0.3	0.58	0.84	0.68	0.39
TiO <sub>2</sub>	0.28	0.01	0.02	0.33	0.11	0.03
CaO	0.06	0.06	0.06	0.13	0.06	0.1
MgO	0.06	0.15	0.06	0.06	0.08	0.22
K <sub>2</sub> O	0.38	0.41	1.97	0.18	0.51	0.8
Na <sub>2</sub> O	0.2	0.2	0.86	0.01	0.07	0.15
L.O.I.	13.8	13.9	11.6	13.6	13.5	13
Mineralogy (wt.%)						
Kaolinite	96	96	76	96	97	93
Mica	4	3	17	0	2	4
Quartz	0	1	1	2	1	1
Albite	0	0	6	0	0	0
Alunite	0	0	0	1	0	0
Others	0	0	0	1	0	2

Table 1: Chemistry and mineralogy of some Chinese kaolin-halloysite deposit compared to a china clay from *ECC International Ltd* in the UK.

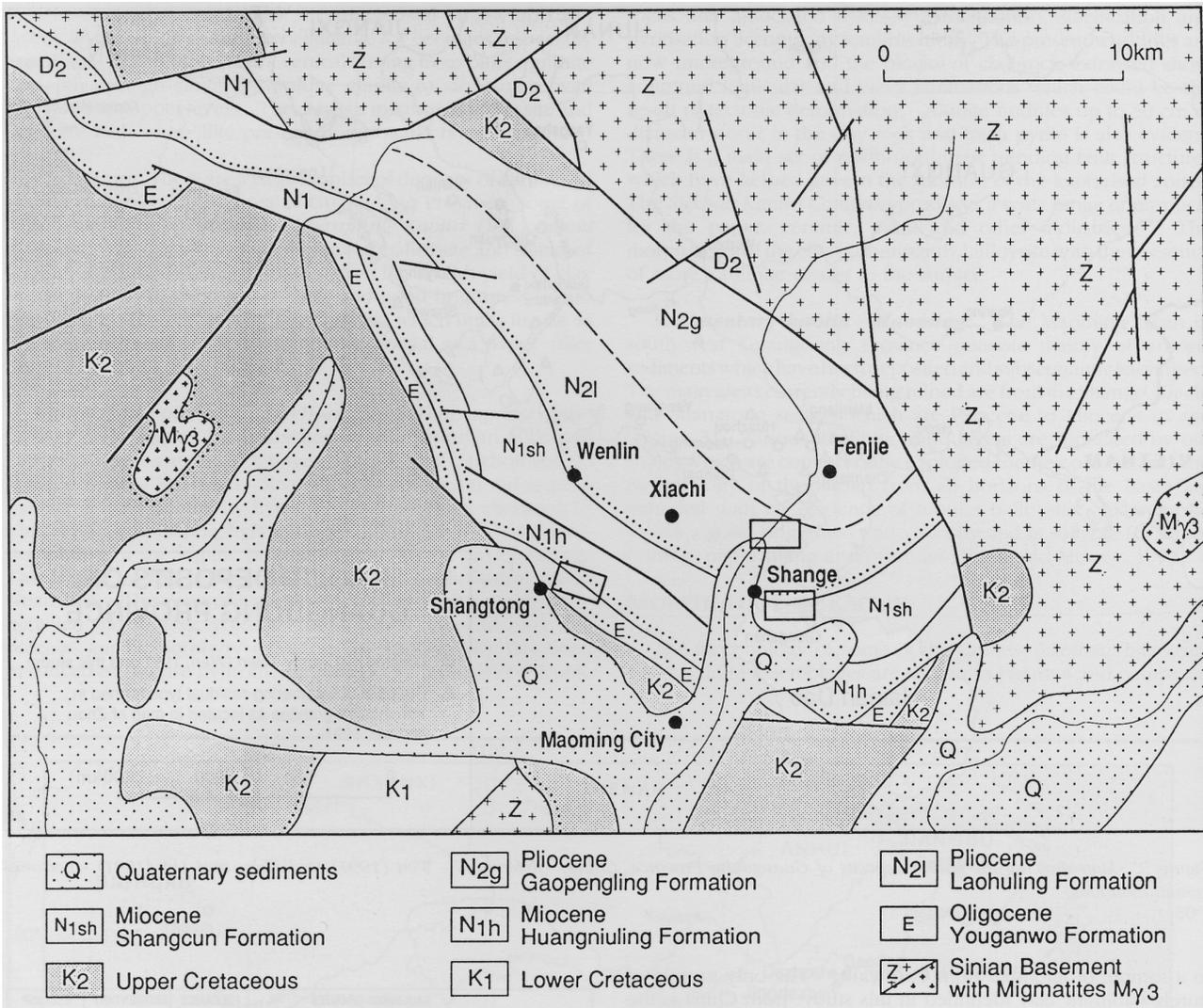


Figure 3. Map showing the geology of the Maoming Basin, SW Guangdong Province, China

Refining level	1 -53μ to +30μ	2 -30μ to +15μ	3 -15μ to +10μ	4 -10μ - +5μ	5 -5μ
CHEMISTRY (wt.%)					
SiO <sub>2</sub>	73	55	52	51	47
Al <sub>2</sub> O <sub>3</sub>	20	31	34	34	38
Fe <sub>2</sub> O <sub>3</sub>	0.4	0.67	0.66	0.65	0.7
TiO <sub>2</sub>	0.38	0.27	0.28	0.25	0.19
CaO	0.06	0.06	0.06	0.06	0.06
MgO	0.1	0.14	0.18	0.17	0.1
K <sub>2</sub> O	1.65	1.35	1.51	1.5	0.36
Na <sub>2</sub> O	0.19	0.2	0.2	0.2	0.25
L.O.I.	3.9	11.1	11.1	11.5	13.7
MINERALOGY (wt.%)					
Kaolinite	33	78	77	82	97
Mica	11	9	10	10	3
Quartz	51	11	10	8	0
Feldspar	5	2	3	0	0
ISOTOPIC COMPOSITIONS OF FRACTIONS					
δD‰ <sub>SMOW</sub>	-110	-82	-85	-72	-71
δ <sup>18</sup> O‰ <sub>SMOW</sub>	12.6	17	16.5	17	19.2

Table 2: The chemistry, mineralogy and isotopic content of different fractions of the same sample from the Maoming Sedimentary Kaolin.

other minerals depending on their origin. For the isotopic study a fine fraction (generally less than 80wt% <2 microns) was tested. The first step in the isotopic study was to illustrate the variation of mineralogy and chemistry from one sample from the Maoming deposit refined to five different levels. In addition δD and δ<sup>18</sup>O levels were measured for each of the increments (Table 2). The isotopic results show that the coarse fraction has the lowest δD and low δ<sup>18</sup>O, the finest fraction (-5μm) has the highest δD and δ<sup>18</sup>O and the intermediate values are similar to the finest. These results of size fractions of a single sample probably represent mixing of detrital feldspar, quartz and mica with kaolinite.

The second step in the isotopic study was to examine samples of kaolinite-halloysite from a wide range of geological environments. Given the variations experienced from Maoming (Table 2) all further samples tested were first refined to approximately 80wt.% <2μ so that the material was dominantly kaolinite and/ or halloysite. The isotopic compositions of kaolinites-halloysites from weathered and altered granites and volcanics and the sedimentary kaolinitic sands from China are plotted in Figure 5 and show a wide variation. Geological evidence suggested that all the investigated deposits are of Recent or Tertiary age formed by surficial processes, or at shallow depth, and the fluid involved was meteoric. The results are surprising as they show lower δ<sup>18</sup>O than expected for the respective δD. All the isotopic compositions which plot near to the kaolinite line are the

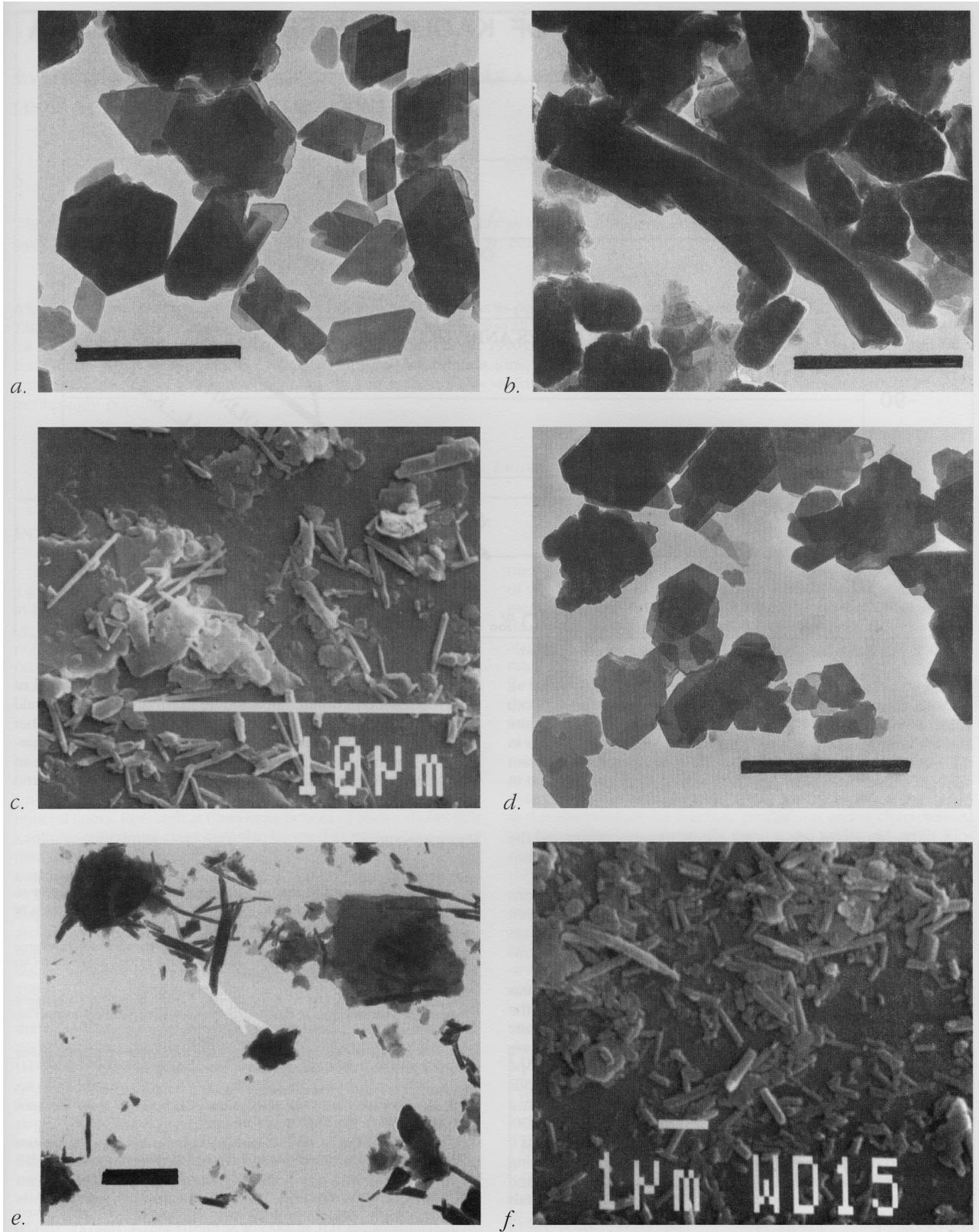


Figure 4. Transmission (TEM) and Scanning Electron Microscopy (SEM) of some Chinese kaolin and halloysites compared to a TEM of a kaolin from south-west England.

Bar scale on all photomicrographs =  $1\mu\text{m}$ , except (C) =  $10\mu\text{m}$ . (A) TEM of Maoming sedimentary kaolin showing well formed pseudohexagonal platy kaolinite. (B) TEM of type locality of Gaoling showing a mixture of large halloysitic tubes with irregular shaped kaolinite. (C) SEM of altered granite from Zhanjiang showing a mixture of stacky kaolinite and tubular halloysite. (D) TEM of kaolinised granite from south-west England showing pseudohexagonal shaped kaolinite. (E) TEM of halloysite and stacky kaolinite from the altered granite at Donggongxia Mine, Longyan. (F) Dominantly halloysitic assemblage from the altered volcanic rocks of Qinshan underground mine, Suzhou Kaolin Company.

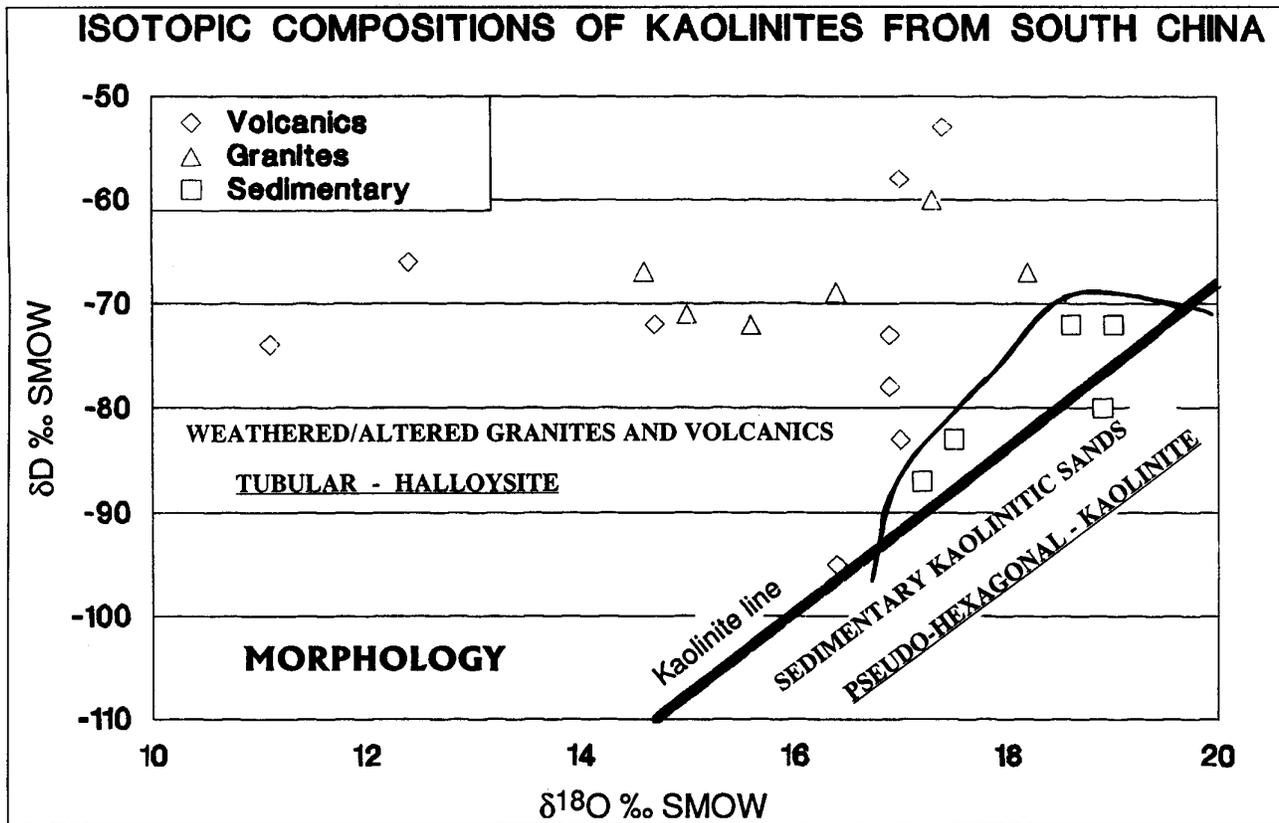


Figure 5. Plot of isotopic compositions of kaolinites from South China

Maoming sedimentary kaolinites and exhibit a platy morphology whilst all of those samples that lie above the kaolinite line are derived from volcanic and granitic rocks and are a mixture of tubular halloysite and kaolinite. The observed pattern may reflect differences in the isotopic composition but also the grain size of the parent material. Two lines of interpretation need to be investigated in more detail:

1. The source of water is not purely meteoric water and the process took place at elevated temperatures such as the kaolins of south-west England (Sheppard, 1977),
2. The kaolinisation process has different isotope reactions for hydrogen and oxygen, and equilibrium has not yet been reached. The observation that the Maoming sedimentary clays are nearer the kaolinite line suggests that weathering of sediments and re sedimentation hasten the process.

Of interest though is the observation that the isotopic values for kaolins from south-west England (Sheppard 1977) and the Czech Republic (Konta, 1969; 1970), both show a similar kaolinite morphology and similar isotopic values to the sedimentary kaolins from Maoming. It was concluded from stable isotope studies that both the south-west England and Czech Republic kaolins are of weathering origin, probably being formed in a tropical to warm temperate climate (Savin and Epstein, 1970; Sheppard, 1977; Bristow 1993; Wilson and Jiranek, 1995) and it is suggested on the basis of the present study that the Maoming kaolins have a similar origin. The link between morphology and isotopic content is an interesting concept and is one that needs to be examined in more detail from a wider range of deposits in differing geological environments.

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