Thermochimica Acta, 200 (1992) 215–255
Elsevier Science Publishers B.V., Amsterdam

Approach to ancient Chinese artifacts by means of thermal analysis [1]

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(Received 24 January 1992)

INTRODUCTION

In the more than 6000-year history of China, arts and crafts played an outstanding role. Ancient Chinese art is notably conservative compared with that of Western culture and is characterized by evolution rather than by revolution. At the early beginnings of its history, Chinese society established a clearly defined social order that assigned appropriate behaviour and obligations according to one's rank and position. Within the framework of this organized and highly civilized society, the main concerns for the production of art were unique technical accomplishment and the dedication to truthful and direct artistic statements. All this is reflected by the perfection, simplicity and symmetry of such objects. The unique achievements which the Chinese attained (e.g. in bronze casting, jade carving, porcelain production and ink paintings) are evidence of a high degree of skill [1].

During recent centuries, exciting discoveries from China's earliest times have been made. Inscriptions on bronze, previously the only authentic records, have been supplemented by the excavation of oracles scratched on bone or shell, a handful of silk manuscripts, some of the wooden strips that formed the earliest Chinese books, and many other artifacts. Compared with the wealth of information on which the reconstruction of the preclassical Middle East has been based, it is still a meagre result, but ancient China is visible now with more clarity.

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[1] Presented at the 23rd Meeting of the Society of Calorimetry and Thermal Analysis, Hiroshima, Japan.

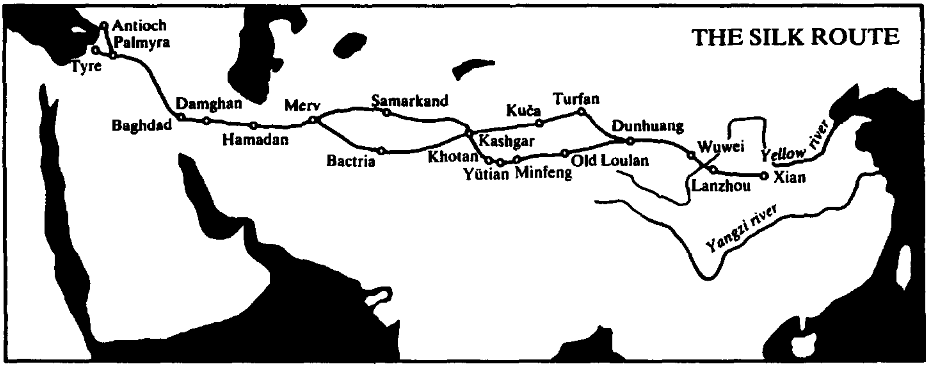


Fig. 1. The silk route.

The link between the Western world and ancient China was established via the famous Silk Road. This adventurous and risky route was used not only by merchants but also by famous explorers like Marco Polo, Sven Hedin, Albert von Lecoq, Paul Pelliot, Aurel Stone and others (Fig. 1).

Some of these people took the troublesome journey through the Pamir mountains, others travelled through the Gobi desert. By means of these important connections and contacts many new materials and products found their way to Europe. This paper will discuss some of the items that originated in ancient Chinese culture and tradition. The experimental work was carried out by use of thermoanalytical methods, such as TG, DSC, TMA and by X-ray diffraction and microscopy. A variety of products and artifacts were selected according to their availability and will be discussed in the order from inorganic to ceramics, metallic and organic materials. Table 1 shows a simplified chronology of the Chinese dynasties from ancient China to the present.

TABLE 1

Chronology

Neolithicum	6000–2000BC	Sixteen Northern-States	304–439
Xia Dynasty	21st–16th Century	Sui Dynasty	581–618
Shang Dynasty	16th–11th Century	Tang Dynasty	618–906
Western Zhou Dynasty	11th Century–771	Five Dynasties	907–960
Eastern Zhou Dynasty	770–256	Liao Dynasty	907–1125
Chunqiu Period	722–481	Song Dynasty	960–1279
Zhanguo Period	481–222	Jin Dynasty	1115–1234
Qin Dynasty	221–206	Yuan Dynasty	1279–1368
Western Han Dynasty	206BC–9AD	Ming Dynasty	1368–1644
Xin Dynasty	9–24	Qing Dynasty	1644–1912
Eastern Han Dynasty	25–220	Republic China	1912–1949
Three Kingdoms	220–265	Peoples Rep. of China	from 1949
Southern Dynasties	221–589		

JADE – THE STONE OF HEAVEN

Jade has been in use in China for almost 4000 years [3]. During that period a variety of semiprecious hardstones (e.g. chalcedone, amazonite, garnet) were collectively called "yu", corresponding to jade (Fig 2). These were fashioned into all kind of objects, mainly ritual and personal ornaments. Later, only two of these hardstones (nephrite (Ca-Mg amphibole) and jadeite (Na-Al pyroxene)) were recognized as fine jade. Of these, nephrite was available in ancient China, from the northern region of the river beds of Khotan and Yarkand. Jadeite was not known before the 17th Century and was brought from Burma for carving by Chinese artisans. Because of its much greater hardness, nephrite is not actually "carved" like jadeite, but ground or abraded. Today both nephrite and jadeite are widely used gem materials, and are difficult to distinguish by mere inspection.

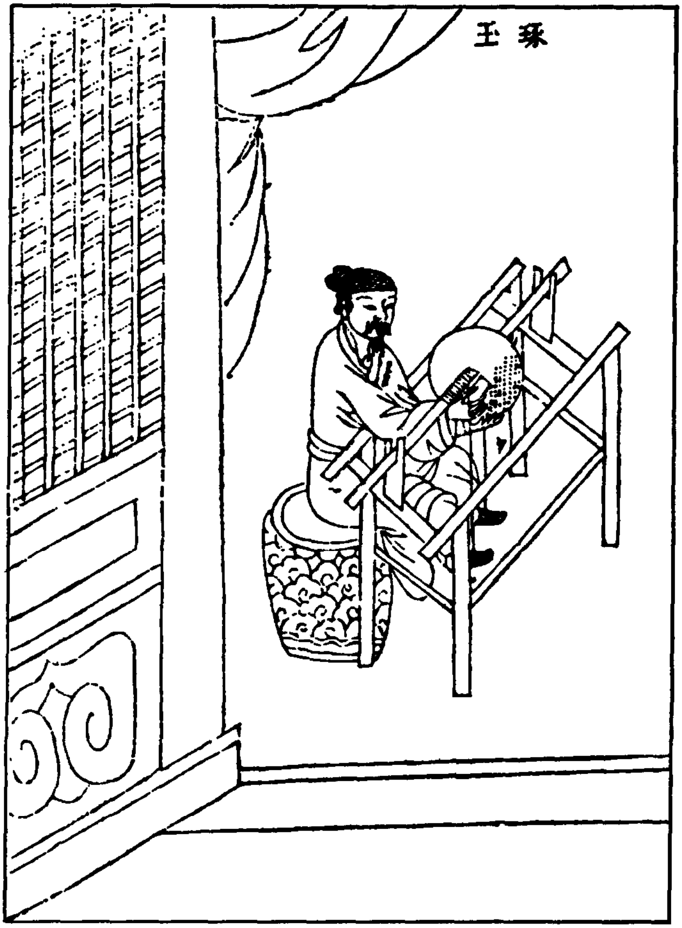


Fig. 2. Cutting jade.

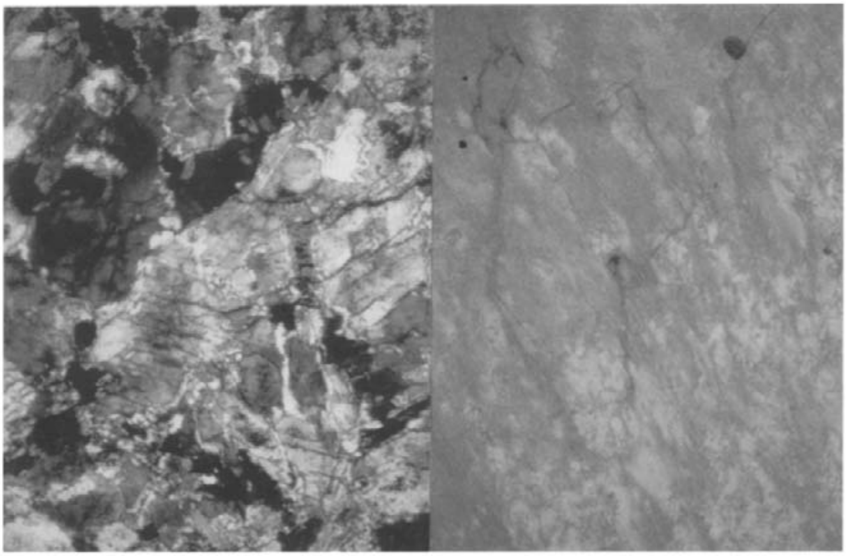


Fig. 3. Polarized light microphotographs of jadeite (left) and nephrite (right).

Thin sections of jadeite and nephrite show quite a strong difference; massive aggregates of interlocking, nearly equidimensional crystals in the case of jadeite and interlocking masses of fibrous crystals for nephrite (Fig. 3). The different structure of these minerals is also evident from their X-ray diffraction patterns. In addition, thermal analysis allows the distinc-

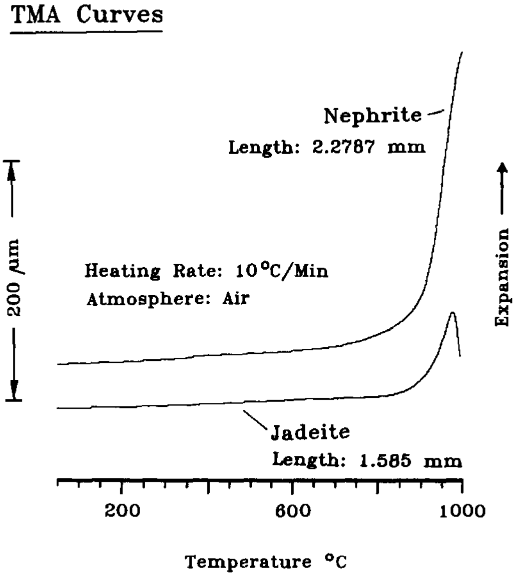


Fig. 4. TMA curves of jadeite and nephrite.

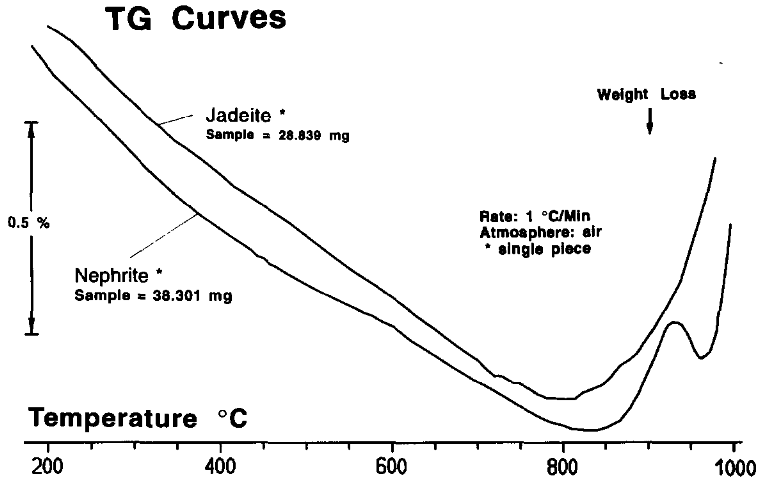


Fig. 5. TG curves of jadeite and nephrite.

tion between jadeite and nephrite. The TMA curves shown in Fig. 4 indicate that the strong increase in thermal expansion found for nephrite is due to the change of oxidation state of Fe and to the decomposition of the amphibole to diopside. This result could be confirmed also by TG analysis (Fig. 5). Jadeite and nephrite (especially) come in a variety of colours. The most valuable gem jade is the emerald green translucent form of jadeite, also called imperial jade. Jade objects were frequently decorated with superficial incisions that followed the general trend of bronze decoration.

Fig. 6. Funeral dress assembled from jade platelets.

Jade played also an important role in funeral rituals because it was thought to prevent physical decay and to help the soul to return to the body. Figure 6 shows a typical burial cloth covered with platelets of jade. Whether such clothes or objects have been exposed to heat can be derived from the change in colour and loss of translucence: from green to brown for nephrite, from green to white for jadeite. (Note: the colour change of jadeite from green to white takes place only with high heating rates of $< 10°\text{C min}^{-1}$, that means with rates of $1°\text{C min}^{-1}$ the colour remains unchanged.)

PEARLS AND CORALS – JEWELS OF THE SEA

The history of pearls is closely linked with the history of China [2]. As far back as 4500BC the Chinese praised and appreciated pearls as a symbol for riches, health and happiness. They were commonly called "tears of the angels". The discovery that fresh water oysters can grow pearls was also made in China in Hoowshow in the 13th Century. They are sometimes called China pearls, and are grown in a variety of shapes with different colours. Like other pearls they show the iridescent luster of the nacre. The art of growing these pearls in their natural surrounding has a long tradition in China. Cultured pearls require much patience and skill, and are grown in very clean waters, e.g. in the Taihu and Shanghai-lake, in the Jangtse and Pearl river. Pearls were also cultivated in salt water in bays along the coast; nowadays in several countries in the Far East and in Australia.

The distinction between natural and cultured pearls is possible by different methods. Under the microscope the natural pearl shows a rather

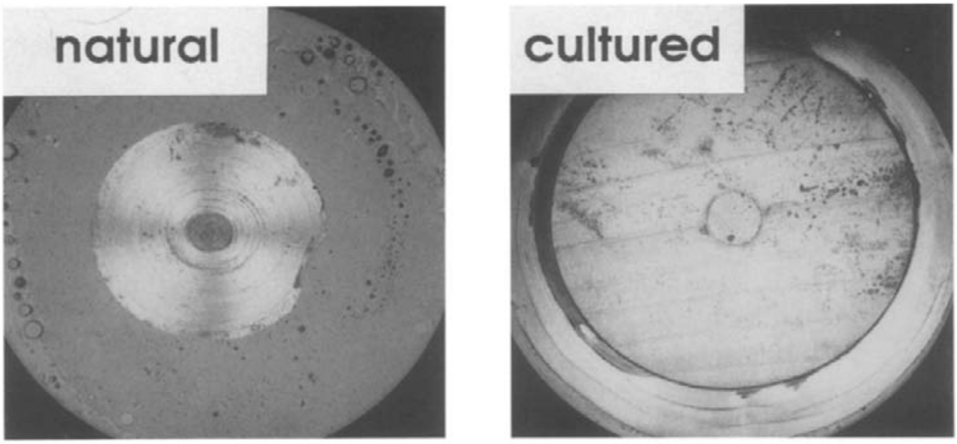


Fig. 7. Thin sections of a natural and a cultured pearl (original magnification ×10).

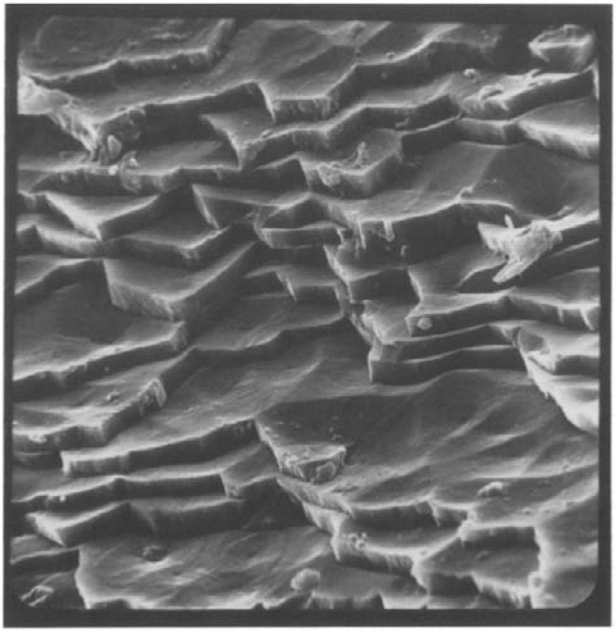


Fig. 8. SEM photographs of coarse crystalline aragonite layers of nacre pearl structure (original magnification ×400).

small core which is overgrown by concentric aragonite layers (Fig. 7). The cultured pearl on the other hand contains a rather big core cut out of mother of pearl which typically shows parallel layers of aragonite crystals. This core is implanted into the living oyster and acts as a seed crystal for the concentrically growing aragonite layers. The typical nacre structure of a pearl with the coarse crystalline aragonite layers can be seen in Fig. 8. All pearls are built up by $CaCO_3$ crystals (in the form of aragonite) bound together by collagen [4].

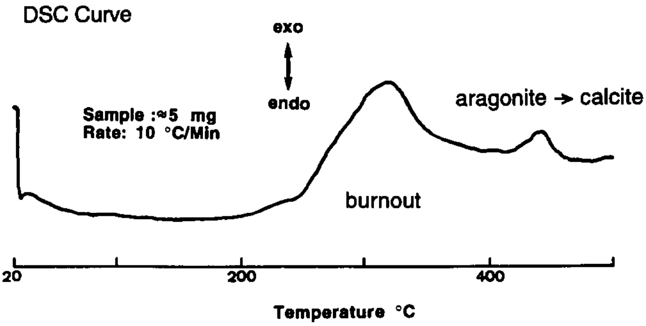


Fig. 9. DSC curve showing the transformation of aragonite to calcite.

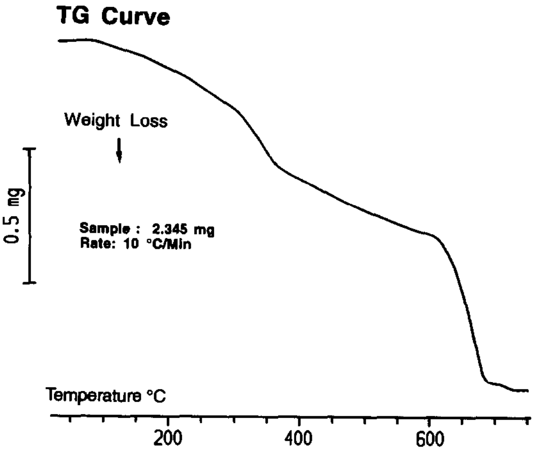


Fig. 10. TG curve of artificial coral.

Fig. 11. Artificial coral elephant.

The X-ray heating photograph of a natural pearl showed typically aragonite which transforms to calcite at about 550°C. DSC runs (Fig. 9) prove the burnout of the organic substance (exothermic peak 255°C) and the transformation from aragonite to calcite (exothermic peak at 410°C).

Another precious organic grown material which was known in ancient China was coral, especially in its red variety. It was used for jewellery, amulets, and as a talisman against all kind of diseases. The chemical composition of coral is similar to that of the pearl – calcium carbonate with conchyn which acts as binder. However, coral contains the $CaCO_3$ in the form of calcite, whereas the structure of the $CaCO_3$ in the pearls is aragonite.

Because of the rarity of the highly valued red coral, many imitations have been tried and are available, e.g. colouring of white corals, ivory, bone, plastics etc. with organic red dyes. These can be easily identified as such by extraction of the red dye with solvents and by various chemical and physical tests. Figure 10 shows a TG curve of a Chinese coral object (elephant) with the decomposition step of calcite at 600–700°C. The weight decrease at 200–300°C is due to the burnout of an organic material. Microscopic inspection proved that this elephant was formed from coral powder glued together with an organic binder. The red colour was artificial and could be extracted with alcohol. This proves that the elephant (which was sold as an antique in China) is an imitation (Fig. 11).

CLOISONNÉ — ORNAMENTAL ENAMEL ART

Cloisonné techniques can be traced as far back as approximately 3000BC to Mesopotamia, where lapis lazuli and turquoise were used for inlaid work. The Chinese enamelling process was developed much later and imported during the Yuan Dynasty, 1279–1368AD from Byzantium [5].

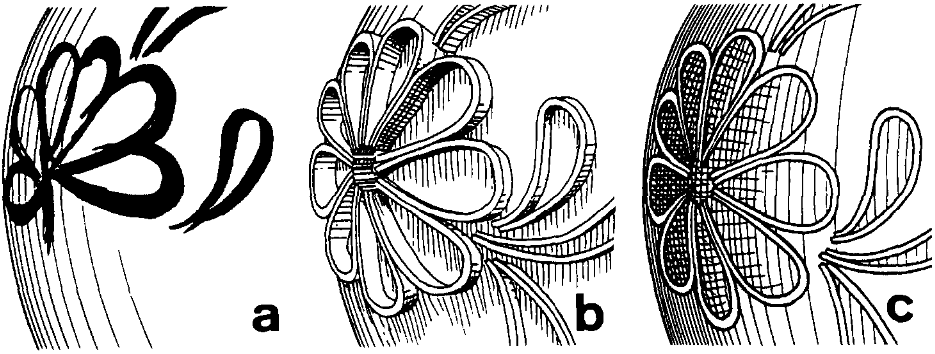


Fig. 12. Production steps of cloisonné: (a) outline, (b) soldering of wires, (c) final enamel.

The basic symbolic colours used by the Chinese were red, yellow, blue (green), white and black. Red stands for happiness and protection, yellow is the Emperor's colour, blue denotes high-rank and the clergy, white signifies sorrow and black is disaster or calamity. This is the reason that black is rarely seen. Of all the colours, blue-green or turquoise predominates and is indicative of Confucianism when used on altar implements, libation cups and sceptres (cult usage).

Calligraphic decors after often found. The common pictographs are: Shou for long life, Chuang XI for reciprocal happiness, and Fu for luck, as well as representation of the male. Here, particularly enjoyable are the representations of the eight immortal (Ba Xian) generals in Chinese history and Taoist sainthood. However, the Emperor and the Empress are never depicted.

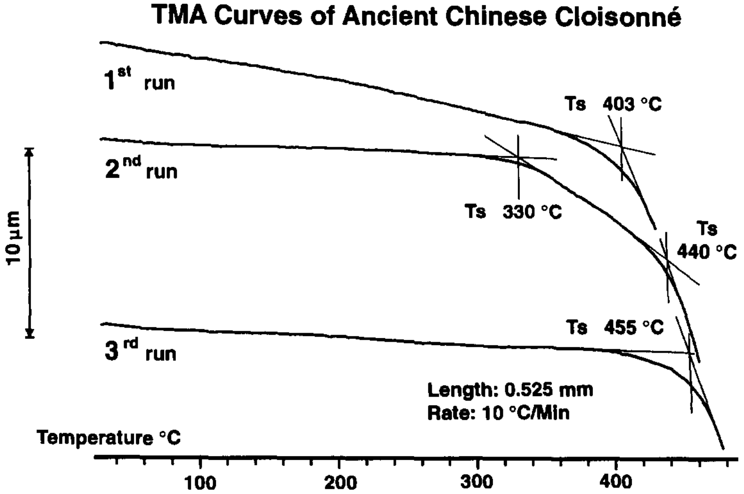


Fig. 14. TMA curves of ancient cloisonné.

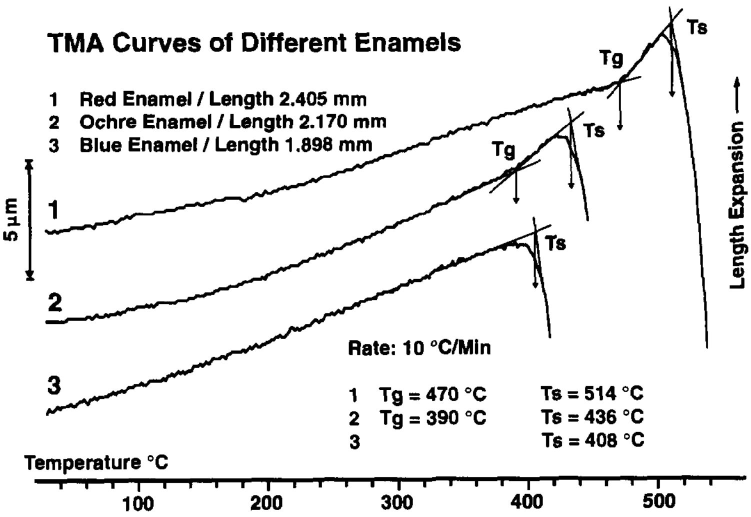


Fig. 15. TMA curves of modern cloisonné.

Cloisonné enamelling involves the preparation of a design of small wires or partitions (cloisons) which is soldered or fused on to the metal surface (Fig. 12). The segments of this design are filled with different powdered glass frits and heated in order to fuse the enamels to the partitions and to the metal substrate. After being ground and polished, this decorated surface displays a coloured enamelled design outlined by thin wires. Our TMA investigations were carried out on an ancient Chinese cloisonné plate (Fig. 13) and on coloured frits as they are used for modern Cloisonné ware. The TMA curves of the ancient Chinese cloisonné (Fig. 14) show a gradual shift of the glass softening point from 400°C to 455°C after repeated heating runs. This points to an unmixing or phase separation in such flux-rich glasses. A second softening point at 330°C could be found in a rapidly quenched sample (2nd run). The TMA curves of the modern coloured frit samples (Fig. 15) show different temperatures for the softening point and also for the transformation point, owing to the variation in the composition. Sample 3 (blue frit with the lowest softening point) was carefully annealed through the transformation range before the TMA run; therefore no discontinuity in the expansion curve is found below T_s.

EARLY MAN-MADE BLUE PIGMENTS FROM CHINA

Blue pigments used in ancient China were mainly made with cobalt-containing glass powders.

Recently, a study of ancient Chinese objects revealed another, so far

Fig. 13. Cloisonné plate (Ming Dynasty).

Fig. 33. Bronze Buddha (probably Cambodian provenance, last century) decorated with pipal leaf (the holy tree of Asia).

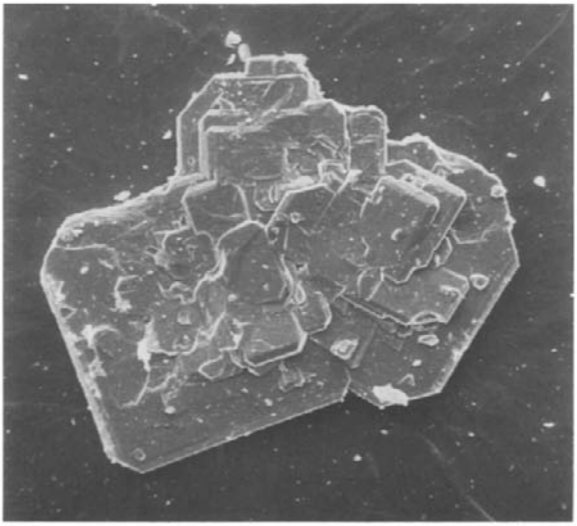


Fig. 16. SEM photograph of single crystal of $BaCuSi_4O_{10}$.

unknown, purplish-blue Ba-copper silicate pigment [6,7]. Its composition has been identified as $BaCuSi_4O_{10}$ (Fig. 16). The interesting point is its analogy to the Egyptian Blue $CaCuSi_4O_{10}$, which was invented and used in ancient Egypt a thousand years BC. Our experiments were carried out on the synthesis and thermal behaviour of such Ca-, Sr- and Ba-copper silicates. TG/DSC runs in different atmospheres proved that the thermal stability of the "Chinese Blue" is much higher than that of the "Egyptian

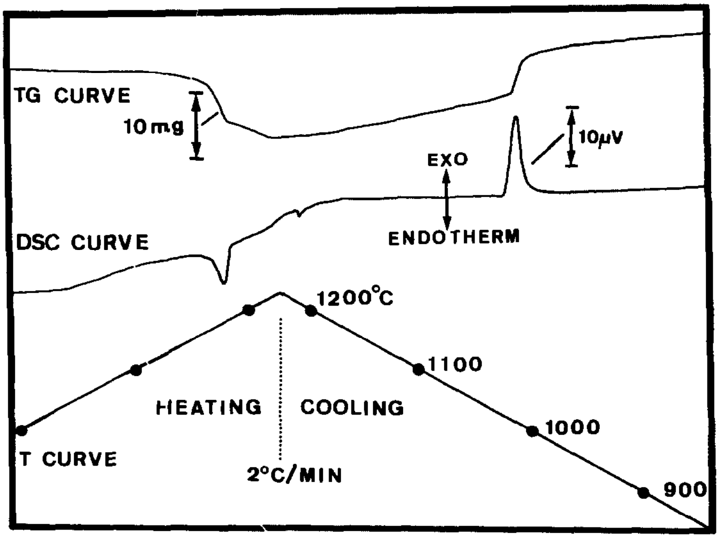


Fig. 17. TG and DSC curves of the synthesis of $BaCuSi_4O_{10}$.

Blue" (Fig. 17). The effect and the importance of adding fluxing agents in order to accelerate the reaction could also be established.

In the caverns of Mogaho near Dunang there exist wall paintings where the Ba-copper silicate was used for colouring. The caverns are known as the "Caverns of the 1000 Buddhas".

Also, a number of the terracotta soldiers of Xiang are decorated with colours which contain Ba-copper silicate.

CARBON MATERIALS FOR MAKING CHINESE TUCHE AND GUNPOWDER

Chinese tuche has been used for more than 3000 years [8]. The main ingredients in Chinese tuche are carbon black for colour and glue as a binder. The carbon black was charcoal produced by burning resin-bearing pine branches. Wood from the tree of life (*Thuya orientalis*) was occasionally used, and it had the advantage of producing a more intense black. The demands for quality inks increased steadily, and as wood became sacred the Chinese were forced to turn more and more towards using oil. By the 10th Century, hemp oil was commonly being used as the source of carbon black. The particle shape and size distribution of carbon is very important because it determines the quality and tint of the ink used for writing and painting. It depends strongly on the primary source, e.g. soot from different

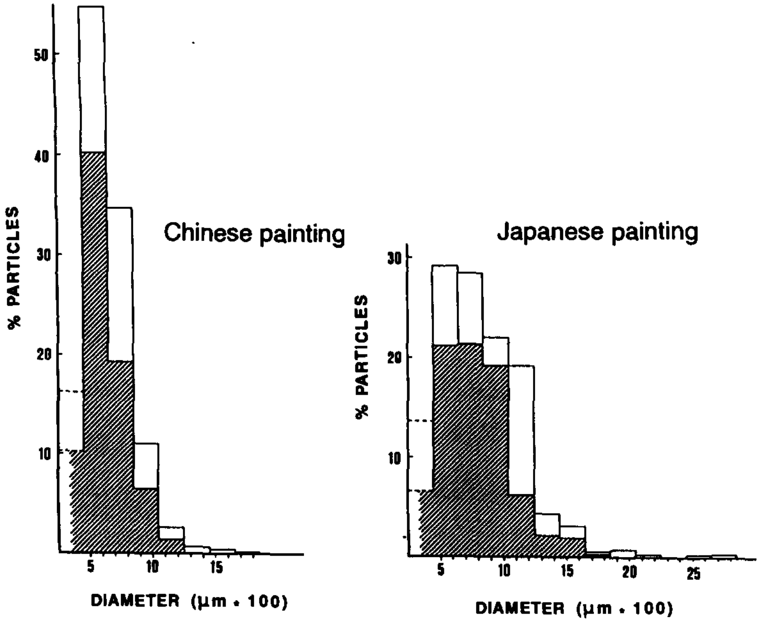


Fig. 18. Graph of the particle size distribution of carbon black of Chinese and Japanese paintings of the 14th Century.

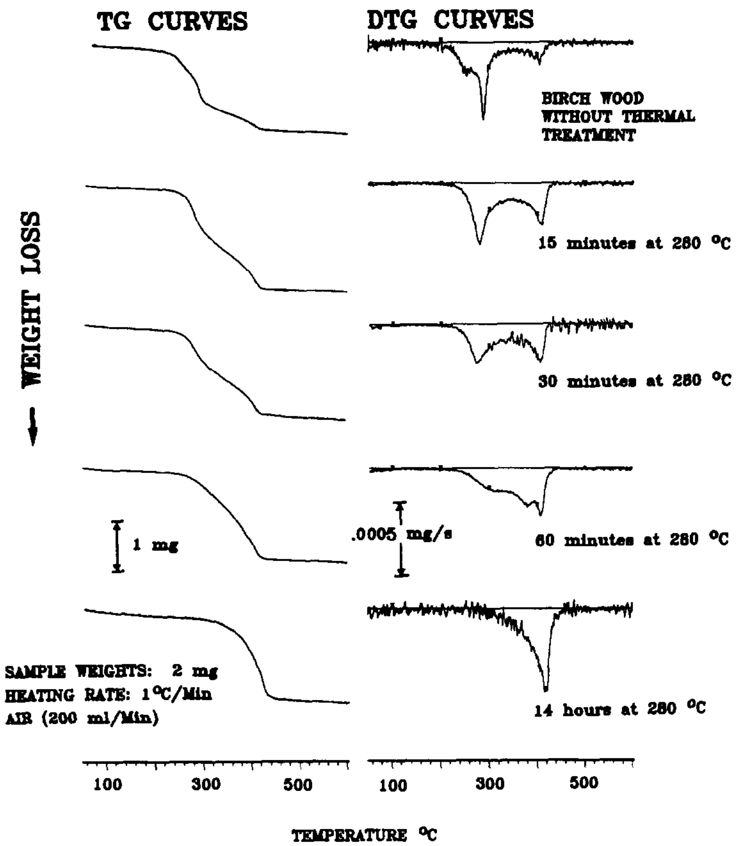


Fig. 19. Carbonization process of birch wood, treated for different times at 280°C, as measured by TG.

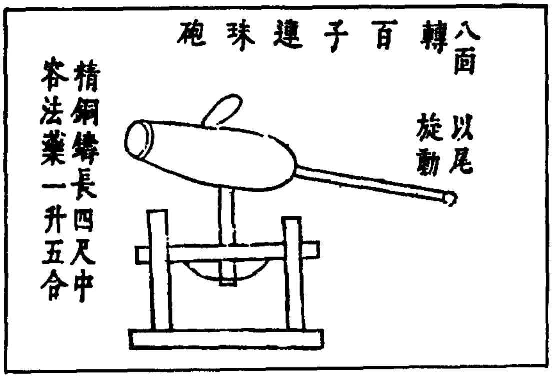


Fig. 20. The eight-direction-rotating string-of-100-bullets cannon.

woods or lamp black from oil lamps. Chinese ink shows a very narrow particle size distribution which is characteristic for lamp black, whereas Japanese ink shows a more equal distribution over a medium range of diameters (Fig. 18). The preparation of carbon black can also be investigated by thermoanalytical methods. This is shown in Fig. 19 which proves that the main reaction responsible for the formation of charcoal [9] is the charring of lignin. The basic component of lignin is coniferyl alcohol, which already contains the six-membered carbon rings necessary for the high-temperature formation of carbon and graphite.

Another application of carbon was in gunpowder. The book of Tian gong kaiwu reported "Gunpowder is manufactured by using saltpetre and sulphur as the principal components, and the charcoal of wood as the auxiliary component. It is believed that saltpetre and sulphur are, respectively, negative and positive characters. A combination of the positive (yang) and the negative (yin) forms gunpowder."

The red-barbarian cannon (hung-yi p'ao), cast of iron and about ten feet long, was used for the defence of cities (Fig. 20). It was packed with several bushels of gunpowder and an iron ball. Upon firing, the iron ball is projected over a distance of two li, so as to destroy any object in its path.

EARLY CERAMICS – SCULPTURAL ART

Chinese ceramics have a very long history. As far back as 8000 years ago, red, grey, black and painted pottery was made. After that period there was a gradual evolution of raw materials selection, forming methods, kiln design, heat treatment and decoration. The initial ceramic products such as pottery and terracotta were porous and rather fragile. Besides vessels for storing and cooking food, these materials were also applied for making sculptures, figures and a variety of objects for ritual purposes.

Our investigations on ancient Chinese ceramics were concerned with terracotta sculptures from the Qin dynasty (Fig. 21). In 1974 an over-2000-year-old subterranean army of some seven thousand men and horses in life-size terracotta was discovered near Xian [10]. This archaeological sensation revealed a level of ceramic technology in ancient China which was previously unsuspected.

The terracotta army was not mass produced from moulds: each figure was individually modelled and was originally painted with bright colours, which today have almost disappeared. The impressive sculptures were made from local clays containing feldspar, quartz and some carbonate. They were probably not fired at high temperature, since they did not show the brown-reddish colour typical of terracotta fired at about 1000°C. The porous, unglazed and comparatively coarse Chinese ceramic is of mud brown-reddish colour and mechanically rather weak. A small fragment of such "terracotta" ceramic from the burial site of the first emperor of Qin

Fig. 21. Terracotta warriors of the Qin Dynasty.

Dynasty, Quin Shi Huangdi, was obtained for experimental investigations. It was claimed to have identical composition and thermal history to the terracotta warriors.

Results from TG, DSC, TMA and XRD proved that the "terracotta" material consists of a mixture of (partially decomposed) Fe-rich clay, K-feldspar, quartz, and probably a minor amount of magnetite. The local sandy loam was probably used as the only raw material (in coarser and finer form) for the manufacture of the terracotta soldiers [11].

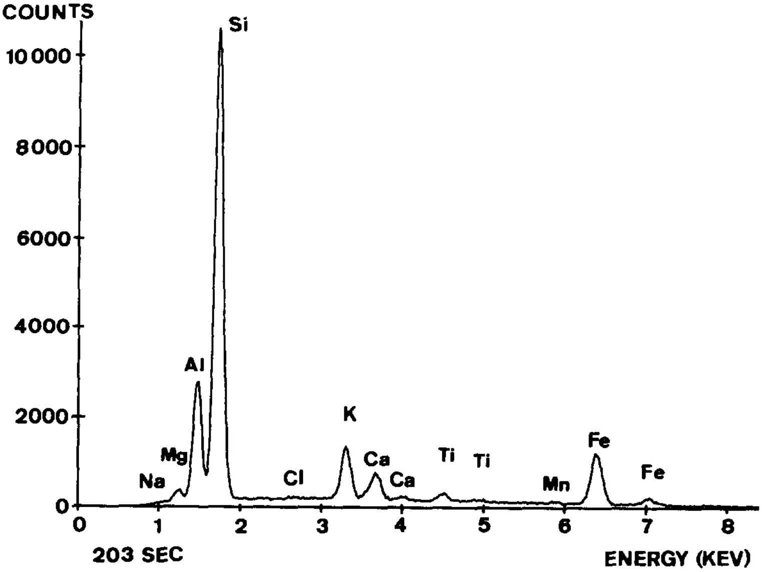


Fig. 22. EDAX analysis of Chinese terracotta.

The relative elemental concentrations in the Chinese terracotta are also shown by EDAX analysis (Fig. 22). The mineralogical composition of the terracotta was established from X-ray analysis which showed the following phases: quartz (VS), K-feldspar (S), partially decomposed clay (mostly amorphous), and magnetite (VW). After firing to 1000°C there is little change in the X-ray pattern, except for the appearance of haematite which is formed by oxidation of the magnetite. This and the following results lead to the conclusion that the "terracotta" has not been heated at all, or only at moderate temperature (500–600°C) due to the outbreak of a fire. For further proof of this assumption, original terracotta samples were fired at different temperatures and also subjected to thermoanalytical investigations. The colour of the original terracotta sample changes gradually after firing above 500°C from muddy grey-brown to a bright red-brown at 1000°C. This is due to the oxidation of Fe^{2+} and to the presence of free haematite.

The TG curve of the Chinese terracotta is shown in Fig. 23 together with the DSC curve and the TMA curve of this material. As expected, the DSC curve shows a continuous drift up to about 600°C owing to the loss of adsorbed water and decomposition of the clay mineral. The broad exothermic peak at around 350°C is due to the combustion of organic material, the sharp endothermic peak at 578°C corresponds to the α–β-quartz transformation. The TMA curve shows expansion up to about 800°C.

The discontinuity at 200–400°C is probably caused by the overlapping effects of H_2O loss, clay decomposition and burn-out of organic material. Contraction of the sample above 600°C is in accordance with the breakdown of the carbonate followed by sintering. Figure 24 shows the TMA

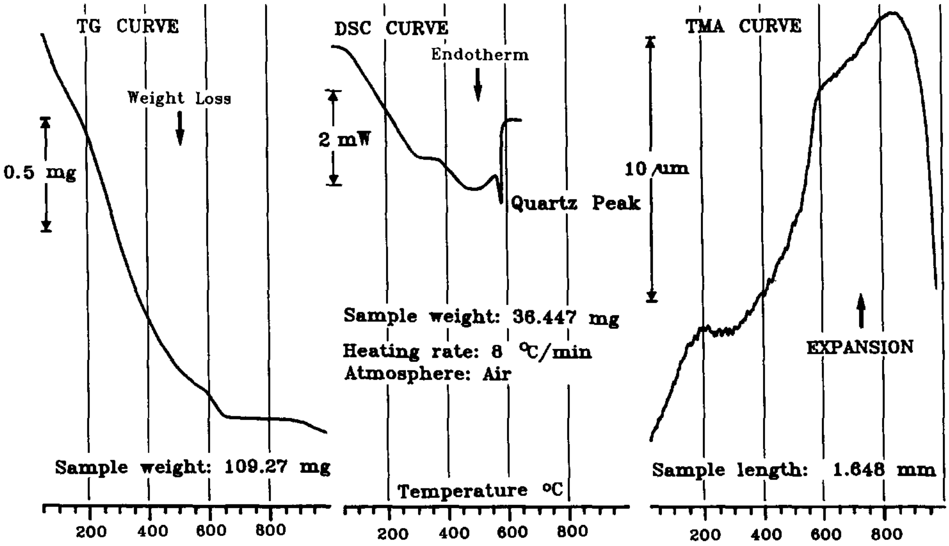


Fig. 23. TG, TMA and DSC curves of Chinese terracotta.

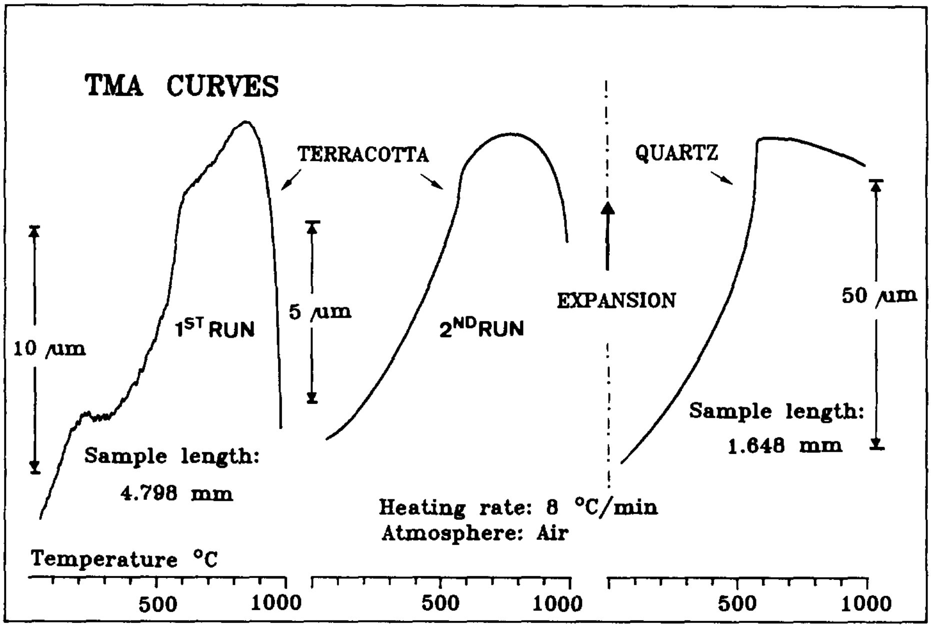


Fig. 24. TMA curves of Chinese terracotta and quartz.

curves of the Chinese terracotta compared with that of quartz. All the TMA curves were recorded under a superimposed load of 0.02 N. After the first run, the TMA curves of subsequent runs become similar to the TMA curve of pure quartz, except for their strong contraction (sintering) above 800°C. Thus, the expansion behaviour of the repeatedly fired terracotta

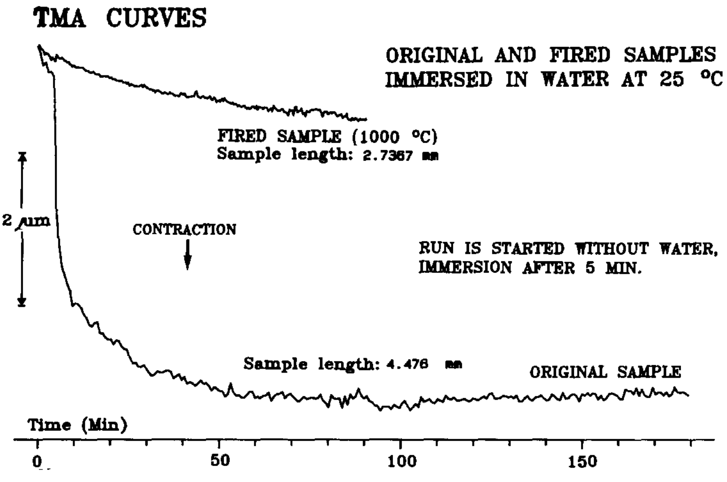


Fig. 25. TMA curves of original and fired Chinese terracotta recorded after immersion in water.

approaches that of quartz. In order to prove that the Chinese terracotta was hardly fired (if at all), TMA curves were recorded for original and fired (1000°C) samples. These samples were immersed in water at room temperature and the TMA curve was recorded as a function of time (Fig. 25). During the runs, the original sample shows a strong contraction owing to the mobilization of the undecomposed and also partially decomposed clay particles. An equilibrium state is reached after about 30 min. The fired sample, however, does not show any contraction when immersed into water, because of its rigid, coherent "framework" resulting from sintering of the grains. Therefore, the original sample of terracotta used in these experiments had only been dried or perhaps slightly heated. It should be mentioned, however, that the firmness of the samples varies from the exterior surface to the interior and also from one figure to another. Obviously, this is caused by the difference in temperature to which the terracotta was exposed during a fire which occurred in the burial place.

Another proof that the Chinese terracotta was hardly fired could be derived from thermomagnetic measurements. TG curves of the original samples were recorded in the presence and in the absence of a magnetic field gradient (Fig. 26). Owing to the existence of a ferrimagnetic component (Fe_3O_4) in the terracotta, the attraction in the magnetic field causes a displacement of the TG curve towards higher weight. Above the Curie temperature (transition to the paramagnetic state) the TG curve approaches the TG curve of terracotta which was recorded in the absence of a magnetic field. This effect occurs at about 600°C, which agrees fairly well with the Curie temperature of magnetite. On further heating (to 1000°C) magnetite is gradually oxidized to haematite (α-Fe_2O_3), which is antiferromagnetic at room temperature [12].

In conclusion, the results of these different thermo-analytical measure-

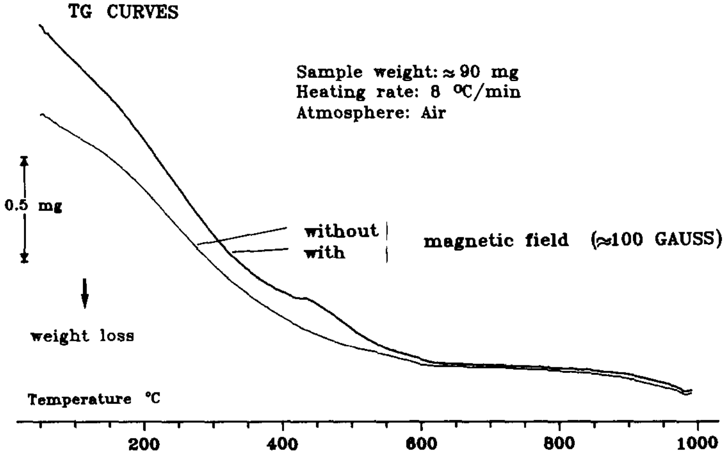


Fig. 26. TG curves of Chinese terracotta recorded with and without magnetic field.

ments on ancient Chinese terracotta indicate that this material was not fired originally and hardened only by drying of the clay component in the raw material. However, these findings may be valid only for the investigated sample. Although it is reasonable to assume that all the terracotta pieces were manufactured with the same local clays, they may have been heated batch-wise and at different temperatures.

PORCELAIN — THE PRECIOUS CHINESE CERAMICS

Ancient Chinese ceramics are often equated with porcelain. In fact porcelain was developed gradually over a time span in the order of a thousand years from stoneware to proto-porcelain. The latter was already very close to porcelain but not white and not translucent. Proto-porcelain was made beginning about 3000 years ago at the time of the Shang and Shou Dynasties. The production of real porcelain began during the Song Dynasty. China was the first nation to produce porcelain. Its delicacy and finesse were admired by the west, when Marco Polo brought it to Europe (1271–1295) on his return from the far east [1,2].

The technology of porcelain manufacture was very highly developed in China. In most cases, two kinds of raw materials were used, being mixed in various proportions by treading and stirring in containers: the non-melting porcelain clay (kaolin rendered plastic by long storage) and the meltable flux (a non-plastic material containing feldspar and mica). The resulting paste was cut, kneaded on slate tables, rolled and dried. The material was shaped by being thrown on the potter's wheel (Fig. 27) or else by pressing it into prefired clay shapes, especially figures or surface reliefs. The glaze was then mostly applied with a brush in several layers before firing or was sprayed on with a small bamboo tube. This distinguishes Chinese from European porcelain, which is hardened by bisque firing before glazing, so that it can be dipped in the glaze. The pigments present in the raw materials or added to colour the glazes were primarily iron oxides (yellow–red–brown with an oxidizing firing process, green–blue with a reducing process, as in the case of celadon); copper oxides (bluish with oxidation, red with reduction); and cobalt oxide (bright blue, or black in combination with iron oxide). Cobalt oxide shows a very special decomposition behaviour (Fig. 28). The original $Co_2^{3+}O_3$ decomposes to $Co^{2+}O$ at about 900–950°C. This reaction is completely reversible in the case of the free Co oxide. The divalent Co^{2+}, however, is fixed or stabilized in the glaze, or by combining (e.g. with alumina) to a strongly coloured pigment (cobalt blue). Cobalt oxide stains were chiefly used for underglaze painting, a method that came into favour in the Yuan period. After preliminary drying the wares were fired.

Suitable kilns had to be developed for the high temperatures required for making porcelain, and glazes melting at higher temperatures were also

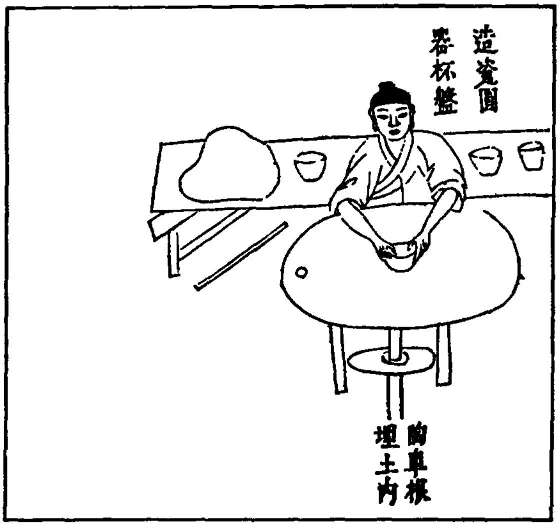


Fig. 27. Shaping clayware with the potter's wheel.

needed. Unlike the lead glazes used in earlier dynasties for low-fired wares, these feldspar glazes were a purely Chinese invention. They had also been used in the Han period on high-fired stoneware.

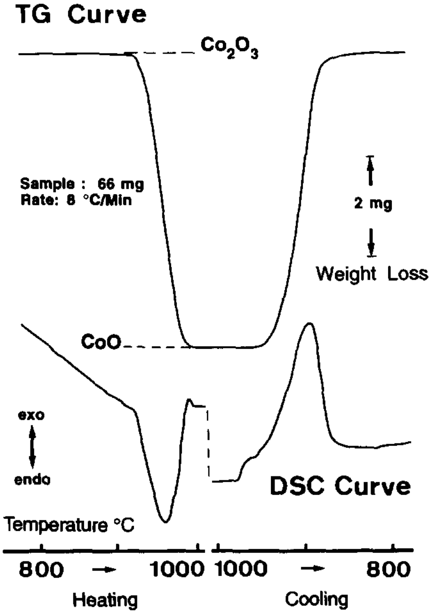


Fig. 28. TG and DSC curves of the reactions of $Co_2O_3 \leftrightarrow 2CoO + \frac{1}{2}O_2$.

The production sites of porcelain in the Tang and Song Dynasties were small individual factories in various regions of the extensive Chinese empire. Chinese porcelain had no competitors worthy of mention and was exported in large quantities, as records going back to the Tang Dynasty show. From the Ming Dynasty onwards the wares were exported not only to neighbouring countries such as India, Japan, the Phillippines and the Sunda Islands, but far to the west: to Mesopotamia, Persia, Egypt and Morocco by way of the old silk route. Stoneware and porcelain were much used as tomb furnishings, small human figures, animals and the main objects of daily life being shaped for this purpose.

Later, porcelain was employed mostly for objects of household use, such as bowls, vases, pots, ewers, tea-cups, censers, ink blocks, paint pots, brush holders, paperweights, lamps, pipes, head rests, and musical instruments. Whereas the Tang Dynasty copied the formerly popular bronze vessels in form, glaze and relief, the Ming Dynasty and later epochs produced imitations of bamboo, wood, jade, horn, mother-of-pearl, lacquer and gold. The Chinese, in their admiration for the earlier shapes and glazes, have succeeded in copying them to perfection, though without any intent to produce forgeries, at least until dealers and collectors from Europe appeared on the scene. It is extremely difficult to distinguish these imitations from the original products, as they often have the same typical features. Modern methods for determining the age of ceramics, particularly by means of thermoluminescence, fail in the case of high-fired porcelain and are usually destructive.

CHINESE BRONZE — ALLOY FOR RITUAL VESSELS AND COINS

The great bronze age of Chinese culture extended from the 17th to the 3rd Century BC (the Shang and Zhou Dynasties). The Chinese forged vessels of unique quality and precision, which were cast in clay piece moulds. Many of the bronzes in the form of weapons and ritual vessels carried inscriptions which prove the high level of Chinese culture and civilization. Unlike in other cultures, where bronze was first used for tools and weapons, in China this alloy of copper and tin was mainly reserved for the manufacture of majestic vessels that played a central role in state rituals and ancestor worship for over 1000 years [1]. We owe the preservation of these ancient bronzes to their burial. During the Shang Dynasty, members of the royalty were accompanied in the afterlife by their bronzes, ceramics, weapons, amulets, and ornaments.

The melting and use of bronze in ancient China is well documented. Possession of bronze vessels became a symbol for the holding of power and prestige.

The decoration of early Chinese bronzes was done directly in the mould or model and cast into the bronzes, not worked into the cold metal

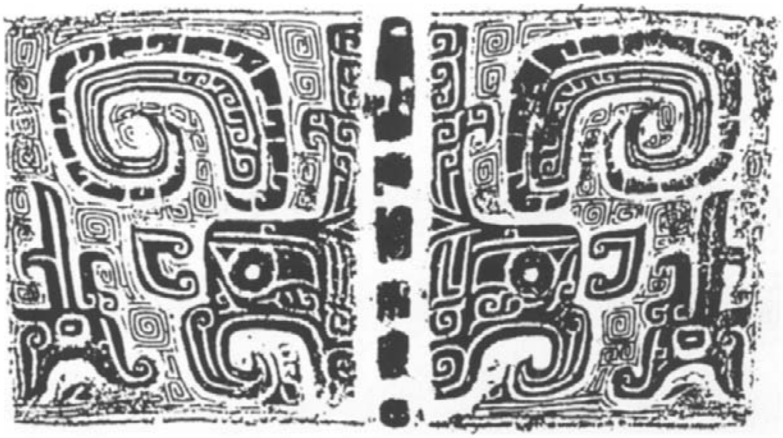


Fig. 29. Rectangular food cauldron with a representation of a Taoti (Shang Dynasty, 12th century BC).

afterwards. The most frequently encountered decoration in the Shang period is a frontal animal mask (taoti). Figure 29 shows a detail of a rectangular food cauldron (fang ding) of the Shang Dynasty (12th Century BC) Henan province. During the Western Zhou period, zoomorphic forms change more and more in abstract forms (Fig. 30). At the same time, handles become sculptural, depicting tigers, dragons, and other beasts.

During the Chou, Chin and Han Dynasties, bronze coins were developed which were also formerly used as weight units. These were calibrated with grains of millet and sometimes also with rice. Table 2 shows the relation of Chinese coins' respective weights and their equivalence in grains of millet and their corresponding weight in metric units (grams).

Knife coins and rounded coins with a central square hole, which were carried on a leather string, are shown in Fig. 31 The upper knife coin is the Tao knife coin which was described by Schjöht [13]. This "three character coin" of Ch'i is frequently met with, whereas those with four and six characters are relatively scarce. The knife shape of these coins indicates that swords or knives have been used in ancient China as a barter. This type of coin had the convenience of a ring at the top, compared with the spade money (coin in the lower part of Fig. 31), which allowed the stringing of the pieces together when carried. All of the metallic coins were cast, as opposed to having been stamped. The alloy was a bronze with a high lead content (see Table 3).

One of samples of ancient bronze has been previously investigated and described by Chase (1979) [14]. It is from a series of Ming-tao knife coins, which were brought back in 1924 from the town of Ichou, Hubei province (3rd knife coin from the top in Fig. 31).

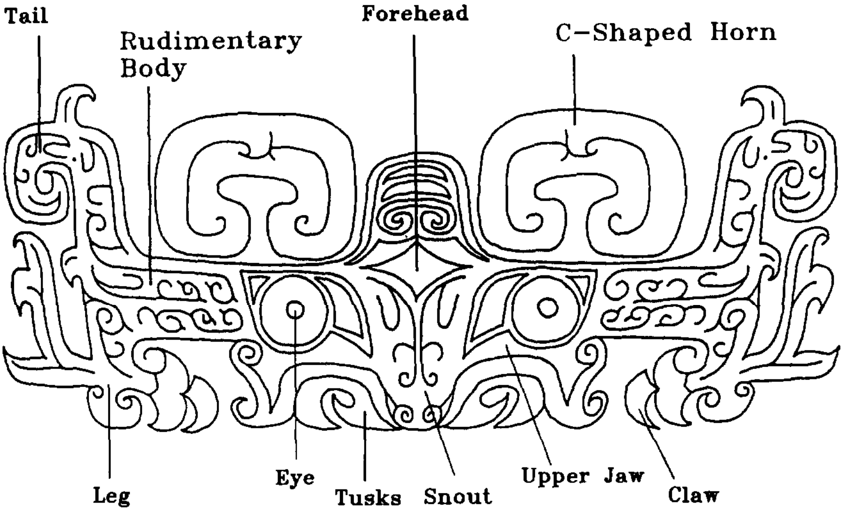


Fig. 30. Sketch of a Taoti and meaning of several details.

All these coins are very high in lead content, except for the more recent imitations. Chemical analysis of the Ming-tao coin showed Cu 47.1%, Sn 0.8%, Pb 49.6%, and Fe 1.0%. The micrographs of Chase [14] proved the existence of large globular inclusions of lead concentrate at the centre of the knife coin. This author assumed that the grey, lead-rich inclusions were originally metallic but have been transformed gradually to lead oxide. The small spherical inclusions which are present within the segregated globules correspond to alpha-bronze.

This alloy had to be poured quite hot, e.g. by injection moulding. As the alloy cools, the lead separates in the liquid phase into an emulsion, while the alpha-bronze (the majority of the alloy) solidifies forming the exterior of the coin. The larger lead globules move to the centre and form the small spherical blobs which appear as large dark areas.

TABLE 2

Equivalence of ancient weights in metric units and grains of millet

Time BC	Chinese weights	Gram	Grains	Coin name	Material
141–78	$\frac{1}{2}$ Liang = 1 Shu	0.659	100	Shu	Bronze
141–78	$\frac{1}{4}$ Liang = 5 Shu	3.480	500	WuShu	Bronze
770–255	$\frac{3}{8}$ Liang = 7.5 Shu	5.150	750	Pu	Bronze
255–206	$\frac{1}{2}$ Liang = 10 Shu	6.960	1000	Ban-Liang	Bronze
770–255	1 Liang = 20 Shu	13.92	2000	Ming-tao	Bronze
1091–255	3 Liang = 60 Shu	41.75	6000	Tao knife	Bronze

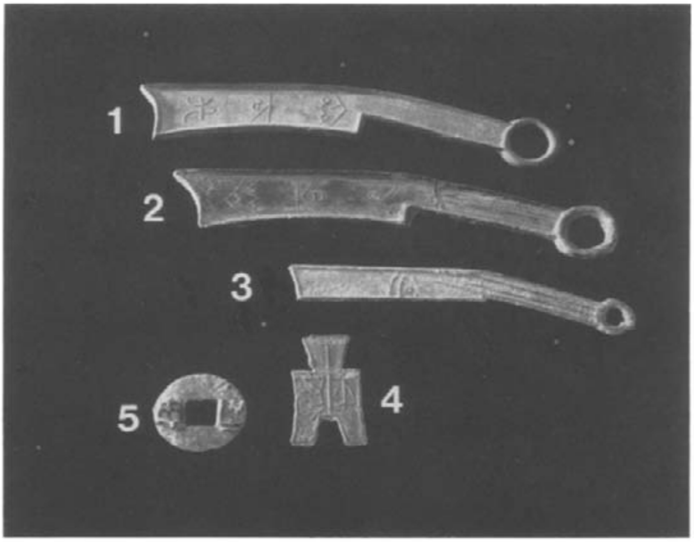


Fig. 31. Several coins/weights of ancient China: 1, Tao knife coin; 2, Tao knife (imitation); 3, Ming Tao knife coin; 4, Pu coin (spade-like); 5 Ban Liang.

TABLE 3

Composition (wt.%) of ancient bronzes of weights and coins

	Cu	Pb	Sn	Fe	Zn	Time BC
Ant nose coin	64.06	24.47	10.32	1.15		351
Tao knife	57.38	39.02	1.16	2.44		1091–255
Tao knife (imitation)	81.24	6.34	2.40	1.41	7.61	(1989AD)
Ming-tao knife coins	55.05	44.94				1122–255
	47.10	49.6	0.8	1.0		
Pu coin	77.83	10.82	7.10	4.64		770–255
Ban-Liang	94.26	5.74				255–206
	91.79	8.21				
WuShu coin	83.91	7.22	4.53	5.0		141–78

TABLE 4

Composition of Chinese bronze mirrors (Riederer [15])

Century	Cu	Sn	Pb	Zn	Fe	Ni	Ag	Sb
6th–4th BC	78.2	18.1	3.19	0.01	0.07	0.11	0.11	0.04
3 BC	73.1	21.9	3.03	0.01	0.07	0.11	0.12	0.03
2nd BC–1st AD	72.0	22.9	5.90	0.01	0.04	0.08	0.14	0.18
6th–7th AD	70.3	24.0	4.13	0.01	1.50	0.03	0.07	0.06
8th–9th AD	67.5	24.9	5.13	0.01	0.06	0.14	0.12	0.18

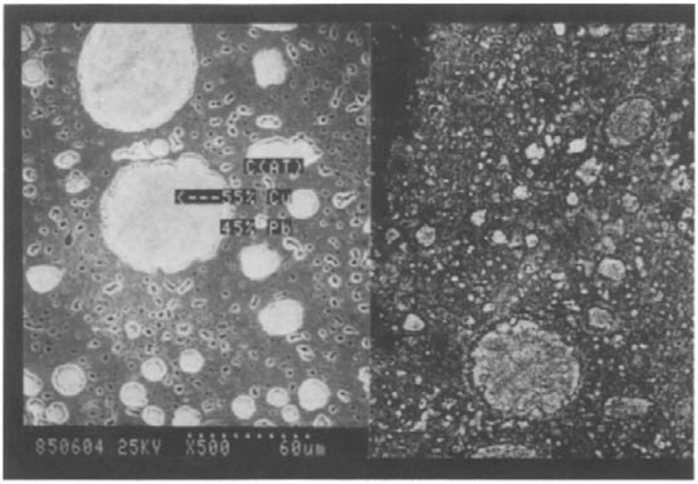


Fig. 32. BSE picture from a cross section of a Ming Tao knife coin shows segregation phenomena of lead globules.

These results by Chase could be confirmed by our experimental investigations. The micrographs from the cross sections of another Ming-tao knife coin (Fig. 32) show identical segregation phenomena. The composition of the spherulites was analysed (Table 3), and showed 45% lead and 55% copper. Copies of such ancient coins (see Fig. 31, 2nd coin) which are sold today in Beijing show a homogeneous, non-segregated bronze texture. Also, these new coins have a fine-grained, greenish patina but with a completely different texture. The analysis of such imitated coins shows their different composition (Table 3) corresponding to a modern bronze.

All the investigated bronze samples proved that the copper and tin content was reduced with historical development in contrast to the lead content, which increased. During the investigation of Chinese mirrors at the Rathgen research laboratory in Berlin, the knowledge of the composition allowed correlation of the age of the mirrors with different dynasties. Table 4 shows a comparison of the composition of analysed mirrors and the respective areas where they were produced. Figure 33 shows a bronze Buddha.

PAPER AND PAPER MONEY — CHINESE INVENTION

The real paper was invented around 105AD in China where Cai Lun produced the first usable writing material from tree bark and plant fibres, and from old rags and fishing nets. Since that time, paper has been in general use all over China. Over the centuries, the technology of paper

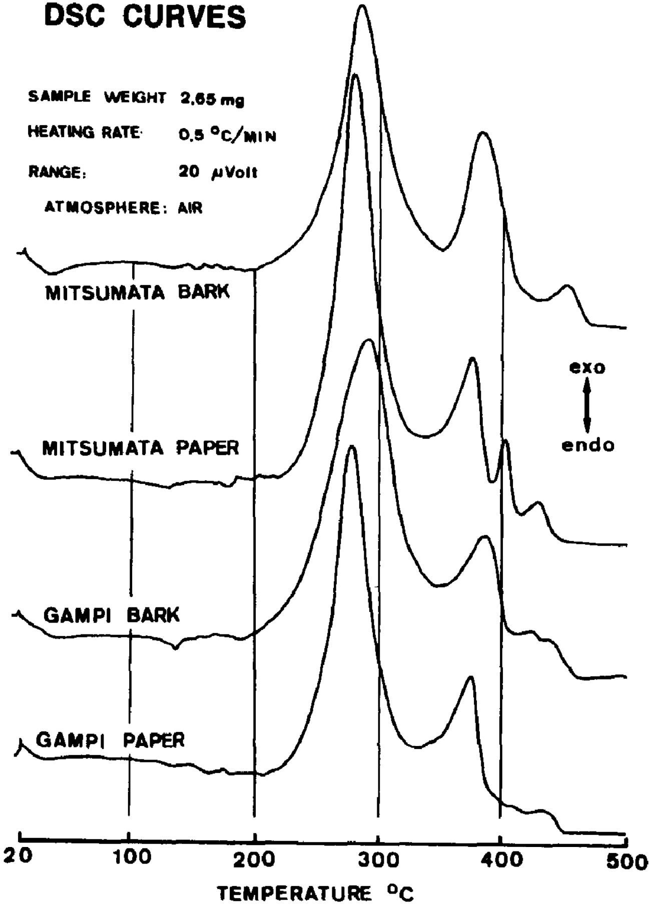
Fig. 34. Boiling of mulberry tree bark strips mixed with ash [17].

manufacturing was constantly refined and modified with respect to the raw materials used in its production [16].

Japanese paper production started in 610AD. They used bark of the mulberry tree, which was cut in strips and mixed with ashes and then boiled in water (Fig. 34). This was followed by various cleaning procedures in which washing played a very important role. The bark prepared in this manner was spread on wooden tables and several labourers then beat the material with hardwood sticks until it could be stirred with water into a kind of pulp. A mixture consisting of rice starch and roots was then added to serve as binder. This Japanese paper is called "Kozo". It is very dense and snow-white. It is still produced today and the dull sheen of its fibrous surface texture is very decorative.

In our experimental investigations we used thermoanalytical methods to compare old historic papers with modern paper. For this, it was necessary to test the raw materials of Eastern paper manufacturing, such as bamboo, mulberry bark, Gampi Shi, and Mitsumata.

Figure 35 shows the comparison between the DSC curves of the bark fibres of Mitsumata and Gampi and those of various types of paper made with these fibers. The similarity is obvious: just below 300°C, the main peak



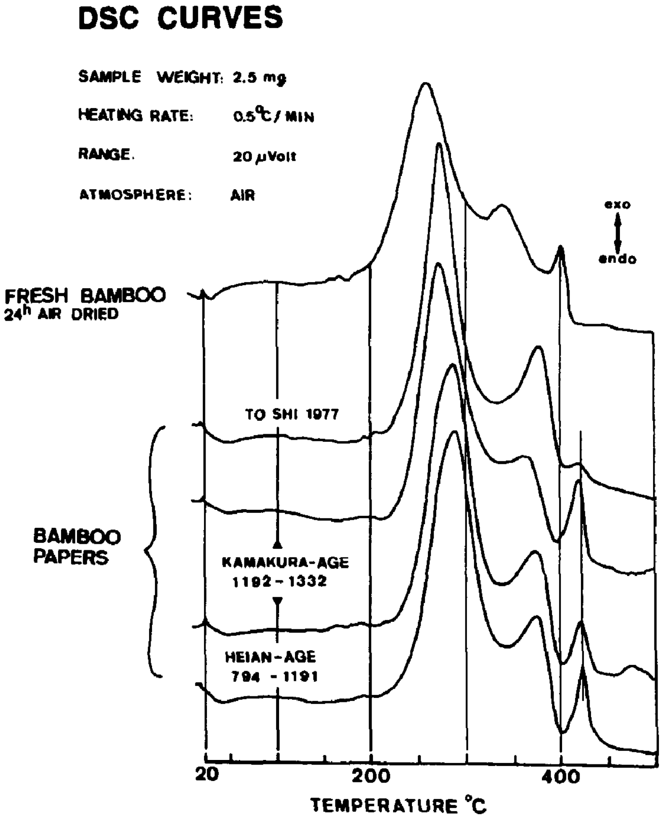


Fig. 35. DSC curves of bark fibres and paper of Mitsumata and Gampi shi.

Fig. 36. DSC curve of To shi paper.

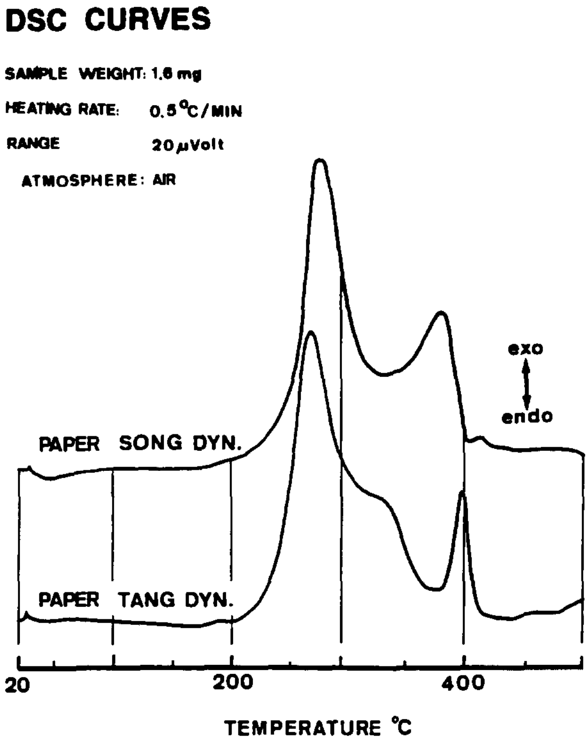


Fig. 37. DSC curve of Song paper.

of cellulose occurs; the lignin peaks at about 350–450°C are differentiated and show splitting because of the varying interlacing of the lignin.

The DSC curves in Fig. 36 show one of the papers made from bamboo pulp, "to shi" called "Chinese paper", which was also used by the Japanese.

When comparing Fig. 37 with the DSC curve of the Chinese Song paper, a certain similarity between the DSC curves of the old Chinese paper and those of the bamboo paper can be noted. Possibly the bamboo fibre was used in those days to manufacture paper. For the Tang Dynasty paper no correlation or similarity with the other papers could be found.

China was also the first country in the world to use paper currency [18]. When Marco Polo came to China, he was surprised to find the circulation of paper currency made of tree bark (Fig. 38). The origin of Chinese paper currency can be traced back to the 4th year of Yuan Shou of the Han Dynasty emperor Wu (119BC) when the painted deerskin note was issued. By the time of Tang emperor Xian Zong (806–820) feiqian or "flying money" made its appearance. It was like today's money order, and is regarded by historians as the precursor of paper currency.

The formal exchange certificate, jiaozi, was created in Sichuan in the 10th Century during the early Northern Song Dynasty. It preceded the Yuan Dynasty paper money by more than 200 years.

Fig. 38. Ancient Chinese paper money (Ming Dynasty).

Fig. 39. Printing plate for paper currency (Southern Song Dynasty).

Fig. 40. Paper money from Ming Dynasty (Da ming tong xing bao chao).

The earliest jiaozi had only a hidden number and a mark on it in red and black. The amount of money was filled in later. Sixteen merchants jointly operated a jiaozi "bank" which issued a much more sophisticated instrument, copperplate printed (Fig. 39) and garnished with a wooden gate and figures. This jiaozi is highly regarded in world history of currency as well as in printing and graphic art history. In 1023 the Sichuan government monopolized the management of jiaozi, which was issued in limited numbers and sustained by gold reserves.

During the reign of the Song emperor Hui Zong, an exquisite money, qianying, copperplate printed in blue, red and black, was issued in 1105, and circulated in Sichuan and other provinces. It inaugurated polychrome printing in China. By the Southern Song Dynasty (1127–1227), paper money was used along with coins in most parts of the country.

Paper money became extremely popular during the Yuan Dynasty. Four kinds of currency were issued at one time, for example the Zhong tong yuan jiao chao. The government proclaimed that paper currency was the only legal tender in circulation, and banned gold and silver from the market. Even foreign merchants had to change their money into paper currency before they could make a deal. Such a system of circulation was centuries ahead of the West.

During the Ming Dynasty (1368–1644) only one kind of paper money, the da ming tong xing bao chao, was issued (Fig. 40). During the reign of the Qing emperor Xian Feng (1851–1861), the da qing bao chao and hu bu guan piao, a silver certificate, were issued. Together they were known as chao piao, or bank note. In 1891, the first modern bank of China, the China Tong Shang Bank, was established. The following year the first modern Chinese bank notes were issued.

CHINESE SILK – A PRODUCT OF INSECTS

The raising of silkworms and the making of silk have held an important place in Chinese cultural history for some five thousand years. Numerous accounts of the origins of silk are found in Chinese history and mythology. The real cradle of silk was the province of Shandong, where silk fabrics were first made at the beginning of the third millenium BC. A little later there are reports on the dyeing of silk and on the emergence of a silk industry. But it is only from the Han Dynasty onwards (206BC–220AD) that we have positive evidence of a really important silk production. Many of the fabrics have patterns (often with interlacing dragons) similar to those on bronze utensils of the Han period. The decorations also include real animals, plants, arabesques and lozenge shapes.

The mulberry tree, the silkworm and the treatment of silk fibres had a prominent place in Chinese culture and literature. Wearing silk was for many centuries the exclusive privilege of the ruling house and the nobility.

Fig. 41. Selection of mature silkworms.

The secrets of silk-making were well guarded by the Chinese over a period of three thousand years. Chinese silks found their way overland to Europe at an early date and were much coveted, for instance, in ancient Rome. The silk trade reached its zenith with the development of the silk route. Yet a few centuries were to pass before the art of raising silkworms became known in Europe and the first sericulture was introduced under the Emperor Justinian in Byzantium in 552. Byzantium was to remain Europe's main silk market till the eleventh century. The expansion of silk was favoured by the advance of the Arabs into the West, for example into Spain. But it was only late in the sixteenth century that silkworm breeding spread widely in Europe, particularly in Italy and the South of France.

The raising of silkworms, the spinning of the silk thread and the weaving of silk fabrics in China are described in detail in the book of the crafts, "Tiangong kaiwu" [2]. It was written by the mandarin Song Yingxing in 1637, shortly before the end of the Ming Dynasty. It is an encyclopaedia of all traditional Chinese technologies: agriculture (grains), textiles, salt, sugar, ceramics, metallurgy, paper, weapons, silk, etc. One figure from this book typically shows the selection of the silk worms, which have reached their maturity after going through different steps of the growth period (Fig. 41).

A comparison of our modern knowledge of the biological cycle of the silkworm, from egg to egg-laying moth through its many intervening metamorphoses, with the historical account given in the "Tiangong kaiwu" reveals no differences worthy of mention.

In early June, the small caterpillars hatch early one morning and creep out of their eggs that have lain till that time in a warm, moist environment. Some of them will not as yet have reached maturity and will therefore wait till the next day or the day after that to break through the walls of their eggs. Development in the egg (≈ 0.9 mm in diameter) takes 12 days. For this time the embryo lives on the egg yolk by which it is surrounded. Two days before hatching the eggshell will have become transparent enough for the occasional movements of the silkworm to be observed through it. To emerge, it has to bite a hole in the shell big enough for the passage of its head. An immense effort is finally required to catapult the silkworm into the full light of day. Its first task is then to secure itself with several silk threads so as to prevent its falling from its breeding place. Under natural conditions this is usually a mulberry twig, on the leaves of which the caterpillar will feed.

The weight of a silkworm 3 mm in length, immediately after hatching, is less than half a thousandth of a gram. But it soon embarks upon a process of rapid growth that is apparent from its increasing length and size. When fully grown it will be 9 cm long and will weigh from 3.5 to 4 g. In other words, its length is multiplied by 30 in 33 days, while its weight increases from 7–8 thousandfold (Fig. 42). The outer skin, consisting of chitin, is not able to keep pace with this enormous development, so the caterpillar has to shed its skin four times. This moulting takes place every 5–6 days. The silkworm becomes immobile, takes on a waxy appearance and interrupts its feeding for one day, after which it begins to grow again and displays a seemingly redoubled appetite. When fully grown each caterpillar spins a cocoon to protect it in the pupa phase. It undergoes several metamorphoses in the cocoon (15 days), after which the moth moistens the filaments and emerges.

Before they spin their cocoons, the silkworms are placed by breeders on special screens on which cocoon spinning cones have been set up. After preparation of the cocoon (storage and the destruction of the pupa by dipping in boiling water), the thread is reeled on a special machine. The silk threads thus obtained are finally spooled on a frame. The spun silk yarn can now be used for weaving into cloth on various types of looms.

The food of *Bombyx mori* L. consists exclusively of the leaves of the mulberry tree. There are several different species of mulberry. Its original habitat, like that of the silkworm, was Asia, where it almost always takes the form of the black mulberry. The original home of the white mulberry has not yet been accurately determined. The practical experience of breeders shows that roughly a ton of mulberry leaves is needed for the eggs of a hundred silk moths (about 500 silkworm eggs per moth). Because the veins of the leaves are left behind, only about half this amount is actually

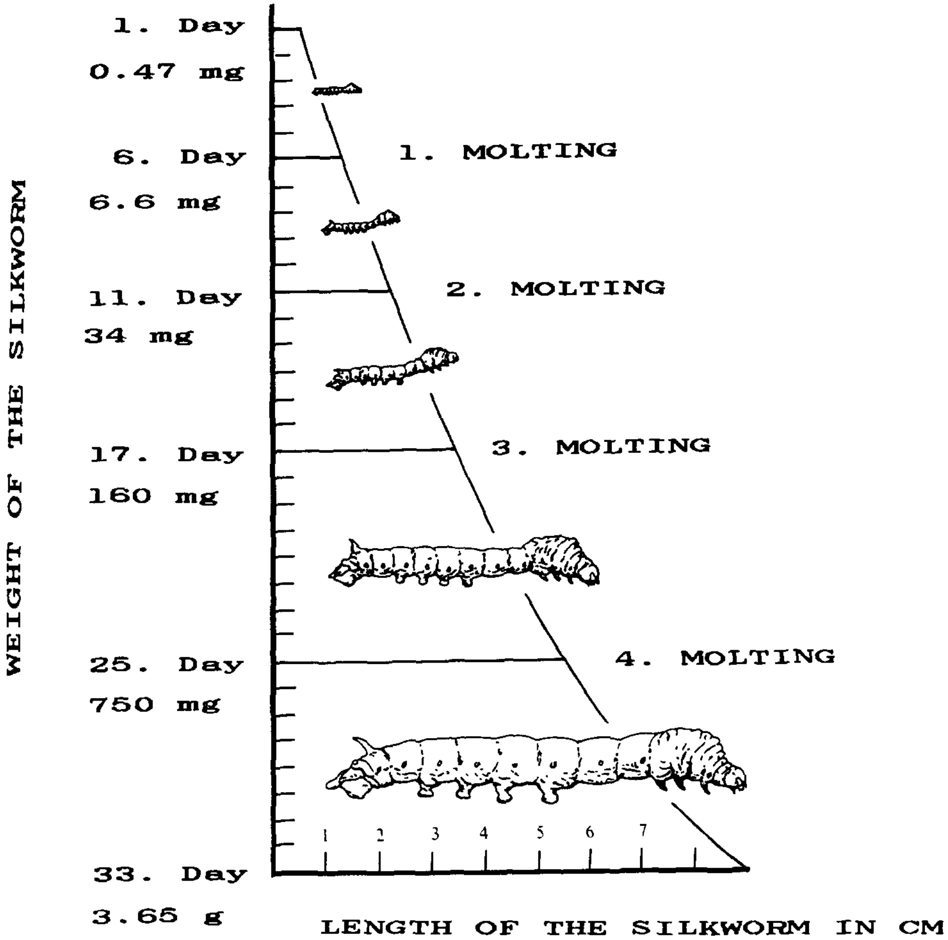


Fig. 42. Silkworm growth.

taken as food. The expected "harvest" from these 50000 silkworms is about 1000 kg of silk cocoons, which yield approximately 120 kg of raw silk. The cocoon filament of the silkworm consists of a double strand of fibroin which is surrounded by sericin holding the strands together and serving as a gum. Fibroin is composed of a crystallized protein (not soluble in water) to which silk owes its outstanding strength. The ensheating substance, sericin, is soluble in water. The fibroin is present in the silkworm's spinning gland in the form of a concentrated aqueous solution known as fibroinogen and crystallizes only when the thread is stretched after spinning, thereby becoming insoluble in water. Silk consists in essence of four amino acids (alanine, glycine, serine and tyrosine) [19,20]. Sericin differs from fibroin in its composition. Figure 43 shows one of the two silk glands of a fully grown silkworm shortly before it makes its cocoon. The glands take up almost three-quarters of the length of the body. Each of them consists of a long

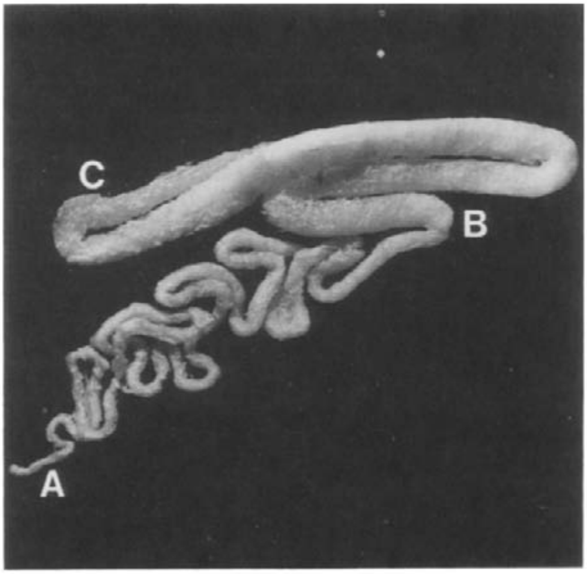


Fig. 43. Silk gland of fully grown silkworm (original magnification ×10). A, B, C marks the sections, where samples for MS analyses were taken.

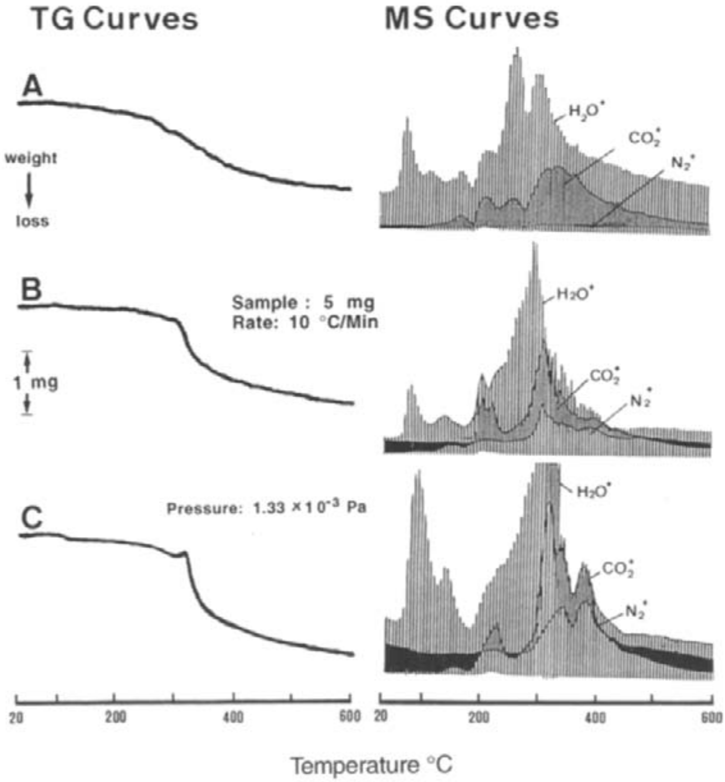


Fig. 44. TG–MS curves taken from the marked sections of a silk gland (see Fig. 43).

tube which runs parallel to the intestine and has many convolutions. The glands are divided into several sections, the last of which connects up directly to the spinneret.

The degradation of different parts of a silk gland from a fully grown silkworm could be derived from TG–MS curves (Fig. 44). The samples show the evolution of different amounts of gases (water, carbon dioxide and nitrogen) during decomposition. That means the composition of the polyamides formed in the gland is not homogeneous. The length of the whole gland is in the order of 28 cm. The first sample (A) was taken very close to the intestine connection. Here the nitrogen content is very low. The second sample (B) was taken where the gland begins to thicken. The MS curves show a much higher nitrogen content. The third sample (C) was taken next to the spinning nozzle. Here the concentration of nitrogen is equal to that of raw silk. During the spinning process of the first part of the cocoon the silkworm reduces its volume by draining an alkaline liquid (2

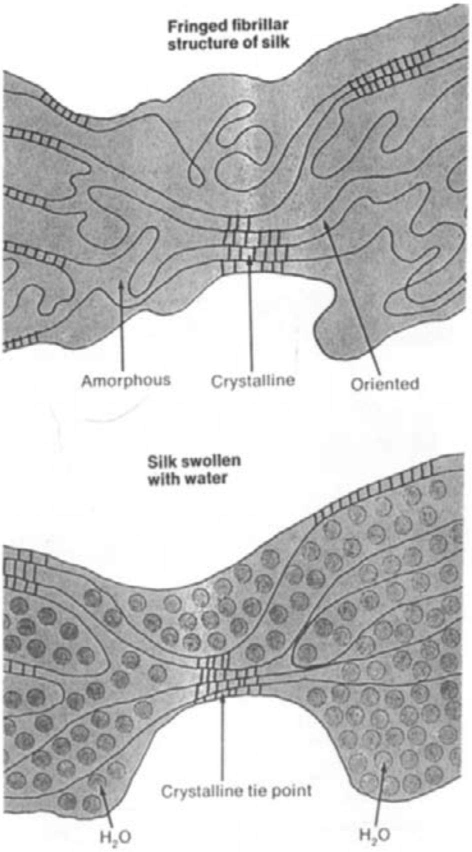


Fig. 45. Supramolecular structure of silk.

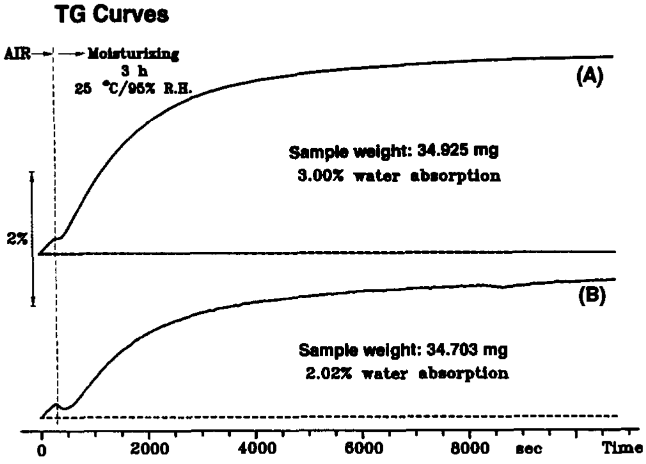


Fig. 46. TG curves of water absorption (moisturizing) of old silk; (A) Japanese silk picture (150 years), and (B) silk of Quin Dynasty (200 years).

cm^3). This liquid is part of the content of the gland, containing the reaction mixture in which the polysaccharides react to the polypeptides that are produced.

The importance of nitrogen for silk production was also recognized by the well-known German chemist Justus Liebig. He writes (in Poggendorf's Annalen) that it is essential to use nitrogen-containing fertilizers for the mulberry trees on which silkworms feed.

Water absorption and its reversibility is one of the characteristic features important to the quality of silk [20]. Silk feels moist only when it contains at least around 30% water. The supramolecular structure of silk [22] contains

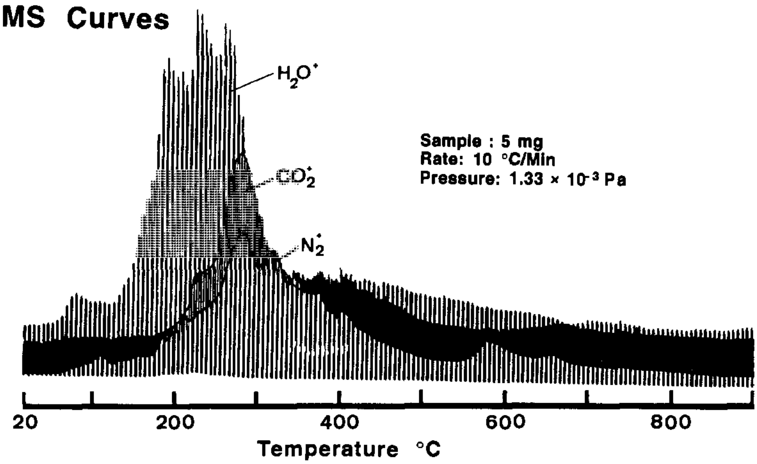


Fig. 47. MS curves of the pyrolysis of raw silk.

protein polymers in crystalline regions, where properly aligned chains are linked by hydrogen bonding. It also contains oriented regions and amorphous regions. As the fibre absorbs water, the chains in the amorphous regions are pushed apart, but the crystalline tie points hold the chains together (Fig. 45). This assumption of reversible swelling holds true only if the silk has not been deserecinized. In other words, the moisture absorption is proportional to the presence of sericine in the silk fibre. This can be seen from Fig. 46 where the water absorption of ancient silk samples is compared. The low values (compared with 6.8% adsorption for untreated cocoons) point to a partial deserecinization. The thermal degradation of raw silk was also investigated by mass spectrometry (Fig. 47), and compares well with Fig. 43 (curve C), regarding amounts H_2O, CO_2 and N_2 which are evolved during pyrolysis.

RICE — NUTRITION FROM CULTIVATED GRASS SEEDS

The book of Tian gong kaiwu [2] reported "There are numerous kinds of rice. Of the non-glutinous kind, the plant is denoted by one word and the

Fig. 48. Hand weeding in a rice field.

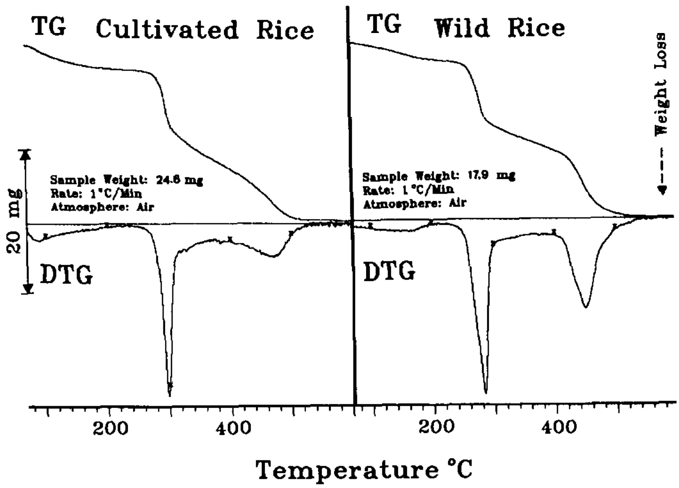


Fig. 49. TG and DTG curves of cultivated and wild rice.

grain by another, both of which are pronounced keng; of the glutinous kind, the plant is called t'u and the grain nuo. Colours of the grain vary from snowy white, ivory, and red, to semi-violet and dappled black." Figure 48 shows farmers pulling weeds in a rice field.

Previous investigations that we have carried out on various kinds of grains showed characteristic differences in their thermal decomposition

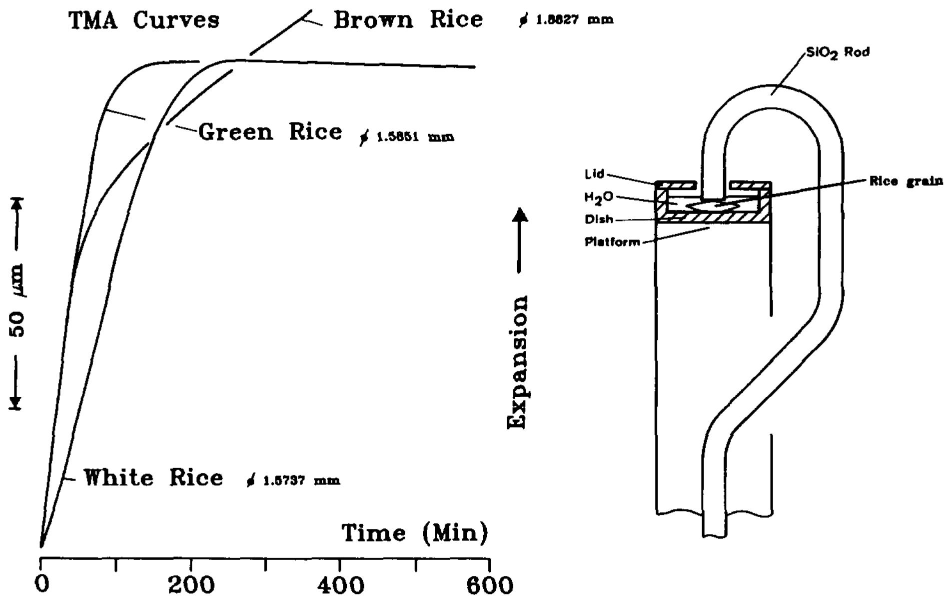


Fig. 50. Swelling behaviour of several kinds of rice.

behaviour. These differences are not only due to compositional variation, but also depend on the age.

Based on these findings, we tried to apply thermoanalytical techniques (TG, DTG and TMA) also for investigating different types of rice. Figure 49 shows TG and DTG curves of wild and cultivated rice, with average grain weight of 18 and 25 mg respectively. The main differences are that the water bonding is weaker in the cultivated rice, and that the decomposition peaks of carbohydrates, fats and protein are shifted to slightly higher temperatures in the case of cultivated rice. Wild rice definitely contains a higher proportion of proteins, and shows ten-fold swelling compared with the cultivated green variety.

The swelling behaviour was measured by means of TMA on three different fractions of whole grains of white, green, and brown rice from Thailand. It is obvious from Fig. 50 that the green rice shows the fastest swelling, whereas the brown rice is much slower and more resistant towards swelling. The white variety is somewhat slower to swell, but shows swelling characteristics similar to those of the green variety. The green variety is intermediate in its swelling characteristics. These differences are caused by the different thickness of the cell membranes which control the water diffusion and therefore the swelling behaviour.

CONCLUSIONS

Experimental results obtained on a variety of ancient objects prove that the application of thermal analysis, X-ray methods and analytical pyrolysis are powerful tools in archeometry.

ACKNOWLEDGEMENTS

We thank Dr. K.A. Jakes for permission to use figures from her paper [21].

REFERENCES

1 C.N. Adams, Wonders from Shanghai, The Lamp, Exxon Quarterly, Summer 1984, pp. 10–15.
2 Ying-Hsing, Sung, T'IEN-KUNG K'AI-WU (1637), The Pennsylvania State University Press, University Park and London, 1966.
3 Wen Fong (Ed.), Treasures from the Bronze Age, Metropolitan Museum of Art, New York 1980.
4 K. Bandel, Biomineralisation Forschungsberichte, 9 (1976) 28–47.
5 H. Brinker and A. Lutz, Chinesische Cloisonné, Museum Rietberg, Zürich, 1985.
6 W.T. Chase, in R.H. Brill (Ed.), MIT Press, Cambridge, MA, 1971, pp. 80–90.
7 G. Bayer and H.G. Wiedemann, Sandoz Bull., 40 (1976) 19.
8 J. Winter, in C.W. Beck (Ed.), Archaeological Chemistry, American Chemical Society, Advances in Chemistry Series 138, Washington, D.C., pp. 207–225.

9 H.G. Wiedemann, R. Riesen, A. Boller and G. Bayer, in Ch.E. Earnest (Ed.), Compositional Analysis by Thermogravimetry, STP 997, Philadelphia, p. 227.
10 K.C. Danford, Journey into China, National Geographic Society, Washington D.C., 1982, p. 170.
11 H.G. Wiedemann and G. Bayer, in E.V. Sayre et al. (Eds.), MRS, Symposium Proceedings, Vol. 123, 1988, p. 129–134.
12 P.D. Garn, O. Menis and H.G. Wiedemann, Thermal Analysis, Proceedings 6th ICTA, 1980, Birkhäuser Verlag, Basel, p. 201.
13 F. Schjöth, Chinese Currency, Andrew Publishing Comp., London, England, 1976, p. 4.
14 W.T. Chase, Proceedings 2nd ISCRCP, Cultural Property and Analytical Chemistry, 1979.
15 J. Riederer, Kunstwerke chemisch betrachtet, Springer-Verlag, Berlin, 1981, p. 42.
16 H.G. Wiedemann, Birkhäuser Verlag, Basel, Experientia Supplementum, Vol. 37, 1979, pp. 242–256.
17 G. Mayeda and Y. Isozaki, W.Fr. Tschudin (Ed.), Praktischer Leitfaden der Papiermacherei, Osaka, 1798, und Rieken bei Basel, Schwarz, Sandoz AG, Basel, 1959, p. 13.
18 China Pictoral, Paper Currency, 6, 1983 Huayuancum, Beijing 28, China, p. 44.
19 R.B. Corcy and L. Pauling, Istituto Lombardo, Rend. Sci., 89 (1955) 10–37.
20 H. Spoor and K. Ziegler, Angew. Chem., 72 (1960) 316–321.
21 K.A. Jakes and J.H. Howard, Advances in Chemistry Series, Historic Textile and Paper Materials Conservation and Characterization, American Chemical Society, Washington, DC, 1984.
22 H.G. Wiedemann, T. McKarns and G. Bayer, Thermochim. Acta, 169 (1990) 1–13.