A PURPLE BARIUM COPPER SILICATE PIGMENT FROM EARLY CHINA

Elisabeth West FitzHugh and Lynda A. Zycherman

Abstract—A purple barium copper silicate, BaCuSi₂O₆, an artificial inorganic pigment, has been identified, sometimes mixed with the known blue barium copper silicate, BaCuSi₄O₁₀. It occurs on painted objects and in octagonal sticks from China attributed to the Han dynasty (208 BC–AD 220). This man-made pigment, for which the name Han purple is proposed, has not been previously characterized.

1 Introduction

There have been remarkably few purple colorants in the long history of pigments. Tyrian purple, in classical times and earlier in the ancient world, was used as a textile dye rather than as an applied pigment and its color could vary from reddish blue to purplish violet [1]. Other red organic colorants such as madder, which were used both as dyes and as artists' pigments in early times, can also take on a purplish color. Purple madder was mentioned as a specific pigment in nineteenth-century Europe [2, p.143]. It has been said that Egyptian blue can be produced with a violet tone [3] and that the Assyrians prepared a purple frit [4], but these statements have not been confirmed by analytical studies. Gold purple, also known as 'purple of Cassius', a precipitate of gold chloride which is more red than purple, was known in late seventeenthcentury Germany and possibly earlier [2, p.128]. The Japanese used a color they called shido (literally 'purple earth') which was evidently a brown iron ochre with a purplish tone [5]. A purplish brown iron oxide has been observed by one of the authors on a small number of seventeenth- to nineteenthcentury Japanese Ukiyo-e paintings in the Freer Gallery of Art.

The lack of a single purple pigment led to

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the use of mixtures of red and blue to produce this color. Islamic paintings from fourteenthto nineteenth-century Persia and India, for example, have various shades of purple rendered with mixtures of ultramarine and a red dye, sometimes combined with lead white [6]. Early Italian painters also made use of the same three-pigment mixture, with azurite sometimes substituting for ultramarine. [7].

It is only in more recent times that single purple pigments have become available. Mauveine (or mauve) was the first dyestuff to be synthesized, in 1856 [8]. Three artificial inorganic purple pigments were developed in the nineteenth century: cobalt violet (cobalt phosphate and/or arsenate), manganese violet (a manganese ammonium phosphate) and ultramarine violet (an altered ultramarine blue) [9]. Purplish-brown artificial iron oxides were known in Europe at the end of the eighteenth century and acquired the name Mars violet after 1835 [2, p.122]; the modern version can attain a true purple color. In the twentieth century several new synthetic organic violet pigments are in use.

In view of this history, it is of interest to note that during a limited period in China, in the Han dynasty (208 BC-AD 220), and possibly somewhat earlier, mixtures of blue and purple silicates were used to paint pottery and metal objects and to make small, facetted octagonal sticks. The blue component of these mixtures has already been shown to be a synthetic barium copper silicate, $BaCuSi_4O_{10}$ [10]. This compound is an analogue of Egyptian blue, the calcium copper silicate, $CaCuSi_4O_{10}$. The purple component of these mixtures has now been identified as another barium copper silicate, $BaCuSi_2O_6$.

2 Sources of material

Samples of this purple compound were avail-

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able for analysis from unfired painted decoration on seven objects and from six sticks of pigment. The pigment mixture consists of blue, purple and colorless components, or sometimes of purple and colorless particles only. The content of the mixture is usually obvious under a stereomicroscope; occasionally it is only revealed at higher magnification in a microscope slide. Attributions were supplied by the owners of the objects and none comes from a controlled excavation.

(1) Hu, dark gray pottery vessel with painted decoration in red, blue, green and white (illustrated in [10, Figure 1]). Attributed to the Han dynasty. Height 33.5cm, maximum diameter 21cm. National Museum of American Art, Smithsonian Institution, gift of John Gellatly, 1929.8.328 (on loan to the Arthur M. Sackler Gallery, Smithsonian Institution, LT1985.1.328). The blue pigment consists of blue, purple and colorless particles.

(2) Hu, dark gray pottery vessel with painted decoration in red, blue, yellow and white. Attributed to the Han dynasty. Height 53 6cm, maximum diameter 38cm. Arthur M. Sackler Foundation, 72.3.33 (on loan to the Arthur M. Sackler Gallery, Smithsonian Institution, MLS1772). The blue pigment consists of blue, purple and colorless particles.



Figure 1 Gray pottery ram's head with painted decoration. Chinese, attributed to the Han dynasty, 100 BC-AD 100. Arthur M. Sackler Foundation, 74.2.1, on loan to the Arthur M. Sackler Gallery, Smithsonian Institution, MLS1775. Reproduced by permission. Sample (3).



Figure 2 Bronze vessel, top of steamer (hsien) with painted decoration. Chinese, attributed to the Han dynasty, second century BC to first century AD. Height 8.5cm. Freer Gallery of Art, Smithsonian Institution, 16.239. Sample (5).

(3) Gray pottery ram's head with painted decoration in black, red and a gray-bluepurple on white slip (Figure 1). Attributed to the Han dynasty, 100 BC-AD 100, $15 \times 30.8 \times$ 23.2cm. Arthur M. Sackler Foundation, 74.2.1 (on loan to the Arthur M. Sackler Gallery, Smithsonian Institution, MLS1775). The purple pigment consists of purple and colorless particles; the presence of the purple silicate was determined by X-ray diffraction.

(4) Gilt bronze vessel with blue-violet painted decoration inside cover. Han dynasty. Height 20 1cm, diameter 17 9cm. Museum of Fine Arts, Boston 48.372. The blue-violet pigment consists of purple and colorless particles; the presence of the purple silicate was determined by X-ray diffraction.

(5) Bronze vessel, top of *hsien* (steamer) with painted decoration in red, light blue and light purple (Figure 2). Attributed to the Han dynasty, second century BC to first century AD. Height 8.5cm, diameter 16.3cm. Freer Gallery of Art, Smithsonian Institution, 16.239. The purple pigment consists of purple and colorless particles.

(6) Bronze bowl with painted decoration in orange-red, white and light purple. Attributed to the Han dynasty, second century BC to first century AD. Height 7.6cm, diameter 15.6cm. Freer Gallery of Art, Smithsonian Institution, 68.33. The purple

pigment consists of purple and colorless particles.

(7) Lintel and pediment of a tomb. Five hollow ceramic tiles painted in ink and colors on white ground. Attributed to the Han dynasty, end of first century BC to first century AD. Excavated from a burial mound near Loyang, China. Length 240.7cm, height 73.8cm. Museum of Fine Arts, Boston, 25.10-25.13, Denmark Waldo Ross Collection; 25.190, gift of C.T.Loo. The light blue pigment consists of blue, purple and colorless particles.



Figure 3 Purple octagonal stick. Chinese, attributed to Warring States to Han dynasty, fourth to first century BC. Royal Ontario Museum, Toronto, 981x5.6. Sample (8).

(8) Purple octagonal stick (Figure 3). Attributed to Warring States to Han dynasty, fourth to first century BC. Length 5.3 cm, diameter, narrow end 0.95 cm, wide end 1.2 cm. Royal Ontario Museum, Toronto, 981x5.6.

(9) Bluish purple octagonal stick. Chinese, date unknown. Length 3cm, diameter 1·1-1·3cm. Östasiatiska Museet, Stockholm, K4069.

(10) Bright purple octagonal stick (Figure 4). Chinese, date unknown. Length 4.7cm, greatest diameter 0.8cm. Östasiatiska Museet, Stockholm, K4070.

(11) Blue octagonal stick. Attributed to the Warring States period or the Han dynasty, fifth to third century BC. Reported to have come from Jincun near Loyang, China. Royal Ontario Museum, Toronto. Chips from this stick, ROM no. 3, were obtained in 1953 and

1956 and stored at the Freer Gallery of Art; the stick itself is no longer available.

(12) Light purple octagonal stick, ROM no.4. Same provenance and sample as (11). Only chips are available.

(13) Dark purple octagonal stick (Figure 5), ROM no. 8. Same provenance and sample as (11). Only chips are available.

3 Macroscopic appearance

3.1 Pigments on objects

The pigments on the objects listed are all a granular pale blue or pale purple. At first glance they appear almost white, and only after further examination is it apparent that they are mixtures of blue, purple and colorless particles or in some cases purple and colorless particles only.

3.2 Octagonal sticks

The three chips from the sticks in the Royal Ontario Museum (11, 12 and 13) are composed of particles firmly attached together to form a hard, gritty material. The character of the attachment is not known. No organic binder is present. The particles are somehow interlocked or fused together, possibly due to the presence of a lead-containing flux (see section 6). Sampling was only possible by the exertion of pressure with a sharp tool. These chips all consist of mixtures of blue, purple and colorless particles. The blue stick (11) is made up chiefly of blue particles and was the primary source of material for the earlier identification of the blue silicate [10]. The purple sticks (12 and 13, Figure 5) consist chiefly of deep purple particles with a few scattered blue ones; there are more colorless particles in the light purple stick. Scattered yellow and brown inclusions are also present in all three chips.

The purple stick from the Royal Ontario Museum (8) has a surface which is predominantly smooth, and facets with sharp edges (Figure 3). The surface is chiefly a mottled brown but the purple color can be seen in some areas, particularly where the surface has become matt and porous due to abrasion. Light and dark purple, blue, white and occasional black and red particles are seen. The

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Figure 4 Bright purple octagonal stick. Chinese, date unknown. Östasiatiska Museet, Stockholm, K4070. Sample (10).



Figure 5 Chips of dark purple octagonal stick. Chinese, attributed to Warring States period or Han dynasty, fifth to third centuries BC. Sample (13).



Figure 7 Photomicrograph, particles from the purple octagonal stick shown in Figure 4. Mounted in Aroclor 5442, n = 1.66. $\times 240$; (top) in transmitted light; (bottom) between partly crossed polars.



Figure 6 Photomicrograph, particles from the purple octagonal stick shown in Figure 5, in transmitted light. Mounted in Canada balsam, $n = 1.53 \times 335$.

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Figure 8 Detail of surface coating, purple octagonal stick shown in Figure 4, Östasiatiska Museet, Stockholm, K4070. × 5.

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particles are less firmly attached together than in the chips from the other three sticks.

The two sticks from the Östasiatiska Museet (9 and 10) are much more worn and porous than those from the Royal Ontario Museum. The edges of the facets are nearly obliterated (Figure 4) and the surface is matt and very friable. The sticks are composed of dark and light purple particles and some colorless particles; the shorter stick (9) also includes scattered blue particles.

4 Identification of the purple component

4.1 Microscopy

4.1.1 Optical properties

Samples were mounted in Canada balsam (n = 1.53) and Aroclor 5442 (n = 1.66). The color of the purple particles by transmitted light varies from deep to light purple to almost colorless, depending on particle thickness. Most are anisotropic to varying degrees. Pleochroism, from purple to colorless, is common, but is not seen in all samples. The particles vary in size and are irregular in shape with rounded edges; straight edges are occasionally seen in larger particles. The refractive index is 1.72-1.74, determined by the immersion method. Photomicrographs of the purple pigment are reproduced in Figures 6 and 7.

4.1.2 Chemical microscopy

The solubility of the purple compound in acids and alkalis was determined. The purple color is destroyed by dilute HNO₃ (1:4 or 1:7 v/v) and dilute HC1 (1:4). The color fades, leaving the outline of the particle intact in most cases. Some effervescence was noted, evidently from surrounding material, when dilute HNO₃ was applied to the samples from the chips of the Royal Ontario Museum sticks. The color disappears slowly, with repeated heating, in dilute H₂SO₄ (1:4). The color is unaffected by heating with 5% or 18% NaOH.

The reaction to dilute acids is in striking contrast to the behavior of the blue barium copper silicate which is extremely acidresistant.

4.2 X-ray powder diffraction

Single purple particles or groups of particles were separated mechanically with a needle

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under a stereomicroscope at low magnification. X-ray powder diffraction patterns were obtained using both Gandolfi and Debye-Scherrer mounts. Intensities were estimated visually. Similar patterns were obtained from the purple material from eight different Chinese objects. The d-spacings of the Chinese purple pigment matched those of the synthetic purple with the formula BaCuSi₂O₆. The structure of this compound has been described by Finger and co-workers [11] and the d-spacings have been calculated [12, 13] (see Table 1); these data will replace JCPDS 39–1267 [14] which was found to be a multi-phase mixture.

Table 1 X-ray diffraction data

Purple barium copper silicate BaCuSi ₂ O ₆ [13]			Purple component of blue pigment on pottery hu, sample (1)		
d(Å)	I/I _o	hkl	d(Å)	I*	
5·964 5·582	25 8	1 0 1C 0 0 2C	5.99	30	
4·989 4·374	20 2	1 1 0C 1 0 2C	5.01	30	
3·719 3·527	90 18	1 1 2C 2 0 0C	3.72	90	
3·2904 3·0363	30 25	1 0 3C 2 1 1C 2 0 2C	3·04	40	
2·9813 2·7899	5	2 0 2C 0 0 4C	2.99 2.80	20	
2·4941 2·4351 2·4056 2·3517 2·3010	50 65 4 3 5	2 2 0C 1 1 4C 2 1 3C 3 0 0C 3 0 1C	2·49 2·44	60 60	
2·2772 2·2308 2·1885 2·1669 2·1283	14 10 5 2 8	2 2 2C 3 1 0C 2 0 4C 3 0 2C 1 0 5C	2.28	10	
2.0895 2.0716 2.0375 1.9871 1.9564	2 30 2 2 2	2 1 4C 2 2 3, 3 1 2M 1 1 5C 3 0 3C 3 2 0C	2.08	40	
1.9273 1.8863 1.8597 1.8220 1.7637	7 2 5 2 20	3 2 1C 2 0 5C 0 0 6, 2 2 4M 2 1 5C 4 0 0C	1.77	40	

Tuble I	comm	iueu		
Purple b silicate BaCuSi ₂	arium .O ₆ [13	copper]	Purple blue pu pottery sample	component of igment on y hu, e (1)
d(Å)	I/I _o	hkl	d(Å)	I*
1.7425 1.7320 1.6913 1.6819 1.6454	40 8 2 2 12	1 1 6C 3 2 3C 4 1 1C 4 0 2C 2 0 6C	1.75	50
1.5934 1.5775 1.5545 1.5179 1.4908	8 8 4 16 7	4 0 3, 3 3 2M 4 2 0C 4 1 3C 4 2 2C 4 0 4C		
1·4712 1·4584 1·4284 1·4233 1·4110	5 2 14 2 2	3 2 5C 4 1 4C 3 1 6C 2 1 7C 4 3 0C		
1·3999 1·3950 1·3832 1·3428 1·3190	2 5 1 7 3	4 3 1C 0 0 8C 4 0 5, 5 1 0M 5 1 2C 4 3 3C		
1·3011 1·2973 1·2795 1·2754 1·2590	3 2 2 2 2 2	5 2 1C 2 0 8C 4 0 6C 5 2 2C 4 3 4C		
1.2395 1.2361 1.2175 1.2098 1.2031	10 2 7 2 7	5 1 4C 3 2 7C 2 2 8C 5 3 0C 4 2 6C		
1.1925 1.1826 1.1758 1.1537 1.1504	3 4 2 2 3	4 3 5C 4 0 7C 5 1 5,6 0 0M 6 1 1C 5 3 3,6 0 2M	[[
1.1386 1.1155 1.1100 1.0936	2 3 8 5	4 4 4C 6 2 0C 5 1 6,5 3 4N 6 2 2C	ſ	

Table 1 continued

*Estimated visually

4.3 Electron microbeam probe

Samples of the chips from the pigment sticks in the Royal Ontario Museum (11, 12 and 13) were analyzed. Major elements present in the

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purple component are barium, copper, silicon and lead. The element ratios of barium, copper and silicon show the sort of variety to be expected from this analytical method, due to the variation in particle size and the nonuniformity and smallness of the samples. The average element ratios are consistent with a composition of BaCuSi₂O₆ (see Table 2). Lead is present in significant but extremely variable amounts and is not part of the purple compound (see section 6). Other elements present as contaminants or trace materials are A1 (1% or below), Fe, Mg, Ca, K and Zn (all below 1%).

Table 2	Purple p	igment:	element	ratios	(number	of
atoms) i	measured	by elect	ron micr	roprobe		

Source of purple from ROM sticks	Sample no.	Si/Cu	Si/Ba	Si/Pb
Blue, no. 3	1	3.9	2.0	48
,		2.1	2.0	
	2	2.3	2.4	31
		2.3	2.4	
	3	3.9	2.4	30
		1.8	2.9	
	4	3.7	2.4	18
Dark purple, no. 8	9	3.2	2.4	6
		2.1	2.0	
Light purple, no. 4	18	2.5	2.4	72
		2.1	2.4	
Average		2.7	2.3	
BaCuŠi ₂ O ₆		2	2	

4.4 Scanning electron microscopy with X-ray analyzer

Qualitative X-ray spectra obtained from the purple component of the chips from the pigment sticks in the Royal Ontario Museum confirmed the presence of Ba, Cu, Si and Al; Ca and Pb were present in all except one case and Fe in all except two. Other elements present as contaminants or trace materials in some samples were Zn (in 2), Sn (3), Mg (2), K (1) and Cl (1).

5 The colorless component and the fading of the purple component

As already noted, a colorless component occurs in varying amounts mixed with the blue and purple components of these pig-

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ments. It is anisotropic, with a refractive index above that of Canada balsam (1.53) and its particle shape is generally similar to that of the purple. The difficulty of separation precluded identification using X-ray powder diffraction. Major elements present in the colorless component, determined by electron microbeam probe analysis, are barium, silicon and lead. Elements present in minor quantities are copper (2%), zinc (1%), and iron, magnesium, calcium and potassium (all below 1%). The range of elements found by determination of the X-ray spectra with the scanning electron microscope was similar to that found in the purple component, except that barium and copper could not be detected in two cases.

Acid treatment was used to remove the color from areas of purple in a cross-section already analyzed by electron microprobe; these areas were subsequently re-analyzed. The appropriate area of the section was treated with 1:4 HNO₃, allowed to stand for two to three minutes, and then well rinsed with distilled water. From two probe analyses it was found that some barium and copper were removed from the purple areas by this treatment. This observation is consistent with the fact that copper is the only element present from which the purple color could originate.

Synthesis of the purple material (see section 7) results in a mixture of blue and purple, or purple alone; sometimes other colors appear but there is never a significant amount of a colorless component. This absence of colorless particles in newly prepared material, coupled with the fact that the purple color can be removed by dilute acids, strongly suggests that the colorless particles were originally purple particles which faded during burial or on exposure to an acidic environment. It should be noted that a bright purple pigment which has not faded has been observed on some Han dynasty objects which have not been analyzed.

Other color changes in pigments due to atmospheric attack are documented. For example, there are numerous occurrences of darkened red lead, known to be caused by the formation of lead sulfide or lead dioxide [15]. Lead white is also known to blacken; this phenomenon has traditionally been attributed to the formation of lead sulfide, but there is evi-

dence that lead dioxide may also be the culprit [16]. Thus, works of art and archaeology need to be examined carefully to ascertain the original coloration. The pale appearance of this blue/purple pigment is a case in point (see section 3.1).

6 The presence of lead

A light brown lead-containing surface coating is present on the three whole pigment sticks (8, 9 and 10). Figure 8 is a detail of one stick (10) showing this surface coating. The material on one of the sticks (9) was identified as lead carbonate, PbCO₃, by X-ray powder diffraction. On another stick (8) the surface coating proved to be a mixture of lead phosphates, $Pb_{5}(PO_{4})_{3}OH$ and $Pb_{9}(PO_{4})_{6}$. Careful examination of this surface encrustation gives the strong impression that this layer formed when the sticks were made and was not a later deposit. As noted above in section 4.3, lead was found to be a major element in the Royal Ontario Museum sticks. One can only conclude that it was present as a flux or separating agent or for some other reason related to the method of manufacture. It does not form part of the pigment compounds.

7 Synthesis of Han purple and Han blue

The purple silicate has been synthesized by several researchers by heating dry materials, which in some cases were ground and reheated. Chase [17] and Douglas [18] used barium chloride, copper carbonate and silica as starting materials, with synthetic natron (a mixture of sodium sesquicarbonate, sodium sulfate and sodium chloride) as a flux, at 870 and 1000°C respectively. Brill used a stoichiometric mixture (for BaCuSi₂O₄) of barium carbonate, cupric oxide and silica at 1080°C, both with and without sodium carbonate. A mixture of the blue and purple silicates, with some other materials, resulted from all of these syntheses. The blue and purple phases could be made to form separately by varying the temperature. Brill also obtained the purple phase by devitrification of glasses with the stoichiometric composition of BaCuSi₂O₄. The diffraction pattern of this frit matched that of the Chinese material, and individual grains

The crystal structure and Raman spectra of the purple silicate $BaCuSi_2O_6$ have been described [11] and the d-spacings have been calculated by Finger [12]. This silicate was formed during the preparation of superconductors in the T1-Ca-Ba-Cu-O system: T1₂O₃, CaO and BaCu₂O₄ (or Ba₂Cu₃O₅) were heated at 880-910°C in a silica sample container [22]. In addition to the two superconducting oxides, the reaction between the oxide mixture and the silica container produced a byproduct, a coating consisting of two phases, one turquoise and the other purple (described as magenta), the latter being BaCuSi₂O₆. Eysel independently obtained the same purple material by heating a stoichiometric mixture of barium carbonate, cupric oxide and silica at 1000°C for three weeks [13] (see Table 1).

The first synthesis of the blue silicate by Pabst was carried out with various fluxes between 850-900°C [23]. Bayer and Wiedemann reported that it will degrade when heated at 1230°C, but will subsequently reform on cooling [24]. Brill noted that the blue phase formed at somewhat higher temperatures than the purple, but that the temperature at which the two phases form appears to depend on the exact composition of the starting materials [20]. The early Chinese method of manufacturing these pigments resulted in a mixture of the two colors in varying proportions, but they sometimes produced an almost pure purple or blue, either by accident or design.

Other blue and purple barium silicates have been reported. Nearly 100 years ago there was interest in these compounds, as indicated by a German patent for the manufacture of a number of pigments which were green, blue and violet barium copper silicates [25]. Two other blue barium copper silicates have been reported, BaCu₂Si₂O₇ (JCPDS 39–253) and Ba₂CuSi₂O₇ (JCPDS 40–84) [14]. No other barium copper silicates, besides the two we have identified, have yet been found on Chinese objects.

8 Discussion

The results of X-ray powder diffraction estab-

lish that the Chinese purple pigment is the same as the material described by Finger and co-workers [11, 12] and Eysel [13]. Polarized light microscopy, scanning electron microscopy with X-ray analyzer and electron microbeam probe analysis help support this identification (see Table 2). It is clear that Brill and his co-workers have also synthesized the Chinese purple silicate, as confirmed by X-ray powder diffraction and microprobe analyses [19, 20].

It has already been noted that the presence of barium, a characteristic component of Chinese glass at this period, is of significant interest [10, 19, 20]. We hope that further research on these compounds will develop theories about the early methods of manufacture of these pigments and their possible relationship to early Chinese glasses and ceramic glazes. To our knowledge, there is no mention of these colored silicates in the Chinese historical literature. Meanwhile one can only marvel anew at this further evidence of the sophisticated technology of the early Chinese.

9 Naming the blue and purple silicates

We propose the names 'Han blue' and 'Han purple' for these pigments. We prefer this terminology to 'Chinese blue' and 'Chinese purple' (although these terms have already been used in the literature [19, 20]) because the name Chinese blue already exists in the pigment literature as one of the names of Prussian blue. These silicates have a definite identity and their naming will simplify reference to them in the future.

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Résumé—On a identifié un silicate pourpre de cuivre et de baryum, $BaCuSi_2O_6$, pigment inorganique artificiel quelquefois mélangé au silicate bleu de baryum et de cuivre et de formule $BaCuSi_4O_{10}$. On le rencontre dans les objets peints et en bâtonnets octogonaux, originaires de Chine et attribués à la dynastie Han (208 BC-AD 220). Ce pigment fabriqué que l'on propose d'appeler 'pourpre Han' n'avait encore jamais été identifié.

Zusammenfassung—Der Beitrag berichtet vom Nachweis eines künstlich hergestellten, violetten Bariumkupfersilikates $BaCuSi_2O_6$, das manchmal zusammen mit dem bekannten blauen Bariumkupfersilikat $BaCuSi_4O_{10}$ vorkommt. Es taucht auf Farbfassungen bemalter Objekte und in oktagonalen Stangen aus China auf, die in die Han-Zeit (208 v. Chr. bis 220 n. Chr.) datiert werden. Für dieses erstmalig nachgewiesene Pigment wird deshalb der Name 'Han purple' (Han-Violett) vorgeschlagen.