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STUDY OF THE COMPOSITION OF A STONE TOBACCO PIPE FROM THE ARCHAEOLOGICAL RESERVE "PAUTALIA-VELBUZHD-KYUSTENDIL", BULGARIA

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ABSTRACT. First data of the composition of a stone tobacco pipe from the archaeological reserve "Pautalia-Velbuzhd-Kyustendil" are presented. The stone tobacco pipe is found in a cultural layer from the Ottoman period during a rescue excavation in the town of Kyustendil. It has no analogue among the museum exhibits in Bulgaria so far. The studied stone tobacco pipe is made of massive homogenous microcrystalline dark green rock with a greasy luster. Its outer surface is polished. The stone pipe is 6.7 cm in length and 4.6 cm in height with a bowl and a stem united at an angle of 66°. The base of the bowl resembles a bud of flower with six petals, and at the top it attains a funnel-like shape with seven sides and faceted edge. The surface of the bowl is engraved with curves resembling onother seven petals. The stem of the pipe has a thickened tip shaped by seven sides and decorated with engraved stylized curves, which edge is also faceted. For identification of the rock used to make the stone tobacco pipe its powder was investigated by X-ray powder diffraction method. The X-ray diffraction pattern of the powder sample is consistent with chlorite. Quartz was observed under the binocular microscope. Thus, the studied rock is determined as a quartz-chlorite stone. The chlorite is iron-magnesian with a close FeO and MgO content, but with predominance of the latter. It is ferrous clinochlore (ripidolite and pycnochlorite according to the nomenclature of Hey, 1954). The approximate temperature of chlorite formation estimated by the compositional chlorite geothermometer of Cathelineau (1988) ranges from 289 to 353°C, and indicates green-schist facies of metamorphism or hydrothermal-metasomatic process. Possible source rocks for the studied stone tobacco pipe are a massive layer of chlorite phyllites and schists or chlorite rocks formed during alteration of ultramafic rocks from Bulgaria or chloritites as a product of hydrothermal alteration of volcanic rocks outside Bulgaria. All these rocks could be worked easily by metal tools and are suitable for miniature products and sculptures. If the studied tobacco pipe is unique for Bulgaria, most probably it is made outside Bulgaria and is imported in the country.

Introduction

During a rescue excavation in the archaeological reserve "Pautalia-Velbuzhd-Kyustendil" a stone tobacco pipe is found as the mouthpiece is absent. It is registered in the Regional Historical Museum in the town of Kyustendil under inventory N964. So far it has no analogue among the known tobacco pipe collections in Bulgaria as material and decoration. That is why it cannot be compared to other tobacco pipes and cannot be classified properly. The only reliable information about the object is that the cultural layer in which it was found is from the Ottoman period.

In Europe the tobacco pipes are known since the V c. BC – Herodotus informed about them. Since tobacco was imported in Europe in the XVI c. until this time dried leaves and grass were smoked. In the Middle East, Central Asia and India opium was smoked instead. In the Ottoman Impire the smoking of tobacco is known since 1599 according to written sources (Robinson, 1983). In Bulgaria during the Ottoman Period and the Bulgarian Renaissance every large craftman centre, including Kyustendil, was producing clay tobacco pipes (Stancheva, Medarova, 1968). In the Regional Historical Museum in the town of Kyustendil there is a collection of clay tobacco pipes for chibouks. The studied pipe is from the same collection but only formally – it is made of stone and obviously has another origin. Tobacco clay pipes were mostly used in England and Canada from the XVI to the XIX century. They were formed in moulds and then were fired in furnaces. Stone tobacco pipes made of sepiolite are known from Turkey – the sepiolite deposits are located in Central Turkey. Ancient white tobacco pipes made of alabaster (mixture of the minerals gypsum and calcite) are also known. The American Indians had a long tradition of smoking with stone pipes, only the mouthpiece was carved of ash-tree. The stone tobacco pipes of the Arapaho tribe were made of black schists from the Rocky Mountains, and those of the Dakota – of catlinite (pelite rock) from the Missouri River valley (SW Minnesota). There are also findings of stone pipes made of talc schists (West, 1935; Brown, 1978; Bates, Jackson, 1987). All these rocks and minerals are worked easily with metal tools.

During the Ottoman period the town of Kyustendil was the centre of a large county ("sandjak" in Turkish) including the towns of Vranya, Kratovo, Shtip, Veles, Strumitsa, Petrich, Melnik, Dupnitsa and Radomir. Kyustendil is situated on one of the most important trade and military roads in the Balkan Peninsula, which in Tatar-Pazardzik was diverted from the main road from Istanbul to Belgrade and via Samokov, Kyustendil and Skopie led to the Adriatic ports in Albania and Dalmatia (Irechek, 1899). All travelers passing through the town of Kyustendil in the XVII-XIX c. have noted its importance as trade, craftsman and administrative centre. That is why it is possible that the studied stone tobacco pipe was imported from a foreign country.

Material and methods

For identification of the rock used to make the studied stone tobacco pipe, a substance from the lower part of the pipe was taken – there were old traces of scraping and a part of the decoration was broken there. The powder sample was taken with a stone knife and was grounded in an agate mortar. The sample was investigated with X-ray powder diffraction method and energy-dispersive electron microprobe analysis. The phase composition of the powder sample was investigated with Dron-3M X-ray diffractometer using cobalt radiation (λ=0.17903 nm) and iron filter in the range from 8 to 70˚ 2Θ at 35 кV и 25 mA. The chemical composition of the powder sample was determined with energy-dispersive spectrometer EDAX 9100/60(5) united with Philips-515 SEM at 20 kV accelerating voltage. The analytical software included ZAF-programmes – FRAME-C and COR-2. The phase and microprobe analyses were made in the Central Laboratory of Mineralogy and Crystallography "Acad. Ivan Kostov". The calculations of structural mineral formulas were made after Bulah (1967), while for determination of the chlorite mineral species the nomenclatures of Hey (1954), Bayliss (1975) and Wiewiora and Weiss (1990) were used.

Results and discussion

The stone tobacco pipe is made of massive, homogenous, micro-grained dark brown rock with dark green nuance and greasy luster. On a fresh surface it is dark green. Its outer surface is polished. Small black spots with metallic luster are observable on its edges (Fig. 1). The type of the rock cannot be identified only by macroscopic features. The base of the bowl of the pipe resembles a bud of flower with six petals, and at the top it has a funnel-like shape with seven sides and faceted edge. The surface of the bowl is engraved with curves resembling another seven petals. The stem of the pipe has a thickened tip shaped by seven sides and decorated with engraved stylized curves, which edge is also faceted. The bowl and the stem are joint at an angle of 66°. The stone tobacco pipe is 6.7 cm long and 4.6 cm high. The outer diameter of bowl is 3.5 cm and the inner one is 1.2 cm. The stem is 5.1 cm long with thickness of the base of 2.1 cm, outer diameter of the tip – 2.8 cm and inner diameter – 1.2 cm. According to the pipe types defined by Stancheva (1972), as well as by other authors, and considering the chronological features and the shape of the studied stone tobacco pipe, we refer it to the bell-like tobacco pipes dated generally from the end of the XVIII to the second half of the XIX century.

The X-ray diffraction pattern of the investigated stone tobacco pipe has distinct peaks and very low background, which allows undoubted determination of the material (Fig. 1). Its X-ray pattern is consistent with this of chlorite (Brown, Bailey, 1962) (Table 1). According to the diagnostic X-ray reflections (Bailey, 1988) the studied chlorite is polytype IIb, which is the most stable chlorite polytype under metamorphic conditions and in hydrothermal processes (Brown, Bailey, 1962). Peaks of other minerals are not present, i.e. the studied powder sample is a monomineral one. Rare quartz grains were observed in the powder sample under the binocular microscope. These results determine the main mineral composition of the rock used to make the pipe as a quartz-chlorite-bearing rock.

Fig. 1. View of the studied stone tobacco pipe from different aspects

The chlorite group comprises several mineral species and varieties, which have similar chemical composition and physical properties and are products of various conditions of formation. The name of chlorite is related to its colour – in Greek "chloros" means green (Godovikov, 1983; Kostov, 1993). The chlorites most often form micrograined to crypto-grained compact, massive aggregates. They are magnesium and magnesium-iron aluminosilicates with a sheet structure, rich of water. All chlorites have similar diffraction patterns and differ only by the weak reflections (Deer et al., 1962). Two subgroups of chlorites were distinguished by chemistry: orthochlorites (pennine, clinochlore, pycnochlorite, ripidollite, brunsvigite, sheridanite, corundophilite, talc-chlorite, etc.) and leptochlorites (turingite, shamosite and delesite). The orthochlorites are predominantly magnesian and well crystallized. The leptochlorites are rich in trivalent iron and are almost ever micro- to cryptocrystalline. Hey (1954) divided the chlorites to non-oxidized (having up to 4% Fe_2O_3) and oxidized ones (having more than 4% Fe_2O_3) and classified them on the basis of the content of silicon in formula units, on one hand, and the ratio $(Fe^{2+}+Fe^{3+})/(Fe^{2+}+Fe^{3+}+Mg^{2+})$, where the contents of cations are in formula units, on the other hand. This division corresponds to their common dividing into orthochlorites and leptochlorites (Kostov, 1993). According to the recent classification scheme the chlorite group includes five end-member mineral species as follows: clinochlore (Mg-dominant), chamosite (Fe-dominant), nimite (Ni-dominant), pennantite (Mn-dominant) and baileychlore (Zn-dominant). The intermediate compositions are being described by chemical elements adjectives (Bayliss, 1975; Wiewiora & Weiss, 1990).

In immersion (glycerin) the studied chlorite is grass-green in polarized light, does not show pleochroism, has grey interference colours, flaky habitus and perfect cleavage along (001) (Fig. 3). The chlorite flakes in secondary scattered electrons show pseudohexagonal outlines and perfect cleavage along the basal pinacoid (Fig. 4-5). From the length of chlorite flakes, which is about 10 μm (Fig. 4), it follows that

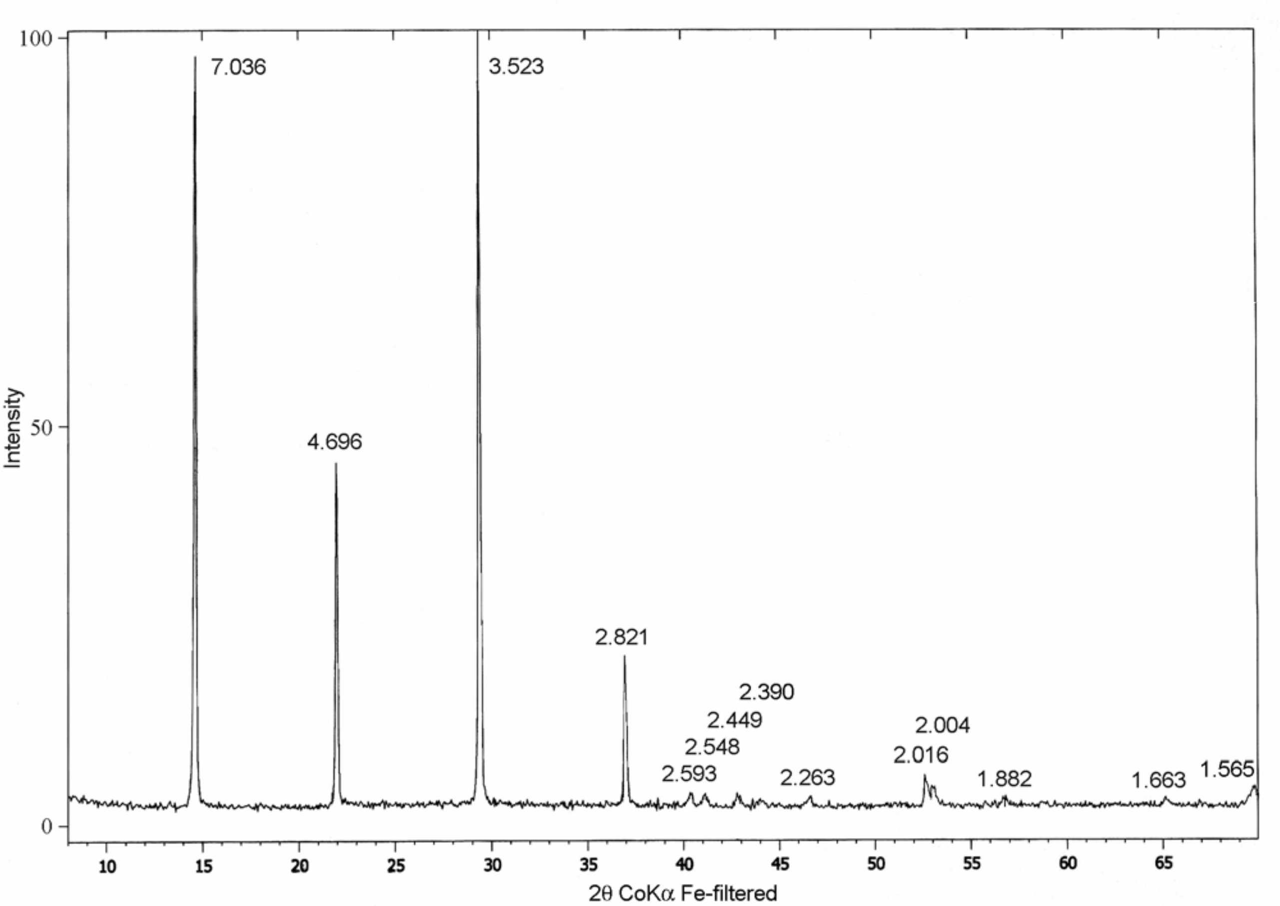

Fig. 2. X-ray diffraction pattern of powder sample from the studied stone tobacco pipe

Table 1. *X-ray diffraction data (d – spacing; I – intensity) for powder sample from the studied stone tobacco pipe and for chlorite (polytype IIb after Brown, Bailey,1962)*

Chlorite		Sample		Chlorite		Sample	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
14.15	8	-	-	2.255	4	2.263	6
7.05	10	7.036	100	2.06	1.5	-	-
4.72	6	4.696	40	-	-	2.016	5
4.60	2	-	-	2.00	6	2.004	4
3.54	10	3.523	100	1.88	2.5	1.882	2
2.83	4	2.821	20	1.82	2.5	-	-
2.66	1.5	-	-	1.74	1	-	-
2.59	5	2.593	2	1.715	0.5	-	-
2.54	8	2.548	2	1.66	1.5	1.663	1
2.44	7	2.449	2	1.565	3	1.565	4
2.38	4	2.390	1	-	-	-	-

the rock is well crystallized – a characteristic feature of the predominantly magnesian chlorites (Kostov, 1993).

For determination of the chemical composition of the studied chlorite energy-dispersive electron microprobe analyses of single micropieces from the powder sample were made. The analyses were normalized to 100% by the software, which unfortunately, does not show the water content in the studied chlorite. Because of this the obtained chemical data should be considered qualitatively. The microprobe analyses showed that the studied chlorite is iron-magnesian with close contents of FeO and MgO. It contains traces of manganese and copper (Table 2).

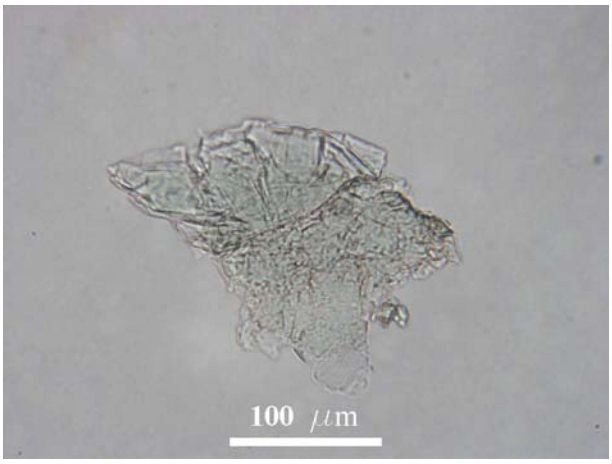

Fig. 3. Flaky habitus of chlorite aggregate from the studied stone tobacco pipe in optical microscope, //N

The structural formulas of the studied chlorite are calculated on the basis of 10 cations. In them (without one) we have an excess of aluminum toward the stoichiometry of ^{VI}Al, that is why this excess is added to the two-valent cations, where there is a deficit accordingly to the structural formula of chlorite (Arden, 1962). At this kind of heterovalent isomorphism the charge balance attains with a vacancy: $3M^{2+} \Leftrightarrow 2Al^{3+} + \square$ (Walshe, 1986). The formula units of Al in tetrahedral site were used for rough estimation of the formation temperature of the studied chlorite using the linear dependence between the formation temperature and ^{IV}Al: $T=-61.9229+321.9772(^{IV}Al)$ (Cathelineau, 1988).

Table 2. *Energy-dispersive electron microprobe analyses of powder sample from the studied stone tobacco pipe (wt. % – weight per cent, s. error, % – standard error of the analyses in per cent; analysist L. Petrov)*

N	Oxides, wt. % / s. error, %						Sum
	MgO	FeO	MnO	CuO	Al_2O_3	SiO_2	
1	18.21	25.95	0.36	0.41	24.94	30.13	100.01
	1.32	0.79	18.75	25.86	0.93	0.78	
2	19.73	22.15	0.01	0.01	26.73	31.37	100.00
	1.38	0.98	980.22	980.56	0.99	0.86	
3	20.00	21.95	0.08	0.10	26.59	31.27	99.99
	0.97	0.64	54.61	68.57	0.72	0.61	
4	19.41	22.39	0.14	0.06	26.44	31.56	100.00
	0.84	0.54	27.44	89.02	0.61	0.52	
5	18.95	26.17	0.33	0.14	24.77	29.65	100.01
	1.29	0.72	18.29	63.58	0.95	0.79	
6	19.34	22.75	0.10	0.00	26.36	31.44	99.99
	1.27	0.80	58.50		0.92	0.78	
7	20.21	20.60	0.00	0.00	26.90	32.29	100.00
	1.15	0.80			0.85	0.72	
8	20.71	19.70	0.02	0.00	27.28	32.29	100.00
	1.08	0.79	221.08		0.81	0.69	

1. $(Mg_{2.41}Fe_{1.99}Mn_{0.03}Cu_{0.03}Al_{0.54})_{5.00}Al_{1.00}[Al_{1.16}Si_{2.76}O_{10}](OH)_8$
T=312° C
2. $(Mg_{2.65}Fe_{1.67}Al_{0.68})_{5.00}Al_{1.00}[Al_{1.16}Si_{2.83}O_{10}](OH)_8$
T=312° C
3. $(Mg_{2.69}Fe_{1.66}Mn_{0.01}Cu_{0.01}Al_{0.64})_{5.00}Al_{1.00}[Al_{1.18}Si_{2.82}O_{10}](OH)_8$
T=318° C
4. $(Mg_{2.62}Fe_{1.69}Mn_{0.01}Al_{0.68})_{5.00}Al_{1.00}[Al_{1.14}Si_{2.86}O_{10}](OH)_8$
T=305° C
5. $(Mg_{2.58}Fe_{2.00}Mn_{0.03}Cu_{0.01}Al_{0.38})_{5.00}Al_{1.00}[Al_{1.29}Si_{2.71}O_{10}](OH)_8$
T=353° C
6. $(Mg_{2.62}Fe_{1.73}Mn_{0.01}Al_{0.64})_{5.00}Al_{1.00}[Al_{1.16}Si_{2.85}O_{10}](OH)_8$
T=312° C
7. $(Mg_{2.70}Fe_{1.55}Al_{0.75})_{5.00}Al_{1.00}[Al_{1.09}Si_{2.70}O_{10}](OH)_8$
T=289° C
8. $(Mg_{2.76}Fe_{1.47}Cu_{0.03}Al_{0.77})_{5.00}Al_{1.00}[Al_{1.11}Si_{2.89}O_{10}](OH)_8$
T=295° C

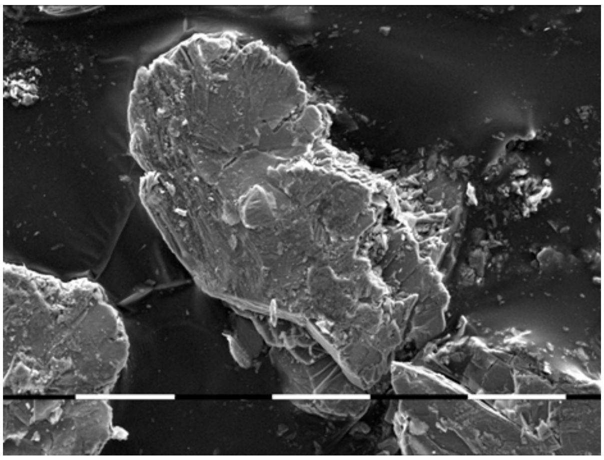

Fig. 4. Chlorite aggregate from the studied stone tobacco pipe with entrance and inner angles characterizing a pseudohexagonal habitus of the chlorite flakes; scale bar 10 µm

According to the nomenclature of Hey (1954) the studied chlorite falls into the border area of ripidolite, pycnochlorite and brunsvigite (Fig. 6), but according to the nomenclature of Bayliss (1975) and of Wiewiora & Weiss (1990) the chlorite is ferrous clinochlore. The approximate formation temperatures (Cathelineau, 1988) are in the range from 289 to 353°C. The obtained temperatures are in the area of the lower temperature part of the green-schist facies of metamorphism (Kostov, 1993).

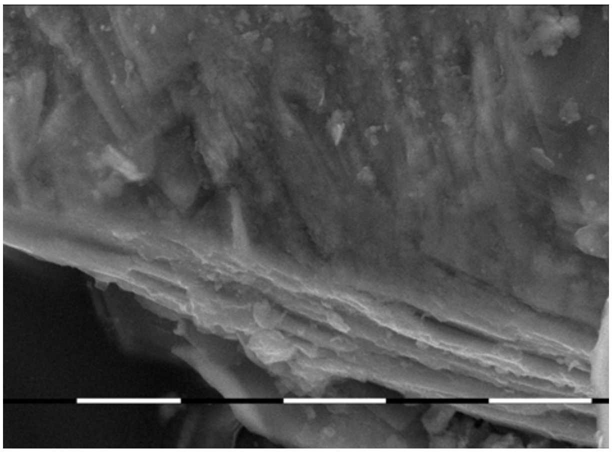

Fig. 5. Perfect cleavage along the basal pinacoid of the studied chlorite; scale bar 10 µm

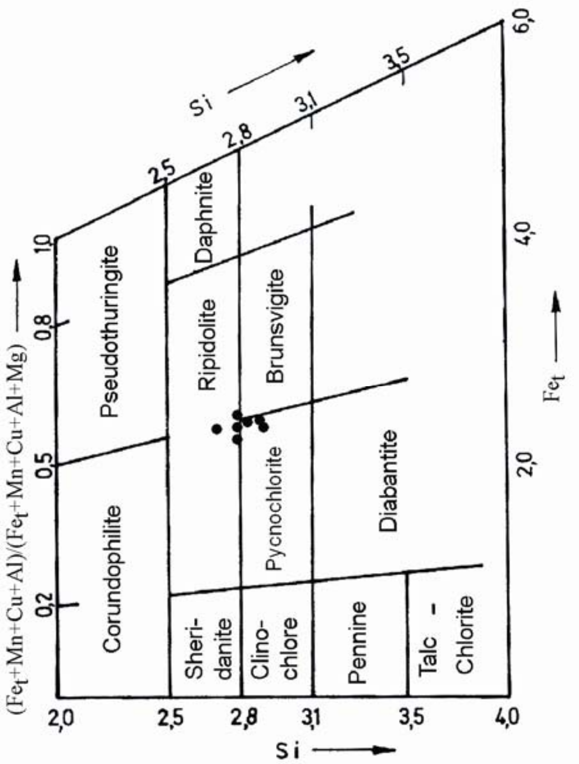

Fig.6. Nomenclature of orthochlorites of Hey (1954, from Kostov, 1993) with figurative points of the studied chlorite, where Al=5-(Fe+Mg+Mn+Cu) formula units

These temperatures are of the same order as those of chlorites (clinochlore, ripidolite and turingite) from hydrothermal quartz and Alpine veins cross-cutting green schists and amphibolites respectively, and of chlorites from pegmatites in high-grade metamorphic rocks in the Bohemian massif (Czech Republic and Poland) (161-379°C, Zimak, 1999) as well as of chlorites from hydrothermally altered rhyodacites transformed into chloritites (ripidolite, pycnochlorite and brunsvigite) from the Archaen green-schist belt Abitibi in Canada (average T=290°C) (Kranidiotis, MacLean, 1987).

The chlorites are the main rock-forming minerals in the chlorite schists and phyllites, which form at low-grade (green-schist) metamorphism of mafic igneous rocks and of clay sediments (Petrova et al., 1981). The chlorites in the chlorite schists are ripidolite, pycnochlorite and brunsvigite (Deer et al., 1962). They form also during metasomatic alterations of volcanic rocks as almost monomineral chlorite rocks (chloritites) can form in some cases (MacLean, Kranidiotis, 1987). The chlorites form also during retrograde metamorphism of ultramafic rocks. They are also widespread products of weathering and are found in many clayey rocks (Deer et al., 1962).

Taking into consideration the aforesaid (the main quartz-chlorite composition of the rock of the studied pipe; the mineral species of the chlorite - ferrous clinochlore; the approximate formation temperatures of the chlorite 289-353°C), it can be supposed that the studied stone tobacco pipe is made of chlorite phyllite, chlorite schist, chlorite zones and veins or chloritites.

The chlorite phyllites and schists in Bulgaria are widespread in West and Southeast Bulgaria, and in the Central Stara Planina. They are product of green-schist facies of metamorphism of Lower Paleozoic, Triassic and Jurassic pelitic and psamitic rocks and of mafic volcanic rocks. On the Geological Map of Bulgaria at 1:100000 and 1:500000 scale they are referred to the Berkovitsa Group, Dulgi Del Group and Frolosh Formation (West Bulgaria, Central Stara Planina), to undivided Paleozoic (Sakar), to Strandja and Sakar types of Triassic, and to the East-Thracian Group (Southeast Bulgaria) (Cheshitev, Kunchev, 1989).

The metamorphosed pelitic and psamitic rocks in West and Southeast Bulgaria and Central Stara Planina are transformed into light to dark green, and black green phyllites with clear schistosity (Dimitrova, Kunov, 1974), which consist of illite-muscovite (sericite), chlorite and quartz. Chlorite and sericite-chlorite phyllites were distinguished. Fe-Mg and Fe-chlorites of IIb polytype predominate. Traditionally a green-schist facies of metamorphism is assumed for them (Dimitrova, Kunov, 1974; Haidutov, 1991) but some authors (Stefanov, 2000; Yanev, Stefanov, 2001; 2002) reported anchi-metamorphism for their formation. The rock of the studied stone tobacco pipe is massive with no signs of schistosity, whereas the chlorite phyllites from Bulgaria are clearly schistosed. But among them there are massive layers enough for working out of stone tobacco pipes like the studied one. Such layers are more often found in the Turkish part of the Strandja Mountain (pers. communication J. Malyakov). These massive layers could be the source for the studied stone tobacco pipe.

The mafic volcanic rocks (spilites) and their tuffs of the Berkovitsa Group during the green-schist metamorphism are transformed into green rocks (phyllites) consisting of uralite + albite + epidote $\pm$ chlorite $\pm$ sericite $\pm$ carbonate (Haidutov, 1991) – a composition much more varied in comparison with the ascertained quartz-chlorite composition.

Chlorite rocks (zones and veins) as a product of retrograde metamorphism of ultramafic rocks crop out in some areas of the high-grade metamorphic terrains of the Rhodope Mountain (the Eastern Rhodopes – near the towns of Ardino, Kurdjali and Krumovgrad; the Central Rhodopes – near the towns of Smolyan and Chepelare; the Northern Rhodopes – between the village of Brestovitsa and the town of Asenovgrad; the Western Rhodopes), Sushtinska and Iztochna (East) Sredna Gora Mountains, the Western and Central Balkan Mountain, the Belasitsa, Ograjden and Maleshevska Mountains (Cheshitev, Kunchev, 1989). But chlorite in these altered ultramafic rocks commonly associates with serpentine, actinolite, tremolite, talc, vermiculite, biotite, and carbonate depending on the degree of alteration. Almost monomineral chlorite zones and veins also found and they are a product of hydrothermal-metasomatic alterations. These zones can reach a meter-scaled thickness (Kozhoukharov, 1966; Zhelyazkova-Panayotova, 1989; Kozhoukharova, 1999, 2000). Kozhoukharova (1999; 2000) described chlorite schists developed metasomatically on serpentinites. These almost monomineral chlorite rocks could also be the source for the stone tobacco pipe studied.

Chloritites as a product of hydrothermal alteration of volcanic rocks are not described in Bulgaria so far. The chlorite rocks are soft, easily worked with tooler and other metallic tools, which allows the working of miniature products and sculptures.

The exquisite workmanship and the particular decoration reveal the features of a stone-cutter school so far unknown in Bulgaria. Due to its unique character the studied stone tobacco pipe most likely has belonged to a wealthy citizen of Kyustendil rather than to a poor one. That is why it is possible that it has been imported as a gift and in this case most likely it has been made of a rock that originates outside Bulgaria.

Conclusion

The studied museum artefact – stone tobacco pipe with inventory N964 from the Regional Historical Museum in Kyustendil, belongs to the bell-like tobacco pipes and it is generally dated from the end of the XVIII c. to the second half of the XIX century.

The stone tobacco pipe is made of massive homogenenous microcrystalline dark green rock of a quartz-chlorite composition, which could be chlorite phyllite, chlorite schist, chloritized ultramafic rock or chloritite. The chlorite is a ferrous clinochlore (ripidolite and pycnochlorite) formed under conditions of green-schist facies of metamorphism or as a product of alteration of ultramafic or volcanic rocks.

Possible rock source for the stone tobacco pipe is a more massive layer of chlorite phyllite and chlorite schist from Bulgaria. Other possible rock sources are chlorite zones and veins in altered ultramafic rocks from Bulgaria as well as chloritites on volcanic rocks outside Bulgaria.

The master of the stone tobacco pipe N964 knew and used the low hardness of the chlorite rock and its ability to be worked with metallic tools.

If the stone tobacco pipe N964 has no analogue in Bulgaria, most likely it was made of a rock outside Bulgaria and was imported as a gift.

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