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Drilling rig, open pit mine "Buchim",
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MINERAL RESEARCHES OF THE EXAMPLES OF THE ARCHEOLOGICAL LOCALITY “STOBI” USING THE METHOD OF THE X-RAY DIFFRACTION

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A b s t r a c t: In this paper examples data is presenting from the mineral researches on couple of examples from moulding decoration (archeological finding) which is found on the Kockarnica at the ancient city Stobi.

Point of the moulding fragments researches is specify if they are all natural stones from mineral origin or parts of them are synthetic. It is very important to give information for their geological origin, more specifically to give information about where we can find them.

Results will serve first for making this artifact, but also for receiving information about its origin. With other words, we need to know whether the artifact is produced in Ancient Macedonia or it is brought from further places. Given results show that the biggest part of the examples originates from Macedonia only beryl appears as an exception.

Key words: moulding; x-ray researches; thermic researches

INTRODUCTION

Stone examples, which were subject of examination, are part of moulding decoration which represents mosaic technique made above wooden base. Moulding is archeological founding from the excavations in 2006–2007 in frames of the conservatoire-researching on the object Kockarnica at the ancient city Stobi.

Stobi, which is one of the most researched locality in Republic of Macedonia is in the middle of the Vardar region between Crna Reka (Erigon) and the river Vardar (Agiuous) and it is assumed that it takes area about 20 hectares.

According to the oldest historical information met in the records of Roman history professor Tit Livij, Stobi originates from Hellenistic period 197 BC (Wiseman, 1971, 1973). According to archeological data from the researches this city settlement is raised 3–2 century BC although many ceramic findings show on a much early period 7–5 century BC. (Mikulčić, 2003, Project elaborat, 2004).

Because of its perfect position on the road “Via Ignacia” that leads from Danube to the Aegean this city settlement represented significant strategic, military, economical and cultural centre (Aleksova, 1997).

In the researched part of Stobi, many architectonic object are found and studied till now and they represent profane and sacral constructions with public function, palaces, baths, antique theatre, parts of city palisade, streets, forum, main entrance of the city and the casino where the artifact that we are talking about is found. The casino represents a hall which floor was covered with mosaic made of geometrical motives. In the middle there was an octagonal fountain covered with marble and above there were three tables for gambling. In the casino there were also a bath with places for seating, and a little pool for drinking water for the guests (Fig. 1, Fig. 2).



Fig. 1. Moulding of the object Kockarnica at the ancient city Stobi



Fig. 2. Part of the mosaic of the object Kockarnica at the ancient city Stobi

METHODS OF EXAMINATION

The analyses are made with scanning electronic microscope JEOL JSM 35CF X-ray micro-analyzer TRACOR NORTHEPN TN – 2000 and we used etalons from JEOL.

X-ray researches are made on the diffractometer Simens D 500 with computer support of Cu monochromatic radiation of 40 KB/30 mA with automatic changeable input shutter. Determination of the mineral phases is made by program package DIFRAK 11 in programs EVAL and IDR.

Quantitative presence of the mineral phases is made by Peter and Kelman's method with already defined coefficients for some mineral phases.

Preparations made for x-ray diffraction are pictured in $2\theta = 3 - 60^\circ$.

Thermal researches are made on derivatograph Q-1500 D under these conditions:

- weight of the experiment 500 mg,
- sensitivity of TT 200 mg,
- sensitivity of DTA 250 μ B, DTT 500 μ B,
- speed of warming up 10 C/min,
- temperature interval of the measuring from 15–20 $^\circ$ C to 1000 $^\circ$ C,
- inert material Al203,
- centre in the oven-air without turbulence.

RESULTS AND DISCUSSION

Subject of examine are 12 samples. In the Tables 1 and 2 chemical compositions are presented of all 12 samples.

Table 1

Chemical composition of the samples 1, 2, 3, 4, 5, 6 and 7 (in %)

	1	2	3	4	5	6	7
SiO ₂	93.45	91.16	62.21	93.36	99.36	0.86	2.42
Al ₂ O ₃	3.38	0.99	5.97	1.19	0.30	<0.01	1.43
Na ₂ O	1.26	<0.01	<0.01	<0.01	<0.01	<0.01	
K ₂ O	<0.01	0.09	1.10	0.20	<0.01	0.14	0.45
CaO	1.09	<0.01	1.04	1.02	<0.01	1.52	5.00
FeO	0.74	7.77	8.12	2.84	<0.01	0.12	0.35
TiO ₂		<0.01	0.05	0.08	<0.01	0.08	0.09
MnO		<0.01	0.14	<0.01	<0.01	0.11	
MgO					<0.01	51.14	1.45
SO ₃							1.18

Table 2

Chemical composition of the samples 8, 9, 10, 11 and 12 (in %)

	8	9	10	11	12
SiO ₂	0.78	65.49	37.35	98.74	0.86
Al ₂ O ₃	0.36	16.96	2.12	<0.01	<0.01
Na ₂ O		0.44	1.74	0.53	<0.01
K ₂ O	0.15	0.08	1.72	0.14	0.24
CaO	0.44	0.03	8.56	0.08	3.36
FeO	0.14	0.16	3.97	0.07	0.27
TiO ₂	<0.01			<0.01	<0.01
MnO				0.07	0.09
MgO	1.05	0.83		<0.01	57.30
SO ₃	<0.01				
PbO			32.08		
CuO			11.45		

In *sample 1* we have presence of the following minerals: quartz, albite and calcite. On Fig. 3 we have crystal of quartz.

On Fig. 4 x-ray diagram of sample 1 is given. Quartz is based under these d-values: 4.24, 3.34, 2.45, 2.27; 2.23; 2.12; 1.97; 1.81; 1.66.

The four most intense d-values for albite are: 3.20; 3.78; 6.39; 3.68, and for calcite are: 3.03, 1.87; 3.85; 2.09

The presence of the minerals is following: quartz 96%, albite 1% and calcite 1%



Fig. 3. Quartz crystal used in sample number 1

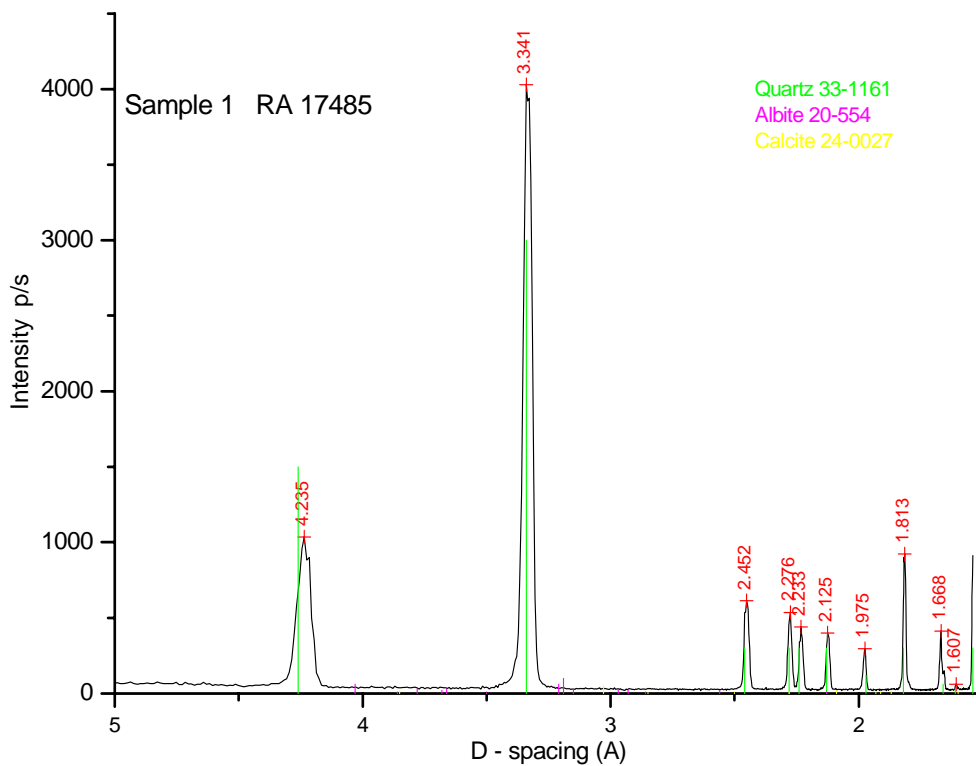


Fig. 4. The powder x-ray diagram of sample 1

Sample number 2: In this sample we have presence of the minerals quartz and hematite. On Fig. 5 we have quartz with hematite. Hematite is based on the following d-values: 2.70; 2.52; 1.69; 1.84 (Fig. 6 and Fig. 7). These values are in accordance with JCPDS 33-664. We have quartz with 90% presence and hematite 9%.

Sample number 3: We have presence of these minerals: magnetite, quartz, dolomite, albite, and

muscovite (Fig. 10). Percentage of the minerals is next: quartz 45%, magnetite 41%, dolomite 7%, muscovite 4%, albite 3%. The x-ray diagram is given on the Figs. 8 and 9.

Characteristic d-values for magnetite are 2.53-1.48-2.97-1.62, for dolomite 2.89-2.19-1.79-2.02, for albite 3.20-3.78-6.39-3.68 and for muscovite 4.50-9.91-2.56-3.62.



Fig. 5. Quartz with hematite from moulding in Stobi

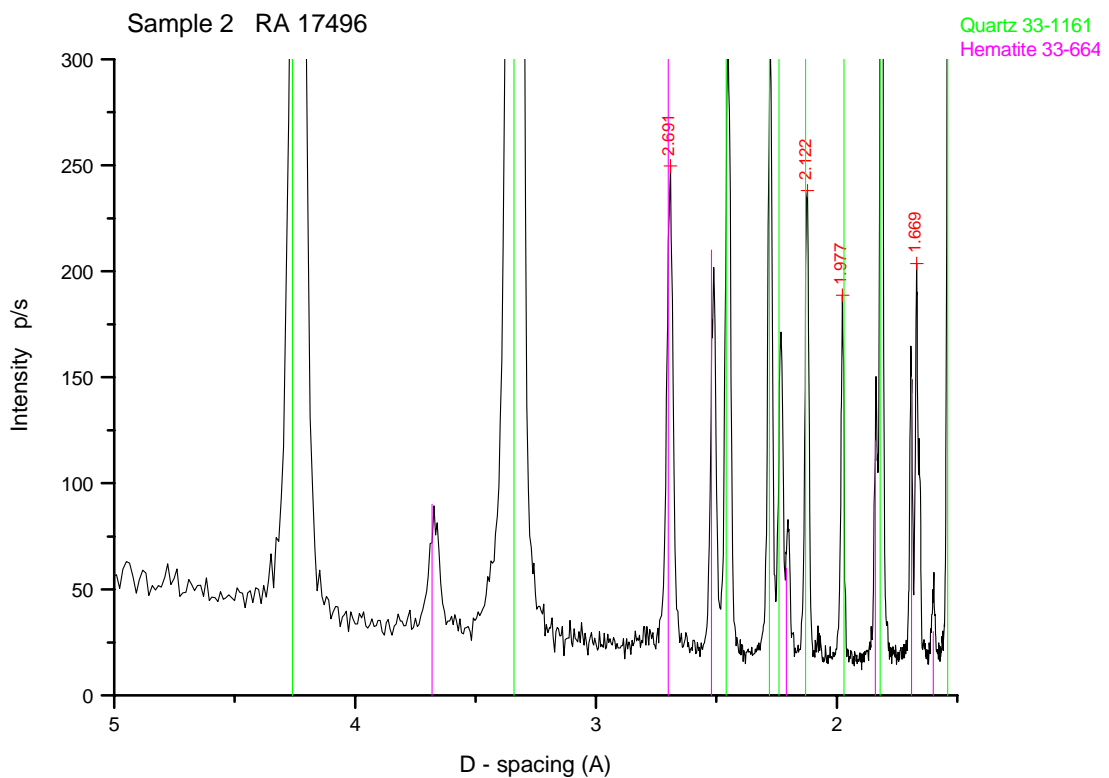


Fig. 6. The powder x-ray diagram of sample 2-1

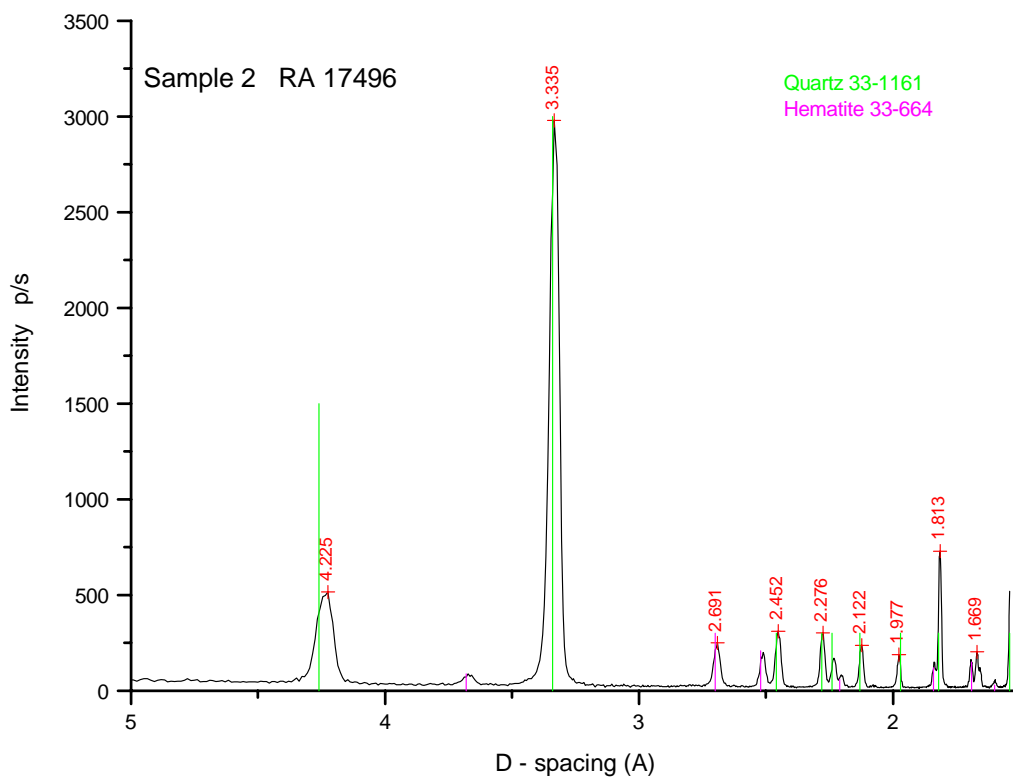


Fig. 7. The powder x-ray diagram of sample 2-2

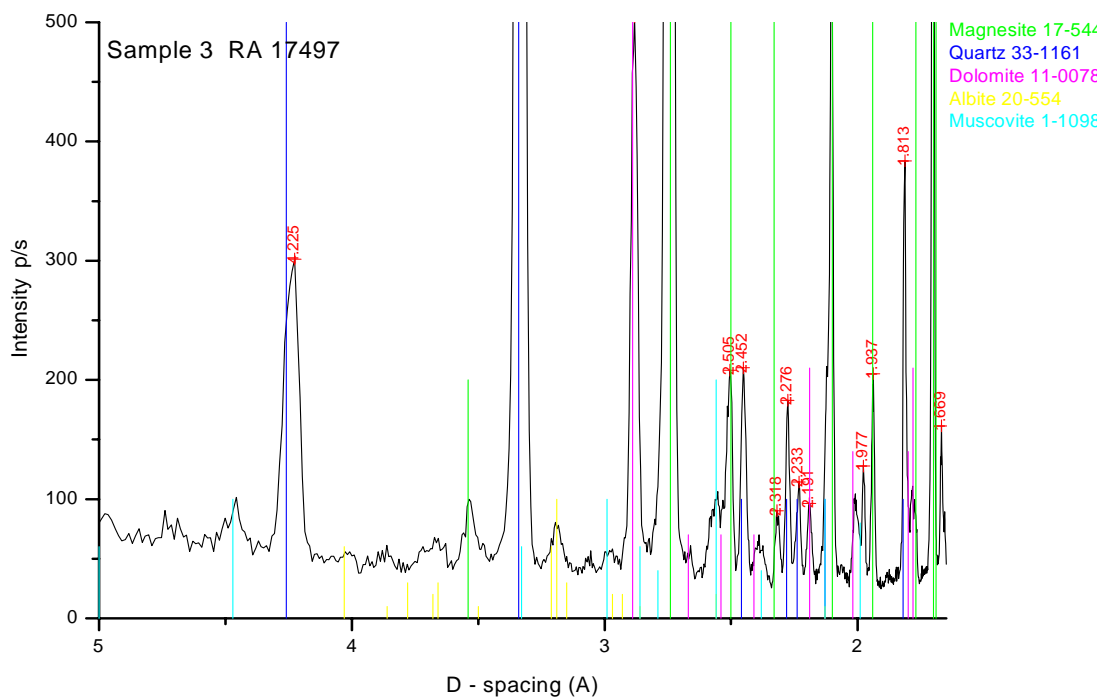


Fig. 8. X-ray diagram of sample 3-1

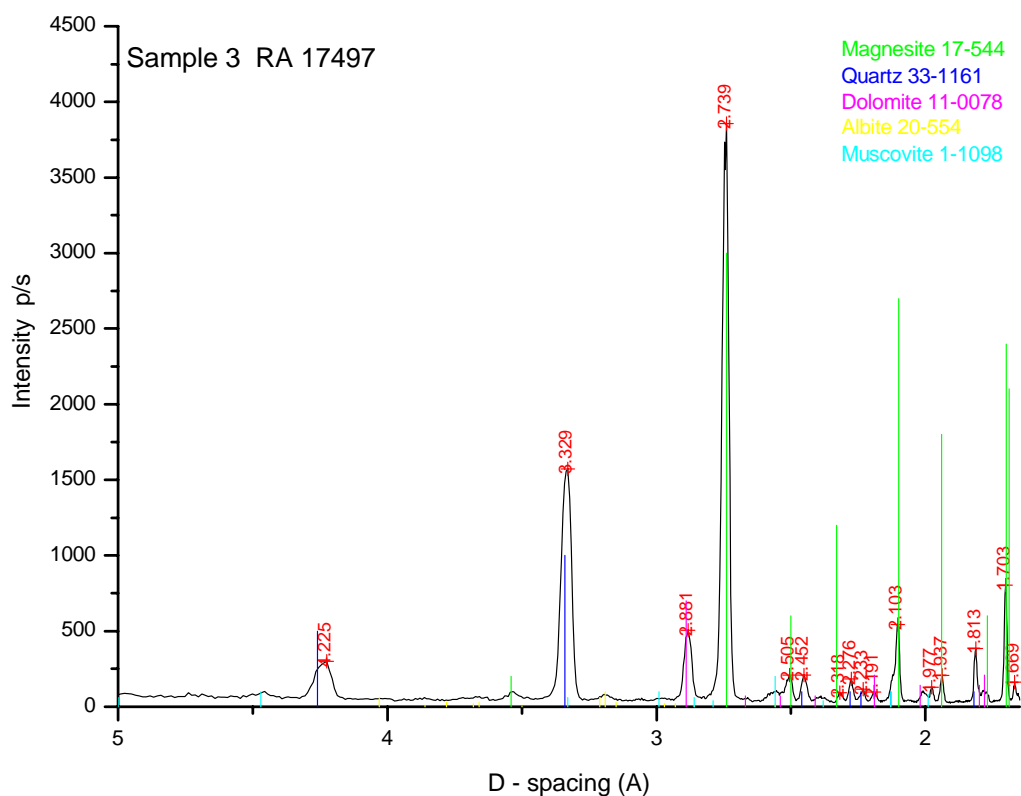


Fig. 9. X-ray diagram of sample 3-2



Fig. 10. Photo of sample number 3

Sample number 4: In this sample we have quartz 76%, dolomite 16%, hematite 3%, calcite 2%, halloysite 2%. We can see some of these minerals on Fig. 11. The x-ray diagram of sample number 4 is given on Fig. 12.

Sample number 5: In this sample we have 99% quartz and dolomite 1% (Fig. 13). X-ray diagram is given on Fig. 14.

Sample number 6: We have the minerals magnesite and dolomite. On (Fig. 16) magnesite is shown. Its presence is 98% and dolomite 1%. The x-ray diagram is given on Fig. 15.



Fig. 11. Photo of sample 4

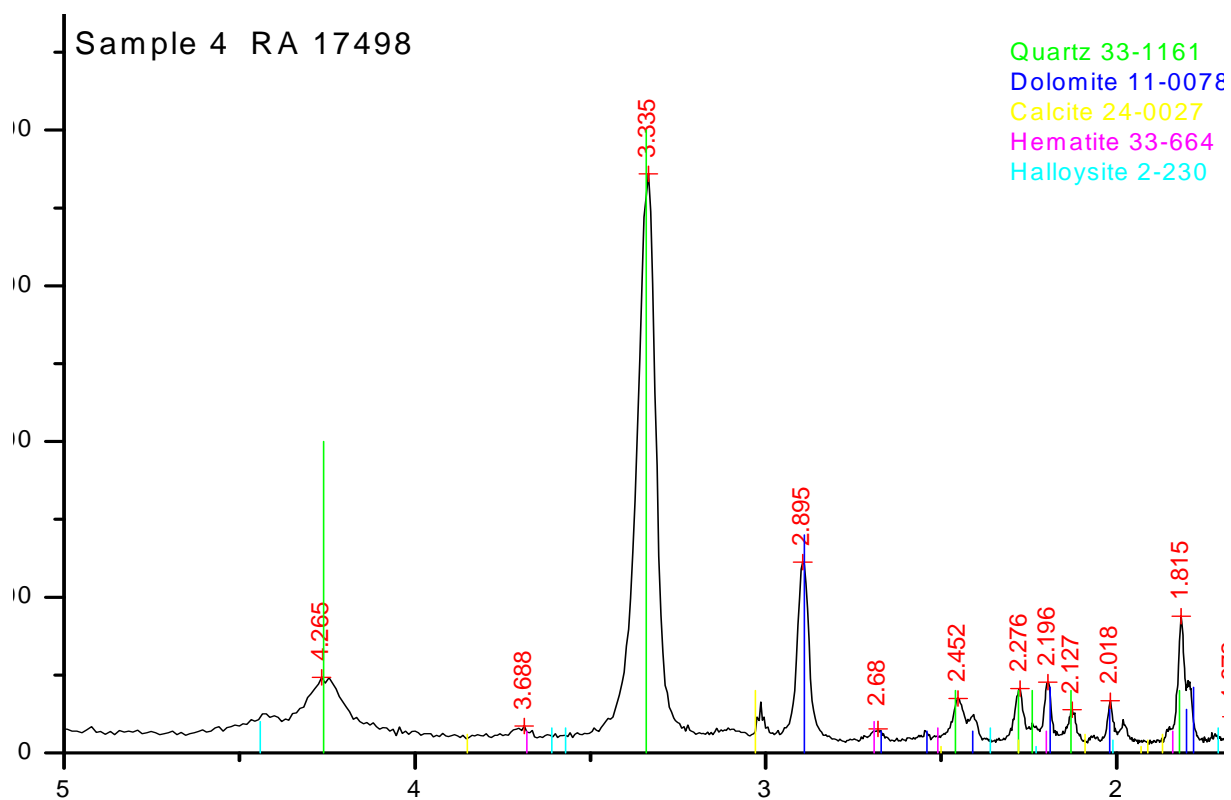


Fig. 12. X-ray diagram of sample 4

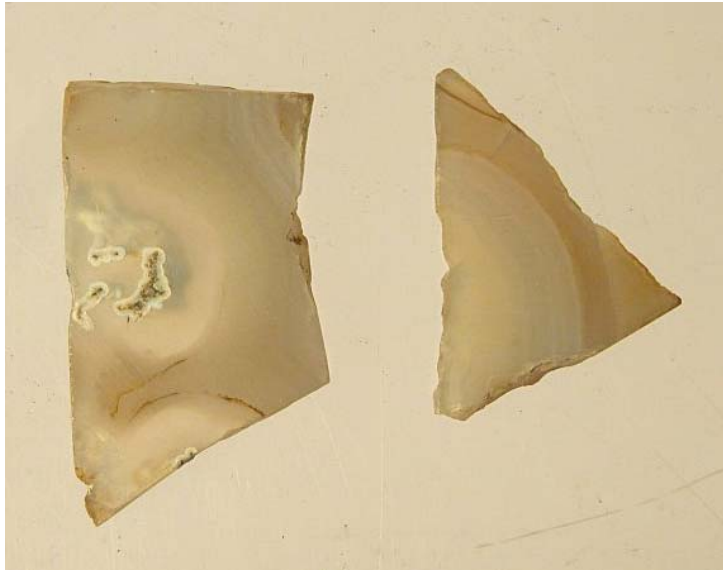


Fig. 13. Achate of sample 5

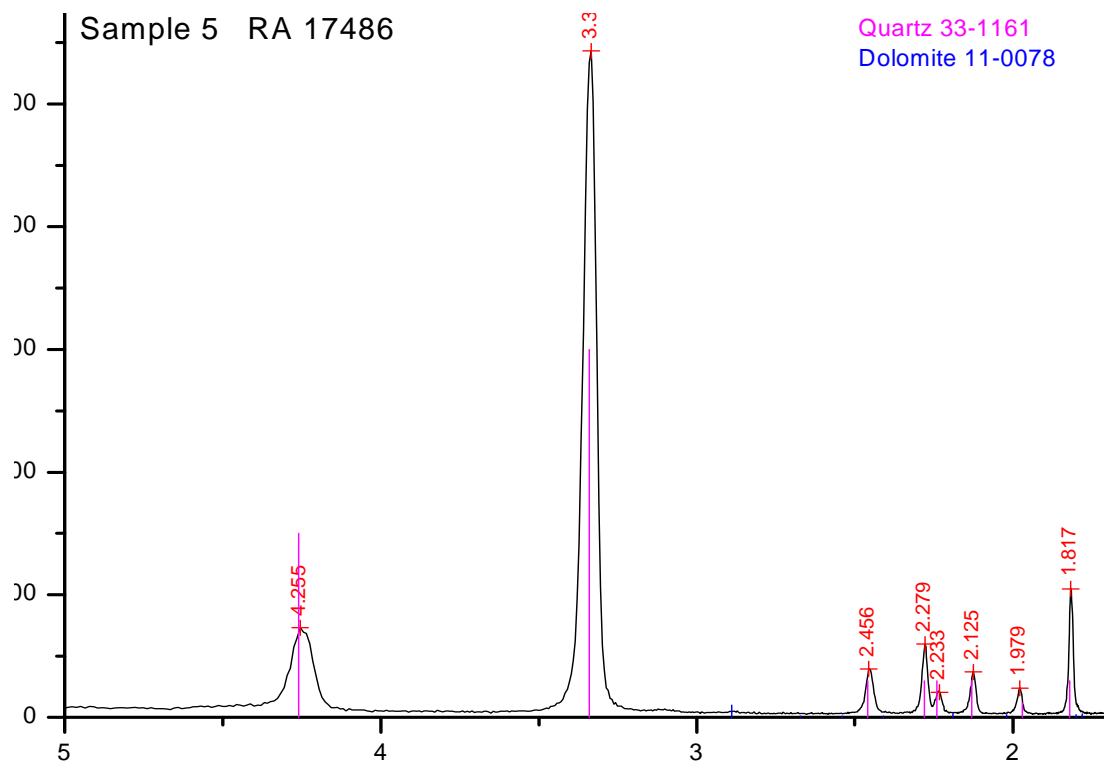


Fig. 14. X-ray diagram of sample number 5

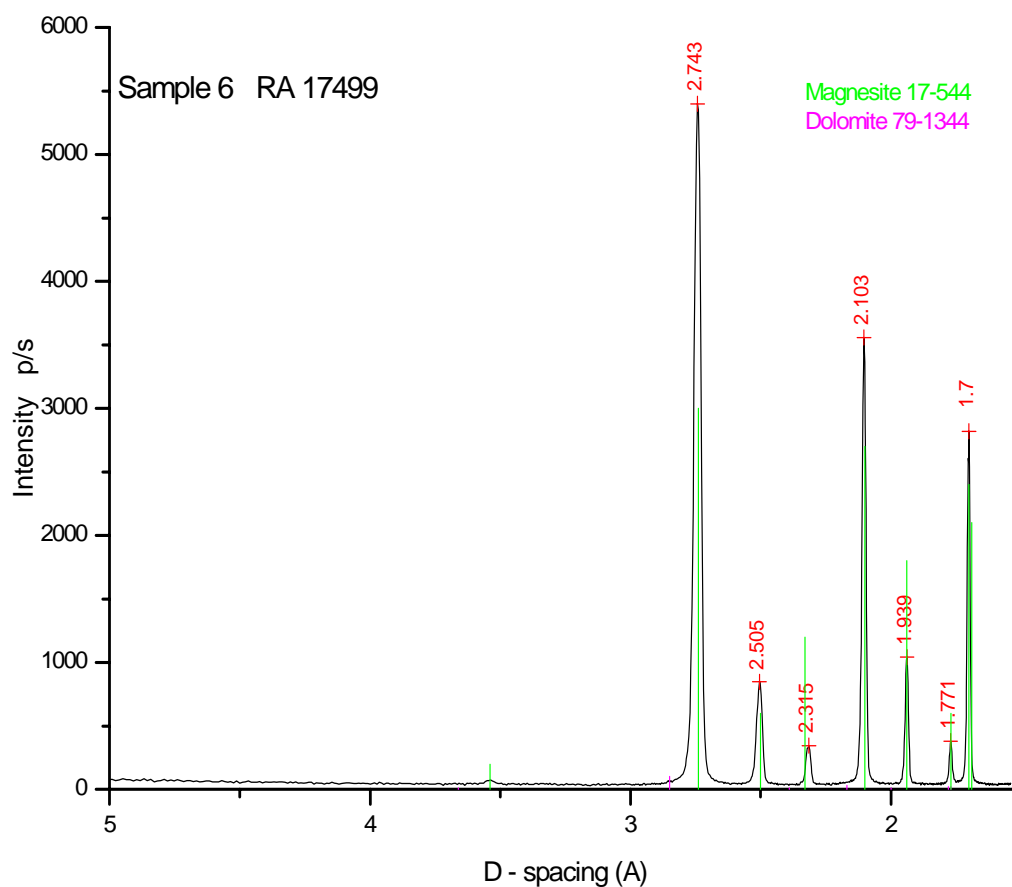


Fig. 15. X-ray diagram of sample number 6



Fig. 16. Magnesite of sample 6

Sample number 7: From the x-ray diagram shown on Fig. 18 we can see that it is about amorphous phase most probably organic material,

with little presence of quartz, calcite and olivine. We have two examples of the sample on Fig. 17.

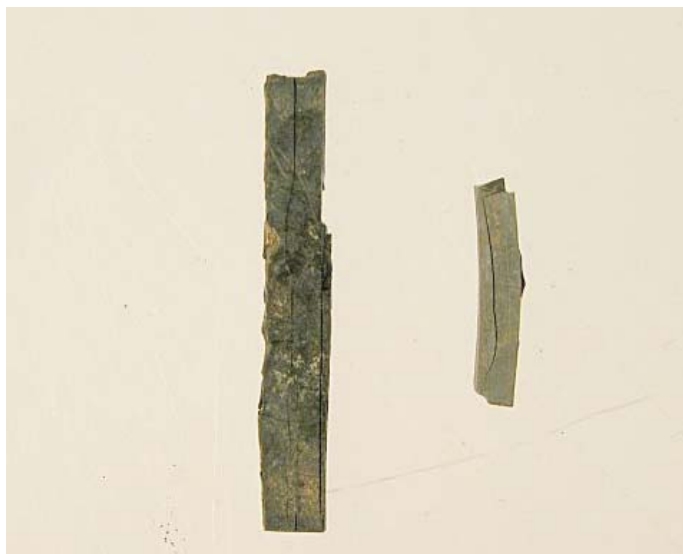


Fig. 17. Organic material with presence of olivine, calcite and quartz

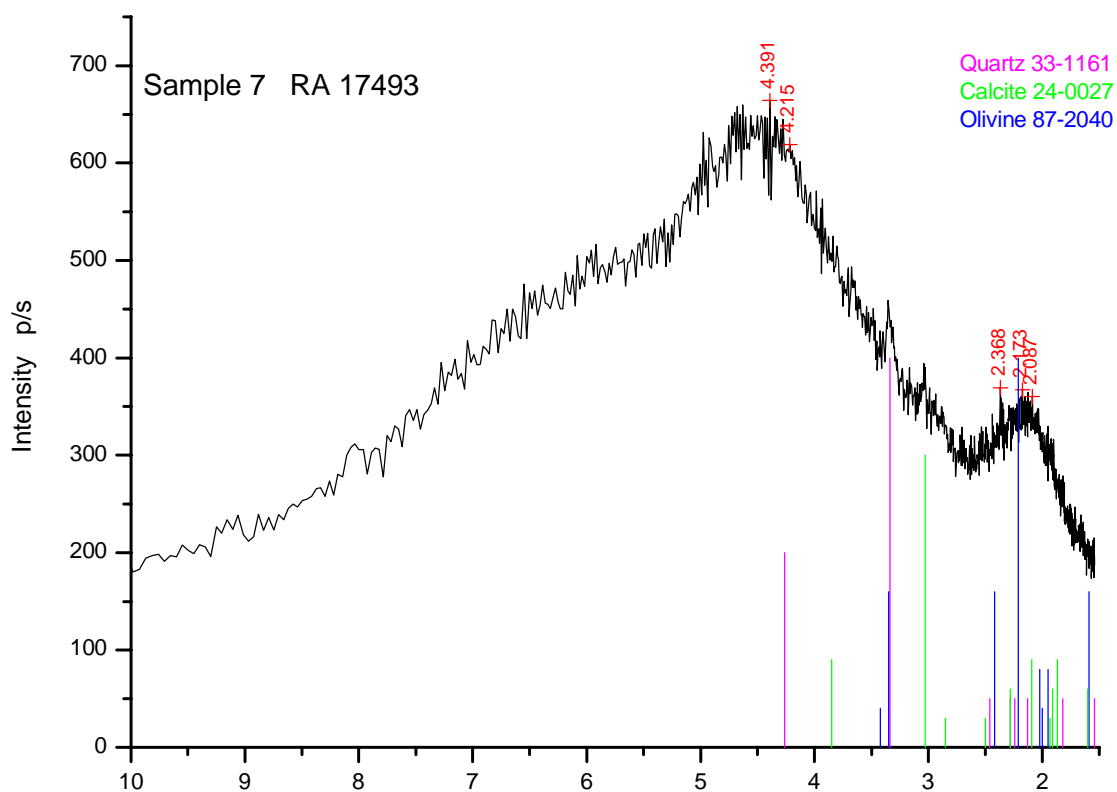


Fig. 18. X-ray of sample 7

Sample number 8: We have amorphous phase with presence of olivine (Fig. 19). The x-ray diagram is given on Fig. 20. For olivine we have these

d-values 2,49-2,41-2,24-1,73 that are in full agreement with JCPDS standards 87 – 2040.



Fig. 19. Amorphous material with presence of olivine

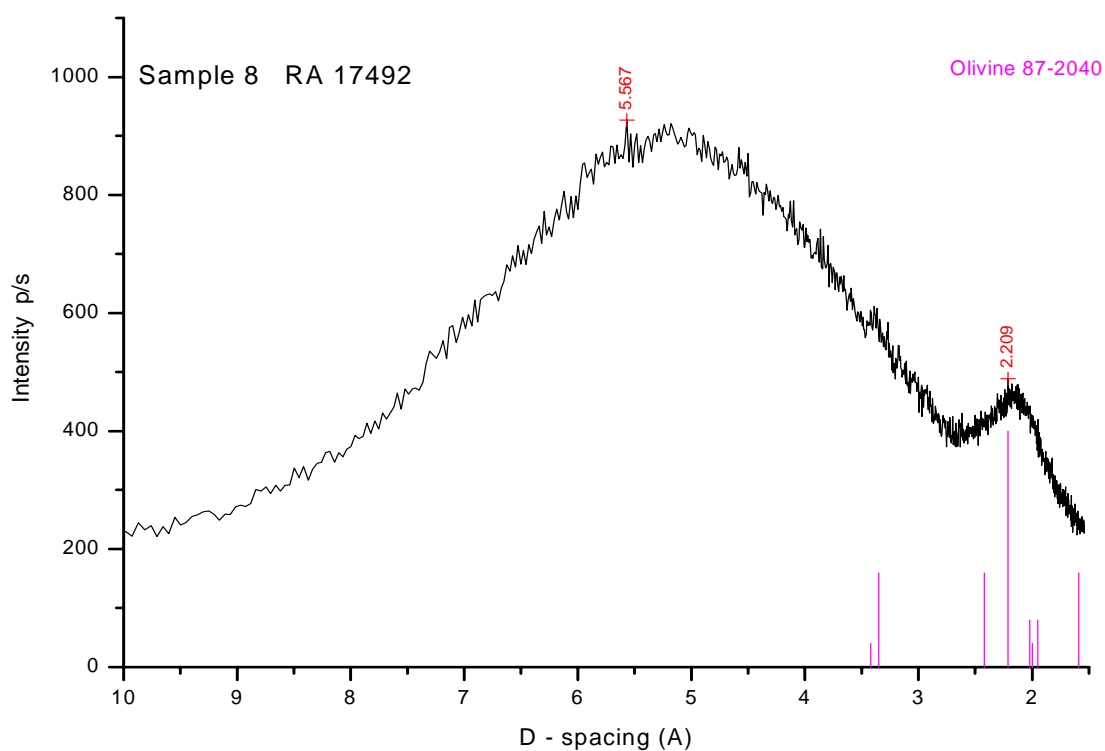


Fig. 20. X-ray of sample 8

Sample number 9: From the x-ray diagram shown on Fig. 22 we can see that it becomes a word about the mineral beryl. The following d-values are given: 7.998; 4.593; 3.982; 3.263; 2.872;

2.529; 2.158; 1.995; 1.744; 1.631. These values are in complete agreement with the data given in JCPDS. On Fig. 21 we have crystals of beryl.



Fig. 21. Crystals of beryl

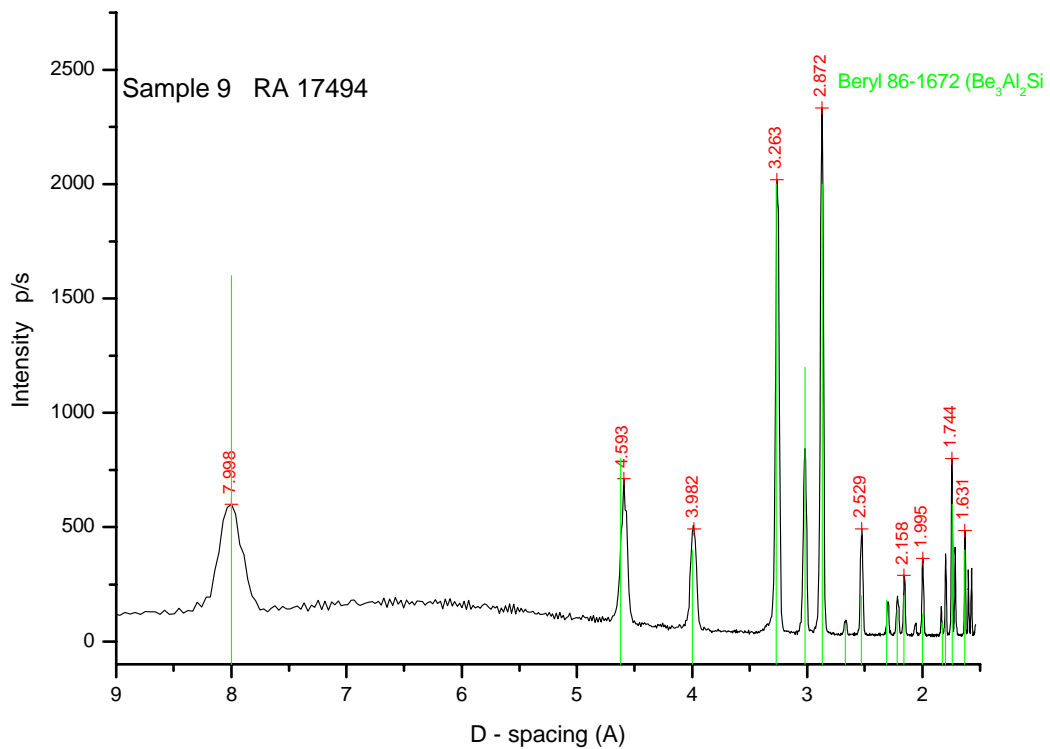


Fig. 22. X-ray diagram of sample 9

Sample number 10: We have amorphous SiO_2 (Fig. 23). From the x-ray diagram (Fig. 24) we can see a presence of cuprites and massicot. d-Values for cuprites are 2.47-2.14-1.51-1.29. Characteristic

d-values for massicot are 3,07-2,95-2,75-2,38. The d-values that we have for cuprites and massicot are in full agreement with the data of JPDS 78-2076 and 77-1971.



Fig. 23. Amorphous SiO_2 with cuprite and massicot

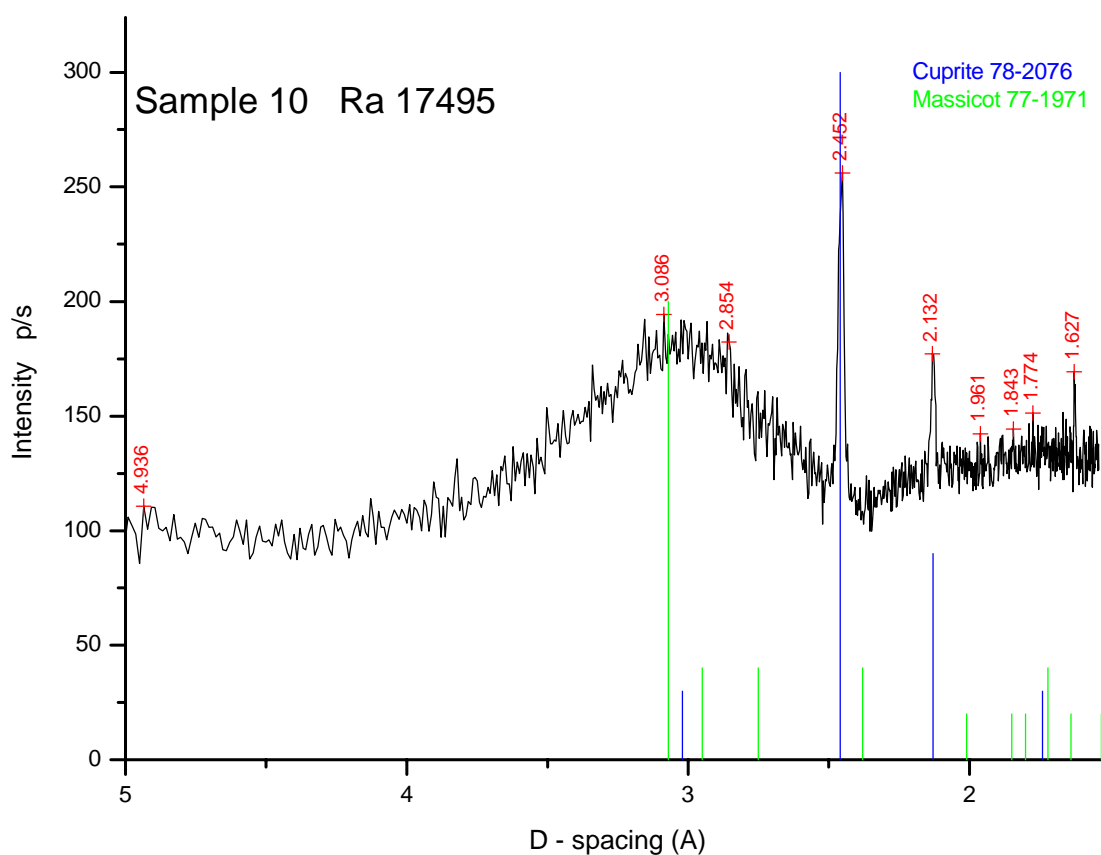


Fig. 24. X-ray diagram of sample 10

Sample 11: In this sample we have quartz with 99%, and muscovite 1%. x-ray diagram is given on Fig. 25.

Sample 12: We have magnesite. Its presence is 99%. From the x-ray diagram we can see that

besides magnesite there is 1% of quartz and dolomite. Most intense d-values for magnesite are 2,74-2,10-1,70-2,50 (Fig. 26)

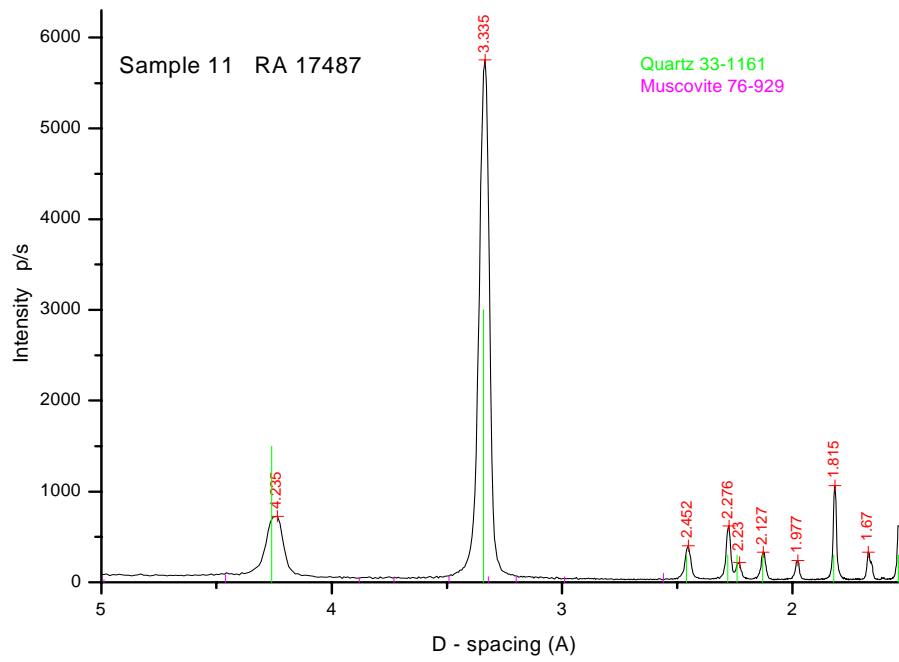


Fig. 25. X-ray diagram of sample 11

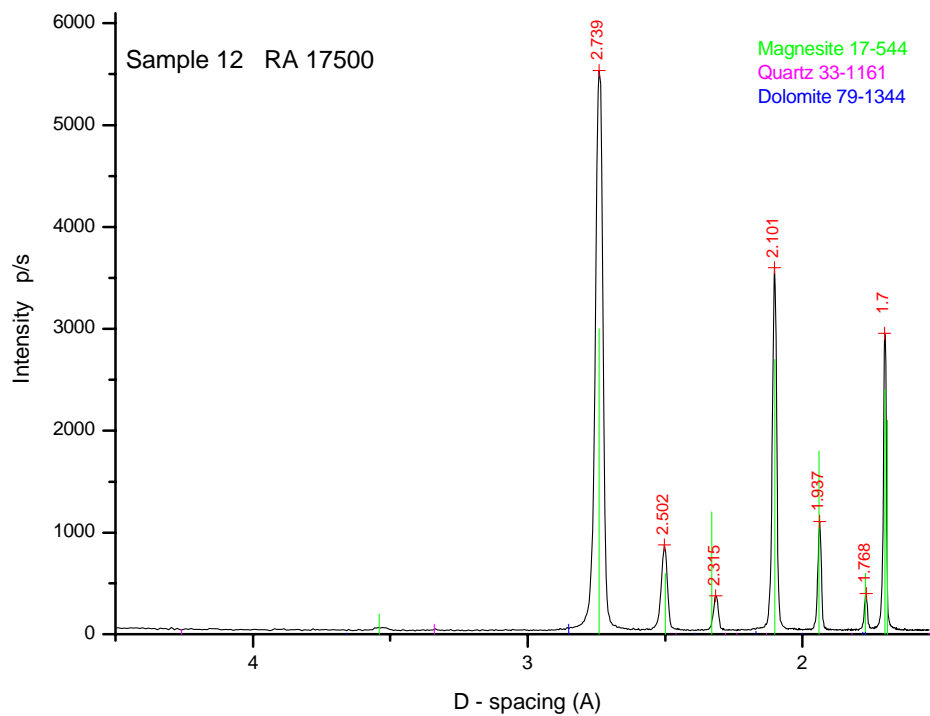


Fig. 26. X-ray diagram of sample 12

CONCLUSION

Making researches that were taken on the moulding examples from the locality Stobi using the method of x-ray diffraction confirmed the presence of monomineral phases (quartz, beryl, magnesite) and also presence of the polymineral associations which in base represents magmatic rocks from the places of the Republic of Macedonia. With these researches it is confirmed that the big-

gest part of the minerals used in moulding decoration in the old casino in Stobi is taking origin from Macedonia. Only beryl which is found in the examples of this locality can be said that definitely is not coming from this region of Macedonia. Beryl as a mineral is brought from the east parts of the previous Macedonian Empire.

REFERENCES

1. Aleksova, B., 1997: *Loca Sanctorum Macedoniae*, Institute for Old Slav Culture, Macedonian civilization, Skopje.
2. Mikulčić, N., 2003: *Stobi, the ancient city*, Skopje.
3. Project elaborat for conservation and restauration works on the object "Kockarnica" in Stobi (IV phase), arh. br. 07-166/39, INDOK-NKC, Skopje, 2004 (in Macedonian).
4. Wiseman, J., 1971: Excavations at Stobi, *American Journal of Archaeology*, **76**, p-p 407-424.
5. Wiseman, J. R., 1973: Stobi: A Guide to the excavations, Beograd.

Резиме

МИНЕРАЛОШКИ ИСТРАЖУВАЊА НА ПРИМЕРОЦИ ОД АРХЕОЛОШКИОТ ЛОКАЛИТЕТ „СТОБИ“ СО ПРИМЕНА НА РЕНДГЕНСКА ДИФРАКЦИЈА

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Клучни зборови: рендгенски истражувања; термички истражувања

Врз основа на извршените минералошки испитувања во неколку примероци од архитектонската декорација на објектот Коцкарница во античкиот град Стоби е одредено присуство на минералите кварц, берил и магнетит. Исто така е одредено и присуство на минерални асоцијации кои се репрезентативни магматски карпи кои потекнуват од територијата на Р. Македонија.

Со овие испитувања е констатирано дека поголем дел од минералите кои се употребени за декорација на

коцкарницата во Стоби потекнуваат од територијата на Р. Македонија.

Само за минералот берил, кој е најден во примерокот бр. 9, може дефинитивно да се каже дека не потекнува од територијата на Р. Македонија. Берилот е најверојатно донесен од источните делови на некогашната Македонска Империја.