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A contribution of INAA to the determination of the provenance of the fourteenth century sculpture

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Abstract The object of the investigation is the so called *Madonna Jackowa*, or St. Hyacinthus's Madonna, a gothic alabaster figurine dated from the XIVth century. The purpose of the investigation is to provide an answer to the question whether *Madonna Jackowa* was made of native alabaster. Samples of alabaster from five various quarries located along the line Cracow-Lvov as well as in Lower Silesia were analyzed and the content of trace elements was compared with that of the sculpture. The determination of trace elements was carried out by means of the instrumental neutron activation analysis.

Key words alabaster sculpture • instrumental neutron activation analysis • provenance study • trace elements

Introduction

The gothic alabaster figurine of *Madonna Jackowa* (Fig. 1), dated from the end of the XIVth century, is an extraordinary work of art. It is one of the earliest representations of *Beautiful Madonna* of a high standard of art and rare, extensive iconographic programme. This small-sized sculpture is recognized as one of the outstanding achievements of that period. This very decorative statuette, full of charm and elegance and of slender proportions, was presumably designed for private contemplation. It is a typical, devotional representation of complex symbolism and rich iconography, as well as an interesting combination of the type of Apocalyptic Madonna with a motive of the Tree of Knowledge and a scene in low relief on the pedestal representing St. George's fight with the dragon. *Madonna Jackowa* is the only known work of art of that period with such an extensive iconographic programme.

It is made of the alabaster stone that rarely occurs in the territory of Poland. Fragile and sensitive to atmospheric agents alabaster sculptures easily suffer destruction. Therefore, the fact that such a small figurine has survived until now makes it even more valuable.

The history of *Madonna Jackowa* itself is very interesting. The figurine can be dated from the end of the XIVth century. Already in 1401 it was worshipped as miraculous at the Corpus Christi Church in Lvov. The extent of its cult was largely due to the legend which connected it with St. Hyacinthus's to whom it owes its nickname. It is believed that before the Tatars' siege St. Hyacinthus's took it from Kiev to Halicz. Later it was brought to Lvov. After World War II, the figurine was brought to Cracow to the Dominicans' Monastery at the Holy Trinity Church where it has remained until now.

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The sculpture has been discussed in a number of scientific studies, including works in foreign languages. Therefore, it is known not only in Poland but also in the world. The mysterious origin of the sculpture has evoked a great interest among researchers, who have attributed its origin to various art centers scattered throughout Europe [5].

The first researchers interested in *Madonna Jackowa* suggested that it came from France and compared it with the XIVth century ivory sculptures. Others attributed the origin of the sculpture to centers in Southwestern Germany, Central Germany or Prague. Still other researchers included the figurine among the Malopolska Region sculptures created under the Czech-Silesian influence and pointed to its direct analogy – the alabaster Madonna from Silesian-Żagań. According to another group of art historians the sculpture originated from Austria, Northern Europe or even England. Recently Jacek Dębicki suggested that the figurine could have been made in Cracow, within St. Hedwig's Foundation and after the death of the Queen was taken to Lvov by Jakub Strepa who later became a bishop of Lvov.

As can be seen, the researchers' opinions differ to such an extent that the origin of the sculpture is still an open question. Identification of the alabaster deposit used for carving the Madonna could be very helpful in solving the problem of its origin and in further studies.

Fig. 1. The gothic figurine *Madonna Jackowa* (XIVth century) – alabaster.

Table 1. Description of the samples examined.

Material examined	Sample No.
Alabaster deposit – Żórawno	ZOR
Alabaster deposit – Kraków Łagiewniki	LAG
Alabaster deposit – Łopuszka Wielka	LOP
Alabaster deposit – Kraków Ruczaj	RUC
Alabaster deposit "Nowy Ląd" – open cast No.2	NIW1
Alabaster deposit "Nowy Ląd" – open cast No.3, NE wall, level +213 m above sea level	NIW2
Alabaster deposit "Nowy Ląd" – open cast No.3, SW wall, level +220 m above sea level	NIW3
Alabaster deposit "Nowy Ląd" – open cast No.3, SW wall, level +220 m above sea level	NIW4
Fillippie's Epitaph – Lvov	FIL
Sample of Madonna's head	M6
Average sample taken from various parts of the sculpture	M7
Sample of the pedestal, reconstructed part	M8
Sample of another part of Madonna's head	M9
Sample from the inside of the sculpture	M10
Sample from the apple	M11

The purpose of the present studies was to answer the following questions:

– is the trace element distribution pattern for the alabaster of which the sculpture was made similar to that of the elements identified in domestic deposits, or is it different?
– do the material differences allow the art historians to draw more precise conclusions as to the attribution, dating, technique and artist's style?

Alabaster is a massive crypto-crystalline form of gypsum deposited by precipitation in inland seas in the last Paleozoic-Permian period and the first period of Mesozoic-Triassic period. Alabaster is a pure substance with a very low trace element concentration [2].

Alabaster was used, particularly in the Middle Ages, as sculptors' material mainly in Normandy, Westfalen, North Netherlands and England. As sculptors' material, alabaster has excellent properties; it can be readily shaped, allows for

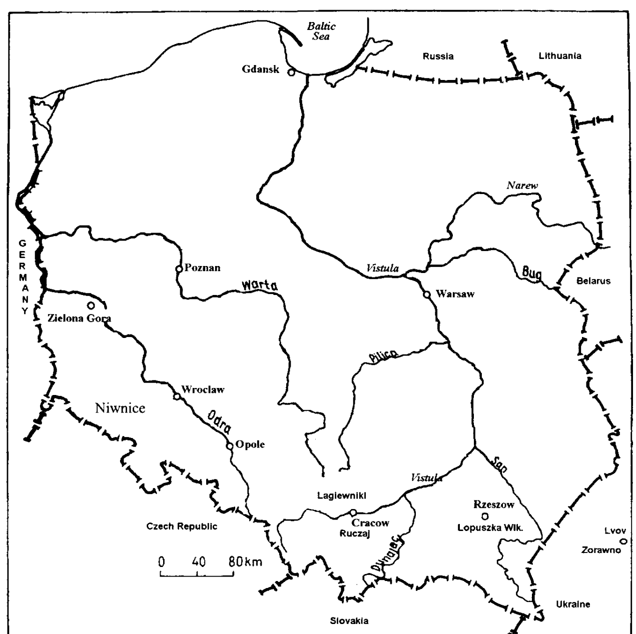

Fig. 2. The geographical locations of the quarries sampled for this study.

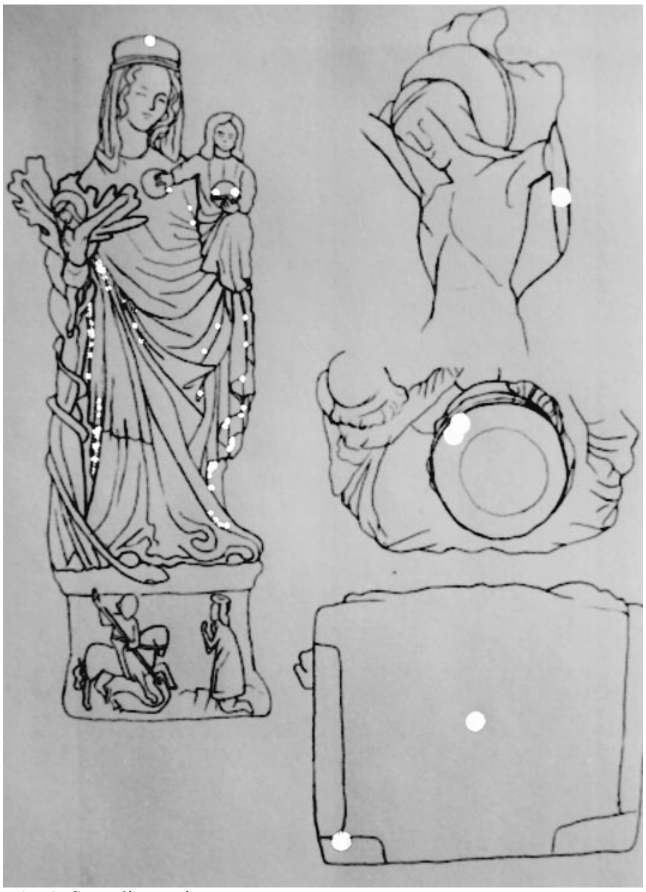

Fig. 3. Sampling points.

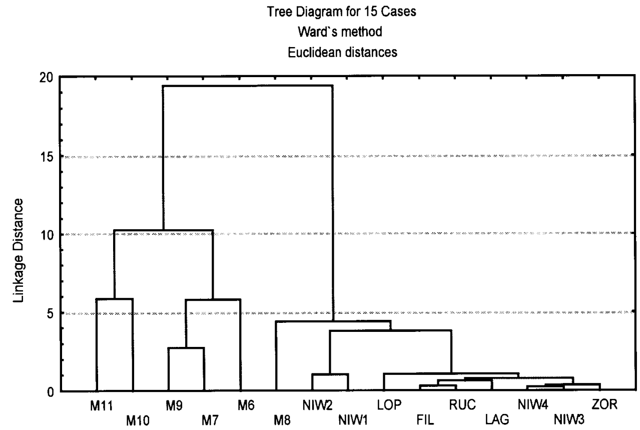

Fig. 4. Cluster analysis of alabaster samples from sculpture *Madonna Jackowa* and deposits.

fine detail, is semitransparent, and can be readily gold-coated or polychromed [3]. Its disadvantages are brittleness and sensitivity to atmospheric agents.

The present examination has been carried out using 6 samples taken from the sculpture of *Madonna Jackowa* (Fig. 3), one sample from Fillippie's Epitaph in Lvov and samples of alabaster from four various domestic deposits located along the Cracow-Lvov line and four samples from the gypsum and anhydrite deposit "Nowy Ląd" at Niwnice in Lower Silesia (Fig. 2). The samples are described in Table 1.

The analysis of the samples was carried out by INAA using standards of the elements to be determined. Major components of alabaster ($CaSO_4 \times 2H_2O$) have a low (n,γ) reaction cross section which is of advantage for carrying out the analysis. By irradiating alabaster with thermal neutrons its main component undergoes the nuclear reaction ^{46}Ca (n,γ) ^{47}Ca→^{47}Sc. The radioisotope ^{47}Ca has a half-life of 4.53 days and emits gamma rays of energies 1290 and 800 keV. On the other hand, ^{47}Sc with a half-life of 3.4 days emits gamma rays of an energy of 160 keV. Its reaction cross section is 0.250 barn and the natural abundance of ^{46}Ca is 0.0033 %.

Experimental

200 g samples of alabaster deposits were ground in an agate mortar. Afterwards, approximately 50 mg samples were taken from the obtained material. Procedure for drilling samples from sculpture makes use of tungsten carbide drills, sometimes small chips break off, which contaminate the sample. This contamination is detected through very intensive ^{187}W gamma lines in the recorded gamma spectrum. The samples were weighed and sealed in quartz ampoules and then packed together with standards of 40 elements. Each packet contained also Sc and Au used as monitors of the thermal neutron flux [6].

The irradiation was carried out in the MARIA reactor at Świerk near Warsaw, at a neutron flux of 8×10^{13} ncm^{-2}s^{-1}. The samples were irradiated for 24 h and cooled for 12 h. The radioactivity of the samples was measured by means of an HP-Ge detector (ORTEC) featuring the active volume of 80 cm^3 and 1.95 keV resolution for the ^{60}Co nuclide energy of 1332 keV. The detector was coupled to a CANBERRA-System S100 spectrometer, controlled by an IBM computer. The analysis of gamma-ray spectra of the samples was performed with the aid of the microSampo program. The measurements were repeated five times within two months after irradiation, the period of time being sufficient for all the short-lived nuclides to decay (Cu, Na, K, W, As, Mn, Ga, Br). The measurement time varied between 300 and 7200 seconds. Table 2 shows the lower limits of detection of some elements in alabaster. The limits were determined using the Currie method [4].

Table 2. Detection limits for alabaster.

Element	Radionuclide	Half life [day]	Gamma energy [keV]	Detection limit M_d [pg]
Na	^{24}Na	0.625	1369	0.75
K	^{42}K	0.5	1525	57.4
Sc	^{46}Sc	84	889	0.434
Cr	^{51}Cr	27.7	320	78.7
Mn	^{56}Mn	0.105	847	2
Fe	^{59}Fe	44.7	1099	780
Co	^{60}Co	1924.28	1173	1.3
Zn	^{65}Zn	265	1115	84.3
As	^{76}As	1.1	559	2.998
Br	^{82}Br	1.5	776	4.43
Ag	^{110m}Ag	250.4	658	11.3
Sb	^{124}Sb	60.3	1691	2.4
Ba	^{131}Ba	11.6	496	193
La	^{140}La	1.7	1596	0.22
Ce	^{143}Ce	1.375	293.6	11.3
Sm	^{153}Sm	2.0	103	0.65
W	^{187}W	0.996	686	1.2
Au	^{198}Au	2.7	412	0.017
Hg	^{203}Hg	47	279	11.5

Neutron flux $\phi = 8 \times 10^{13}$ ncm^{-2}s^{-1}; irradiation time – 24 h; decay time – 12 h; counting time – 2 h; mass of alabaster sample – 50 mg.

Table 3. Concentration of trace elements in the alabaster samples examined [ppm].

Sample No.	ZOR	LAG	LOP	RUC	NIW1	NIW2	NIW3	NIW4	FIL	M6	M7	M8	M9	M10	M11
Na	60.4	33.2	34.3	35.6	47.5	52.5	57	54.5	60.1	156	389	78.8	415	1020	687
K	34.1	78.9	66.3	44.4	107	55.5	55	58.5	50.2	159	420	157	391	863	730
Sc	0.015	0.018	0.016	0.012	0.2	0.1	0.06	0.2	0.011	0.034	0.056	0.012	0.012	0.196	0.190
Cr	10.3	8.61	9.37	8.48	6.8	11.1	7.7	7.4	7.04	22	58	67.5	61.9	113	52.1
Mn	14.1	17.1	17	12.7	9	21.5	10.8	8.7	10.7	36.6	69.9	12	67.2	130	48.4
Fe	132	284	196	141	155	210	95.5	150	61.3	420	611	116	646	933	665
Co	0.113	0.162	0.14	0.156	0.3	0.3	0.3	0.2	0.168	0.442	5.04	6.15	1.53	4.27	4.02
Zn	2.31	1.45	1.06	0.86	3.4	20.8	1	1.3	2.43	6.5	41.2	14.2	19.9	5.62	104
As	1.46	1.2	1.1	0.84	0.5	0.7	0.9	0.6	0.84	1.65	14.7	0.65	6.31	9.05	5.70
Br	3.88	1.92	79.6	4.59	12.6	11	17	21.5	4.79	25.8	36.1	8.32	44	292	368
Zr	–	45.4	47	42.4	–	–	2.8	–	84.2	356	431	47.1	549	28	66.4
Ag	0.069	0.014	0.016	0.026	0.003	0.001	0.0004	0.0009	0.031	82	14.5	1.22	26.1	0.63	13.07
Sb	1.22	0.83	0.69	0.74	0.2	1	0.5	0.3	1.14	2.67	6.74	1.14	7.57	3.50	1.53
Ba	3.61	4.43	4.61	4.53	34.5	39	30	29	3.14	5.92	16.6	1.97	22.9	25.0	265
La	0.15	0.19	0.15	0.11	0.09	0.6	0.2	0.3	0.085	0.31	1.42	0.19	1.24	2.89	1.98
Ce	1.03	0.61	0.71	0.47	0.6	1.1	0.5	0.8	0.34	1.92	3.52	1.06	1.93	2.43	39
Sm	0.03	0.033	0.035	0.21	0.2	0.3	0.02	0.04	0.024	0.074	0.22	0.043	0.18	0.17	0.089
W	0.16	0.37	0.42	0.45	0.1	0.3	0.2	0.1	0.3	0.65	–	–	–	3.81	1.68
Au	0.0028	0.0013	0.0006	0.0009	0.003	0.004	0.003	0.004	0.0008	4.21	1.9	0.252	3.82	0.026	0.514
Hg	–	–	0.22	0.3	–	–	–	–	0.33	2.98	17	1.7	3.6	0.27	81.3

Discussion of the results

Nineteen elements were identified and determined in the samples examined. The concentrations of the determined elements in the samples are presented in Table 3. Data are given as the average of three or more independent determinations. The average measured precision, which is depending upon inhomogeneity, variations in the neutron flux and counting errors is about 10%, ranging from 5 to 17%. The analysis has given the following results:

1. The content of gold in the Madonna alabaster is three orders of magnitude higher (samples Nos. M3, M4 and M1) than in the deposits (samples Nos. ZOR, LAG, LOP, RUC, NIW1,2,3,4). This may indicate that the Madonna was gold-coated or that the alabaster used for the carving contained high amounts of gold. In order to explain this problem we applied to the conservator for alabaster samples to be taken from the inside of the sculpture.

2. It turnes out that the content of gold in the alabaster (sample No. M10) is two orders of magnitude lower than in the alabaster taken from the outer layers of the sculpture. We can, therefore conclude that the sculpture was gold-coated.

3. The content of gold in the alabaster of the sculpture pedestal (sample No. M8) is one order of magnitude lower than that in the Madonna alabaster, but higher than in the deposits (samples Nos. ZOR, LAG, LOP, RUC, NIW1,2,3,4). This may indicate that the pedestal was gold-coated as well.

4. The alabaster of the sculpture contains more silver than that from the deposits. Also the content of silver in the pedestal is lower than in the Madonna, as in the case of gold. It may be supposed that the gold used for gilding contained silver impurities.

5. It follows from a comparison of the determined concentration of such elements as Na, K, Cr, Mn, Zr and Sb present in the alabaster used for sculpture and for the reconstructed parts of the pedestal (M8) that they were made of different kinds of alabaster.

The elevated contents of mercury in some parts of the sculpture indicates that the statuette was polychromed. The artist used probably red pigment: mercuric sulphide (vermilion).

In order to determine the degree of similarity, the analysis of clusters, based on their features, was carried out [1]. The results from the average linkage cluster analysis of 15 objects, described by 19 features, representing 19 elements, are shown in Fig. 4. On the basis of this analysis, a high degree of similarity has been found only between sample M8 (pedestal) and the alabaster samples taken from the quarries. Material taken from the sculpture *Madonna Jackowa* did not come from the deposits analyzed so far, which limits the number of hypotheses regarding the origin of alabaster used in the analyzed object.

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