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Abstract	The paper considers the possibility of using X-ray fluorescence analysis as a non-destructive express method for determining the deposit of a collection sample of malachite. This method can be used as an additional method.

Keywords (separated by '-')	Malachite - Deposit - X-ray fluorescence analysis - Spectrum

Determination of the Validity of a Collectional Malachite Deposit by an X-ray Fluorescent Analysis

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Abstract. The paper considers the possibility of using X-ray fluorescence analysis as a non-destructive express method for determining the deposit of a collection sample of malachite. This method can be used as an additional method.

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Keywords: Malachite · Deposit · X-ray fluorescence analysis · Spectrum

1 Introduction

Nowadays, a lot of private mineralogical museums and large private collections are being created. The founders of museums and collectors, when acquiring samples from spent historical deposits, the question arises about the reliability of the acquisitions. There are samples that are represented by individual crystals or aggregates without the presence of host rocks. Rarely come across rarities - specimens that have survived in limited quantities. Their cost can reach several tens of thousands of dollars. Information on the presence of various trace elements in most minerals (rocks) indirectly indicates the region of origin of the presented samples. Information on the presence of various elements-impurities and may indirectly indicate the region of origin of samples or raw materials. This information can be used to determine its deposit.

2 Research Methods

To solve this problem, it was decided to use X-ray fluorescence analysis and optical method. The studies were carried out using an EDX-8000 energy dispersive X-ray spectrometer from SHIMADZU (Japan) (Fig. 1). The presence of elements from Na to U in the samples was determined using the qualitative-quantitative method (standard software

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of the device). The quantitative content of the element was determined by the method of fundamental parameters. During the survey, a collimator with a diameter of 3 mm and a camera were used to highlight the area of interest for analysis. The work was carried out in the laboratory of the IGG UB RAS (analyst N.P. Gorbunova). The optical properties of the texture, structure, and features of malachites were studied using an MBS-10 magnifying glass.

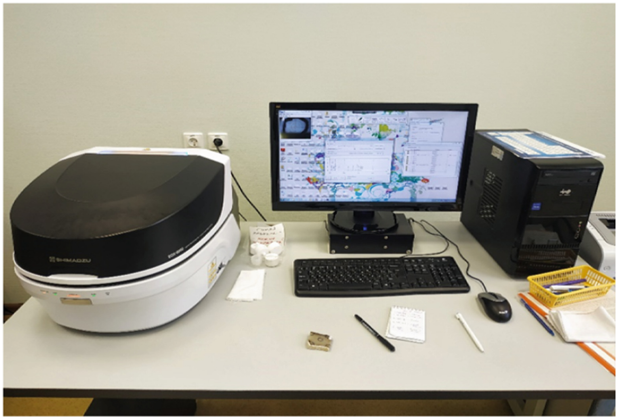

Fig. 1. General view of the workplace (XFA method)

3 Factual Materials

Malachite is a mineral, basic copper carbonate, the composition of which can be expressed by the chemical formula $Cu_2 (CO_3) (OH)_2$, corresponding to 72% copper oxide, 19.9% carbon dioxide and 8.1% water. Malachite constantly accompanies various copper ores, being a product of their weathering, due to which it often forms pseudomorphs over chalcopyrite, minerals from the group of fahlores, cuprite and other minerals. Most often it is observed in the form of crusts, spherocrystals, sintered kidney-shaped aggregates of a radial-radial, parallel-columnar and zonal-concentric structure. Minerals of host rocks and minerals are often found in malachite as mechanical impurities. Malachite is prized as a beautiful ornamental stone (Kievlenko 2000, Samsonov et al. 1985).

In the Urals, two deposits are known, from which the world-famous ornamental malachite was mined in the 18–20 centuries, which became a symbol of the mining of the Urals. This Mednorudyanskoye malachite deposit is located within the city of N. Tagil (Sverdlovsk region). And the Gumeshevskoye field, which is located 55 km south-west of Yekaterinburg, on the territory of Polevskoy. Ural malachites are famous for their patterned color and are valued as a collectible and valuable ornamental stone (Semenov 1987).

The Mednorudyanskoe malachite deposit is located in the southern part of the Vysokogorsky ore field among interbedded tuffs and limestones. The length of the ore body is about 700 m, the maximum thickness is 40 m. On its territory, iron hat ores are mainly developed, traced to a depth of 100 m, below which primary magnetite ores with disseminated pyrite and chalcopyrite lie in garnet skarns and epidosites. In the southern part of the deposit, redeposited ores are developed, consisting of clayey weathering products of limestones and tuffs, impregnated with carbon dioxide and oxygen compounds of copper, among which malachite predominates (Kievlenko et al. 1983). In addition to malachite, many other secondary ore minerals have been found in oxidized ores: native copper, chalcocite, cuprite, tenorite, azurite, hematite, martite, atacamite, turyite, and various copper phosphates (Popov et al. 2015).

The Gumeshevskoe deposit can be attributed to the magnetite-bearing skarn-copper-porphyry genetic type. Lenticular bodies of pyroxene-garnet skarns 3–11 m thick with quartz-carbonate, magnetite and copper-sulfide mineralization are developed along the contact of diorite with marble. The primary ore minerals are dominated by pyrite, chalcopyrite, fahlores, and copper-bearing magnetite. Copper-iron ores are oxidized to a depth of 120–170 m. (Grabezhev et al. 2000) Malachite is found mainly in redeposited cuprous clays filling a karst funnel in marble from the western hanging flank of the dike. The length of this funnel is about 600 m, width 150 m, the depth towards the diorite dike increases from 10–30 m to 130–150 m. The ore-bearing clays are variegated, in places calcified and contain fragments of brown iron ore. Chrysocolla, earthy malachite, azurite, tenorite, and native copper represent copper mineralization in them. Segregations of dense ornamental malachite were noted at the bottom of the crater under clays at a depth of 70–130 m, where they covered the marble surface with crusts and nodules, closely associated with red copper ore and azurite. On the very surface of the marbles, malachite crusts abundantly covered karst depressions and cracks. In some places, such depressions looked like real malachite cellars filled with finely exhausted clayey matter (Vertushkov 1975).

In the modern stone market, there is a large amount of malachite from the Katanga copper-cobalt deposit located in Kolwezi district (Republic of the Congo, Africa). The western end of the Katanga copper belt contains mineralized zones located mainly in the late Proterozoic meta-sedimentary rocks of the system, as well as in deposits with small volcanic, volcanic and intrusive rocks. Primary mineralization occurs in the form of sulfides within the Lower Royan, in a low-grade ore body. Primary minerals, copper sulfides, are found in the form of bornite, chalcopyrite, and sometimes native copper. An increased content of cobalt minerals (carrolite, cobaltocalcite, etc.) is noted (Dewaele et al. 2006; Wit et al. 2015) Sometimes, at mineralogical exhibitions, highly decorative African specimens (sinter, kidney-shaped) specimens are "passed off" as rare Ural specimens.

Malachite from the Ural deposits is a brand with a history and is in demand in the market. However, since its main reserves have already been worked out, and new developments are not carried out or are carried out privately, there is a shortage of Ural malachite on the market, and therefore the prices for samples or raw materials are several times higher than for similar Zairian malachite. In February 2020, a wealthy private collector who decided to purchase a large ore (36 × 40 × 15 cm) of sintered malachite from a private collection (St. Petersburg) approached us. According to the seller, the sample was mined in the 19th century at the Gumeshevskoye field. The experts were given the task, in addition to studying external signs (morphology of aggregates, color, decorativeness, paragenesis), to try to prove belonging to the declared deposit.

For research, a collection of control samples from known deposits was created: Gumeshki (Polevskoy, Wed. Ural), Mednorudyanskoe (N-Tagil, Wed. Ural), Chokpak (Kazakhstan), DR Congo-Zaire deposits (Africa), malachite deposits in China… The size of the samples was 3–6 mm, which consisted of malachite of various morphological differences (buds, crusts, crystals, earthy aggregates) without visible inclusions of foreign minerals (Fig. 2). 4–5 spectra were taken from each sample.

Fig. 2. The investigated samples of malachite

4 Results

To determine the deposit of the samples, the method of comparing the obtained spectra was applied. The greatest similarity of the spectra of the studied unknown sample (ER-1) was found with the spectra of the sample from the Gumeshevskoye field (sample ER-5) (Fig. 3).

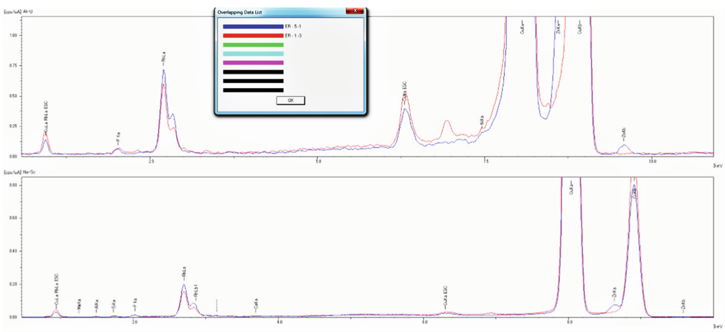

Fig. 3. Comparison of the spectra of malachite samples from the Gumeshevsky deposit (ER - 5 - blue) and the investigated unknown malachite (ER-1 - red)

Additionally, the spectra from the sample (ER-2) of African malachite (DR Congo) clearly show the peaks of cobalt, a characteristic element for the Katanga deposit (Fig. 4).

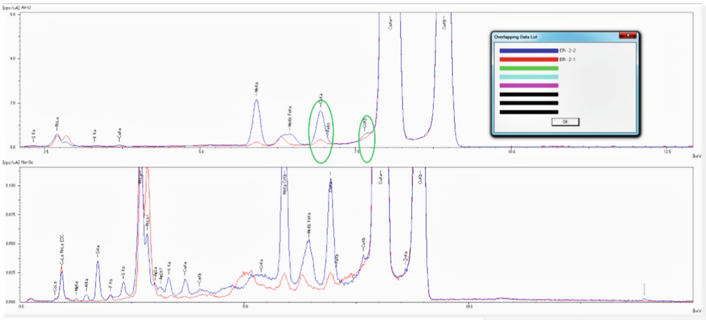

Fig. 4. Spectra from a sample (ER-2) of African malachite, green - peaks Co

5 The Discussion of the Results

In terms of geochemical features, malachite is characterized by a high content of elements such as CuO, SiO_2, Al_2O_3, MgO, P_2O_5, SO_3, CaO, Fe_2O_3, K_2O, MnO, ZnO, NiO, Na_2O, V_2O_5, Co_2O_3, Cr_2O_3. The samples of malachite from different deposits contain mineral inclusions that are characteristic of each object. The Ural objects are characterized by the presence of such minerals as magnetite, sphalerite, clay minerals, copper phosphates (pseudomalachite, elite, tagilite). Pseudomalachite is a mineral, copper phosphate with hydroxyl $Cu_5\ (PO_4)_2\ (OH)_4$. It got its name because of its similarity to malachite, from which it differs in composition and bluish tint. For the first time, I.F.L. Gausmann described pseudomalachite in 1813 (Popov et al. 2015). Gives the Ural malachite a special turquoise color.

African malachite is characterized by the presence of cobalt minerals, chromium-containing minerals. When plotting the ratios of some elements, the data for the known deposits vary quite well. In the press and on the Internet, discussions and disputes constantly arise about the correspondence of this or that stone material to a certain deposit. Decorativeness (figure), physical properties, and forms of excretion (gem stones, 2019) are used as diagnostic signs. The proposed technique makes it possible, with a high degree of probability, to answer the question - "is the sample from the Urals or is it a foreign analogue".

6 Conclusion

 X-ray fluorescence analysis can be used as a non-destructive rapid method for determining the deposit of the studied sample. This method should be used as an additional method. The main thing is visual diagnostics of mineral ore.

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Chapter 73

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