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CHEMICAL WEATHERING OF CHALK STONE MATERIALS FROM BASARABI CHURCHES

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Abstract: *The Basarabi whole cave has been recognized as the first religious monument from medieval Dobrogea. This ensemble is built from amorphous calcium carbonate and very sensitive to humidity, frost, salts etc. Usually, calcium carbonate is occurring as limestone, chalk and biomaterials. Mg^{2+} (from $MgSO_4 \cdot 7H_2O$, called epsomite) being one of them as a major cation in seawater and groundwater, SO_4^{2-} (from pollution-related atmospheric SO_2 are responsible for calcite conversion to gypsum) and NO_3^-, responsible for stone wall solubilization, are the main undesired processes for church degradation. Processes as crystallization and dissolution of salts take place, new pores being generated in a self-acceleratory process through some stone micro-cracks. In this paper, the effects of the environment on this monument can be evaluated through different analytical investigations: thermal analysis, XRD, EDXRF, ion-chromatography.*

1. INTRODUCTION

The Basarabi whole cave has a special place in terms of chronological data, being recognized as the first religious monument from medieval Dobrogea. Discovered on 1957, the Basarabi - Murfatlar Ensemble is one of the most impressive archaeological sites of Europe, consisting of churches dated from 9th - 11th century. Situated in the cliff of a chalk stone hill, this ensemble is built from amorphous calcium carbonate and very sensitive to humidity, frost, salts etc. Atmospheric pollution and acid deposition materials are recognized as the most important and common causes of decay the heritage monuments. [1] Usually, calcium carbonate is occurring as limestone, chalk and biomaterials. It can adopt three polymorphs forms: calcite, aragonite and vaterite. [2] It is known that calcite (the variety of calcium carbonate detected by XRD) dissolution is affected by the presence of foreign substances Mg^{2+} (from $MgSO_4 \cdot 7H_2O$, called epsomite) being one of them as a major cation in seawater and groundwater.

Also, SO_4^{2-} (from pollution-related atmospheric SO_2 are responsible for calcite conversion to gypsum) and NO_3^-, responsible for stone wall solubilization. Processes as crystallization and dissolution of salts take place, new pores being generated in a self-acceleratory process through some stone micro-cracks. These salts have a significant danger to cultural heritage, generally.

Dissolution rates are significantly increased in the presence of NaCl solutions, due to electrostatic considerations. In this paper, the effects of the environment on this monument can be evaluated through different analytical investigations: thermal analysis, XRD, EDXRF, ion-chromatography. The temperature ranges correspond to the weight loss due to absorbed water (<120 °C), where don't exist hydrated salts, to the loss of chemically bound water (200-600 °C), when there are no other compounds that undergo weight loss in this temperature range and to the loss of CO_2 (>600 °C) due to the decomposition of carbonates, higher for the most degraded stones of the church.

2. EXPERIMENTAL PART

The samples prelevated from Basarabi Church (samples collected from the exterior of the monument, without any value for this church. Samples were obtained by taking a minimum part of the archaeological object, with the aid of a scalpel with diamond tip, to minimize any damage and contamination. These samples were ground in an agate mortar and pestle before analyses, in order to reduce the particle size and to secure homogeneity.

The samples were analyzed using Ion Chromatography, X-ray diffraction (XRD), energy-dispersive X-ray fluorescence (EDXRF) and thermal analysis (TG), in order to characterize the salt mixture associated with surface damage.

Ion Chromatography was used to identify the soluble salts as cations and anions present in the samples. The analyses have been performed on a DIONEX DX-500 Chromatograph. The eluent was sodium carbonate and sodium bicarbonate with a flow rate of 2 ml/min, and a 4 mm column for the separation of anions.

The diffraction analysis has been carried out in a DRON UM1 diffractometer using an iron filter for the CoK_α radiation (1.79021Å).

Thermal analysis have been performed on a Mettler Toledo Thermo-gravimetric Analyzer TGA/ SDTA 823^e, in the range of temperature 25°C to 1000°C, in dynamic air, with 60 ml/min, at a heating rate of 10°C/min, in alumina crucible, for all the paper samples, of 3mg to 5mg. DSC was performed on a Metter-Toledo Instrument DSC 823^e. Samples (1-2 mg) were loaded into sealed aluminum pans with lids and heated to 600°C at a heating rate of 10°C min^{-1} in oxygen flux (100 ml min^{-1}). The empty aluminum pan was used as reference and the heat flow between the sample and reference pans was recorded. Measurements were repeated at least three times.

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