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Complex study of composition of building stones of the historical objects in Tallinn (Estonia) and assessment of stone deterioration on the base of geochemical data

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On the territory of the Old Town of Tallinn there are located many historical and cultural Middle Ages' objects that are included on the UNESCO World Heritage List. For buildings in Tallinn there are traditionally used the Ordovician carbonate rocks quarried in the vicinity of Tallinn. High quality and good physical properties permitted to use the local carbonate rocks for building of many churches, town halls, strongholds and city walls.

Unfortunately, damage of building stones is widely observed in the biggest cities of Europe where the pollution situation is quite serious. The problem of buildings' decay is also very actual for Tallinn as the biggest industrial centre of Estonia. The deterioration of building stones takes place under the influence of the chemical attacks (leaching and dissolution under rain water, different kinds of the industrial pollutants, etc), mechanical destruction under pressure in the pores, cracks by the freezing of water, vibration, corrosion and other negative natural factors and industrial pollutants.

Mineral-weathering reactions are the most important in the destruction processes. The carbonate minerals as the most sensitive ones to acidification participated very actively in the reactions of dissolution. The most intensive destruction takes place on the surfer part of the building stones and in the fractures. The admixture of silicate materials plays also an important role in destruction of the carbonate building stone. The weathering rates of the carbonate minerals control the mechanical properties of the building stones.

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was started in Institute of Geology at Tallinn University of Technology in the year 2002. In order to diagnose quantitatively the stone deterioration and assess the weathering damage, the building stones from several selected Middle Ages historical objects in Old City of Tallinn were sampled. The samples were taken as from building stones as from so-called "black crust" formed on their surface. The samples were studied by lithological, chemical (13 major and 42 trace elements measurement by XRF-fluorescence, ICP-MS and ACP-ASP technique) and mineralogical (8 parameters by XRD-technique) methods. For determination of the different valence forms of iron it was used a classical chemical analysis.

In some cases when the size of the samples permitted, there were measured the physical properties (density and porosity). In case if the size of the samples was sufficient the thinsections were made from the samples. Detail descriptions of the thinsections and their photos under microscope were used for detalisation of the results.

The first results obtained on the base of lithological, chemical and mineralogical investigations (Bityukova, 2003; Bityukova et al., 2003) showed large variability of the building stones' composition and their conditions.

There was estimated the trend in variation of chemical composition and its influence on physical properties of the rocks, studied the relationship between chemical and physical parameters. The comparative analysis of natural unaltered Ordovician carbonate rocks, damaged building stone and samples from surface of building stone was carried out. For this purpose it was used the database created for Ordovician carbonate rocks collected from main outcrops and boreholes in Estonia. The study permitted to mark the specific geochemical features typical for weathered limestone, quantify the intensity of destruction and reveal the objects with the most intensive deterioration of the building stones.

From the studied building stone of St. Catherine‘s, St. Olaf's and St. Mary‘s Churches, City Hall and City Wall the building stones of St. Catherine‘s Church are represented by the most pure carbonate rocks. The content of SiO_2 in these carbonate rocks varies from 3,58 up to 7,9%. For the samples from the black layer the higher level of the content of $SiO_2$is typical. The carbonate rocks from St. Olaf's Church and in some samples from City Wall are characterised by relatively high content of silicate admixture. The level of SiO_2 is close to 10% there. Level of Al_2O_3 is relatively stable and varies as a rule in the limit 1-2%.

The iron takes part very actively in the alteration processes and is characterised by change of their valence form depending on the environment conditions. The total content of iron (Fe_2O_3tot)variesin the limits from 0,4 up to 2,32% (the average value is 1.11%). In the studied building stones iron is presented mainly in three valence forms.

The content of the bivalence iron form is very low and as a rule is in the limit of 0.03-0.11% (the concentration 0.05-0.06% prevails). Distribution of bi- and three valence forms of iron showed that the samples from black layer as a rule have the highest content of three-valence iron. It is connected with oxidation of iron and formation in black crust the three valence-iron minerals (hematite, limonite and others hydroxides). The presence of these minerals is observed in the thinsections and is confirmed by the mineralogical analyses. The presence of iron hydroxides assists adsorption of trace elements in the black layer. The content of iron as in building stone as in black layer correlated with content of SiO_2 (insoluble residue) for all studied objects. It could be indicated that iron is included in silicate admixture in carbonate rocks and that the processes of alteration with concentration of iron in black layer took place in the rocks with higher content of silicate admixture.

One important component of carbonate rocks is MnO. MnO is found mostly as isomorphous admixture in carbonate minerals. MnO shows the clear positive correlation with content of MgO. MnO correlation with content of silicate admixture is not so clear for building stones from City Wall and St. Olaf’s Church and it has the negative tendency for building stones of St. Catherine‘s Church. It is necessary to note that in building stones from City Wall and St. Catherine‘s Church the MnO content is as a rule lower or close to MnO content in black layer. For the samples from black crust of St. Olaf’s and St. Mary‘s Churches the higher level of MnO content relatively altered building stones is typical. The former studies showed that MnO has a positive correlation with iron content (Bityukova et al., 2003).

As it is well known the alteration processes are accompanied by the formation of gypsum ($CaSO_4$•$2H_2O$) and accumulation of sulphur in the black layer. The studied altered building stones are characterised by values of S from 0,0n up to 0,n% and as a rule it does not increase 1%. The lowest concentrations of S were determined in the City Hall and St. Mary‘s Church building stones. The main elements distribution in studied altered building stones in Tallinn showed the growth of sulphur in the black layer in several times. The concentration of S in the black crust varies in the limit of 0.7-4.1% and gypsum from 1,3 % up to 14.1% (in St. Olaf’s Church). These data are similar to data by Nord (Nord et al., 1999). The content of gypsum in undamaged limestone in Swedish cities is less than 0,2% and its content increased in the black layer up to 17,5%. In the studied building stones there were determined low contents of glauberite (Na_2SO_4•$CaSO_4$) and bassanite ($CaSO_4$•$0.5H_2O$) that could be seen as the product of “dewatering“ of gypsum (Deer et al., 1962).

Phosphorous varies in the studied building stones in the limit of 0.09-0.80%. This is very close to content in the limestone building stones in Stockholm and Norway (Nord et al. 1994).

The combination of the natural and anthropogenic factors leads progressively to destruction and degradation of the structure and physical properties of the stones of the historical objects in the industrial areas. The porosity of studied samples varies from 2.6 up to 13.6%. The positive correlation of porosity with content of insoluble residue in the building stones was observed.

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