

Weathering reactions on rocks in polluted urban atmosphere developed in wet and dry deposition environments

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Weathering reactions zones on the Middle Muschelkalk dolomite used commonly as building material in Kraków (S Poland) since 17th century was studied. The dolomite was often used at the beginning of 20th century what gives an opportunity to compare material with comparable time of exposition to atmospheric influences. Samples were collected from two localities situated at the distance of ca 1 km between them. Both localities are characterized by similar, relatively high air pollution level and similar composition of air pollution. One set of samples was collected from wall exposed to direct rainwater washing (wet deposition environment) and the second from wall sheltered against rainwater washing (dry deposition environment).

On the surface of rock exposed to rainwater washing typical black and white zones are formed. Black zones are related to the cover of brittle gypsum crust often subjected to blistering and spalling. Black crust contains numerous particles of atmospheric dust and black pigment. Voids are present both in gypsum crust and in the rock beneath the crust. Gypsum accumulations and veinlets are present in the outer part of the dolomite in substratum. The surface of the rock sheltered against the rainwater washing is covered by gray crust. Gray crust is soft and powdering. It tightly cover rock surface and blistering is absent. The crust is composed of atmospheric dust with dispersed gypsum crust. Small nest of gypsum are present in the rock beneath the crust.

Both types of crust contain subordinate dolomite. In samples from environments sheltered against rainwater washing soil derived dust (quartz, micas, feldspars) as well as anthropogenic dust particles are present. Calcite and whewellite occur in small amount. On rainwater washed surfaces authigenic, non-stoichiometric dolomite ("protodolomite") is present. In sheltered against rainwater samples authigenic calcite is present. This difference suggests that dissolution of the dolomite rock occurs on rainwater washed surfaces. Whewellite originates from the metabolism of microorganisms.

Gray crust from surfaces sheltered against rainwater is relatively rich in Si, Al, K, Ti and Fe, Pb, Zn, Ni, Mn, Cr, V what is related to accumulation of atmospheric dust particles of natural and anthropogenic origin. Values of $\delta^{34}\text{SCDT}$ (1.88-5.75‰) and $\delta^{18}\text{OSMOW}$ (4.99-8.60‰) in gypsum from both groups of samples are very similar. $\delta^4\text{SCDT}$ values are very close to those measured in rainwater in Kraków. Isotopic composition of sulphur indicates that fuel combustion is its dominant source.

Results indicate that mechanism of formation of dark crust in wet and dry deposition environments differs significantly. Gray crust (dry deposition environment) is formed by deposition of fine dust particles on the rock surface. Layers of dust are consolidated by crystallization of gypsum promoted by adsorption of sulphate aerosols and SO₂ adsorbed on the rock surface. The role of atmospheric moisture condensed on the rock surface is very important in gypsum crystal growth. In wet deposition zone dissolution and recrystallization of dolomite occur and formation of gypsum crust by crystallization from rainwater solution is a dominant process. Reaction of sulphur containing components on the rock surface typical of dry deposition environment occurs during periods without atmospheric precipitation.