

Crystallographic transformations in malachite used as a pigment in paintings

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The work presents XRD analyses on the crystallographic transformations on 4 samples of malachite: untreated, CO₂, NO₂ and SO₂-treated malachite. The unit-cell parameters refined for the untreated malachite sample are $a = 9.503(3) \text{ \AA}$, $b = 11.982(8) \text{ \AA}$, $c = 3.239(1) \text{ \AA}$, $\beta = 97.75(2)^\circ$ and $V = 364.45(1) \text{ \AA}^3$. The treatment of the sample with NO₂ and SO₂ will cause the replacement of a part of the C⁴⁺ ions with N⁵⁺ and S⁴⁺, respectively, inducing slight distortions of the structural blocks due to the contraction or the expansion of some of the (XO₃) groups in the structure. The structure of malachite is built up by ribbons of edge-sharing CuO₆ octahedra running along the c-axis; the ribbons are linked together through corner-sharing giving rise to corrugated layers parallel to (010) that are interconnected through carbonate groups. Carbonate triangles are inserted between these corrugated layers, assuring an interlayer linkage. The carbonate trigonal groups are located in the (100) plane, so as the substitution of the ³C⁴⁺ cations by smaller or bigger cations will mainly influence the a and b unit-cell dimensions. Treatment of malachite with NO₂ causes N-for-C partial substitutions. As a result, in the N-substituted malachite, both a and b parameters are smaller than those in the untreated malachite, whereas the c unit-cell parameter remains practically constant, in the limit of errors. The shrinkage of the unit-cell volume is also visible. For the SO₂-treated malachite the unit-cell parameters show practically no changes considering the limit of errors. A slight decrease of the sample crystallinity is due to a reaction producing a copper sulfate and explains the “lose” of some small reflections from the malachite pattern. No changes in the malachite structure could be imagined, since the coordination number of the S⁶⁺ cation could be only 4 and 6, which precludes a step-by-step replacement of the three-fold coordinated C in the carbonate groups, as in the case of N. Malachite treated with CO₂ shows a visible change in unit cell parameters explained only by structural changes. The sample of malachite used for the study is more hydrous than expected for assuring the stoichiometry based on the ideal formula. The only possible way to locate more water than that corresponding to the ideal formula is by partial substitution of the hydroxyl anions by H₂O molecules, balancing the substitution with corresponding vacancies in the octahedral sites. By consuming water, the gas treatment reduced these vacancies, resulting in a more “monoclinic” cell, with smaller β angle. Particularizing for the CO₂-treated sample, it seems that the octahedral distortion of the two independent Cu²⁺ sites in the malachite structure, attributed to the Jahn-Teller effect of Cu²⁺ increased, which is normal considering that the initial vacancies in the octahedral sites were occupied by copper cations. As a result, the Jahn-Teller elongated axes of CuO₆ octahedra expanded, which a normal increase of the a and decrease of the b unit-cell parameters. As in the other cases, the c unit-cell parameter remains practically constant, in the limit of errors.