

MALACHITE-ROSASITE GROUP: EVIDENCE FOR TWO DISTINCT STRUCTURAL TYPES THROUGH RIETVELD REFINEMENTS

Natale Perchiazzi and Stefano Merlino

Department of Earth Sciences, Università di Pisa. Via S.Maria 53, I-56126, Pisa, Italy
natale@dst.unipi.it

The malachite-rosasite group, with general formula $Me_2^{2+}(CO_3)(OH)_2$, includes both common minerals, such as malachite ($Me^{2+}=Cu$) and rosasite ($Me^{2+}=Cu, Zn$), together with rare species such as mcguinnessite (Mg,Cu), glaukosphaerite (Cu,Ni), kolwezite (Cu,Co), nullaginite (Ni), pokrovskite (Mg), zincrosasite (Zn,Cu). The similarities of their powder patterns, and their chemical relationships, suggest close structural relationships between these phases. Cu-Zn malachite-type carbonates are employed in the hydrogen production by steam reforming of methanol.

Space group symmetry and cell parameters obtained through single crystal studies are available for malachite and rosasite [1] only, whereas for the other phases, characterized by microcrystalline fibrous habit, they were mainly deduced from powder pattern indexing; the resulting crystallographic data present some degree of uncertainty. As an example, the mineral glaukosphaerite is described as monoclinic, with a malachite-like cell in its original description [2], as well as triclinic, isostructural with kolwezite [3].

An accurate structural model of malachite is available since long time [4], whereas the crystal structure of rosasite and of the isostructural mineral mcguinnessite were only recently solved from powder data [5]. Malachite is monoclinic, $P2_1/a$, with $a=9.502$, $b=11.974$, $c=3.24$ Å, $\beta=98.75^\circ$, whereas rosasite, $P2_1/a$, displays cell constants $a=12.897$, $b=9.370$, $c=3.162$ Å, $\beta=110.26^\circ$. Both structures are built up by the same “modules”, namely “octahedral” walls of edge-sharing Me^{2+} polyhedra, linked together through corner sharing to form infinite layers, and “triangular” CO_3 groups, which assure the interlayer connection. Although the two structures are quite similar when seen along [001], they are actually distinct due to the different ways of module connection.

Powder data scans suitable for subsequent Rietveld structural investigations have been collected for glaukosphaerite, kolwezite, pokrovskite and zincrosasite, and a close scrutiny of these scans suggest a rosasite-like structural assessment for all of these phases. So far, the glaukosphaerite structure has been refined, starting from the rosasite model, up to $R_p=4.49$, $wR_p=6.25$, $RF^2=8.22\%$.

Intermediate compounds in the malachite-rosasite compositional range will be synthesized and their crystal structure determination will be undertaken, to possibly clarify the crucial influence of the regularly octahedrally coordinated cations, such Zn^{2+} , in the transition from the malachite to the rosasite structure type.

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[4] Zigan, F., Joswig, W., Schuster, H.D., Mason, S.A., (1977), *Zeit. Krist.*, **145**, 412

[5] Perchiazzi, N. (2004). EPDIC European Powder diffraction conference Praha **2004**, **11**, 76.