

Crystal structure determination and Rietveld refinement of rosasite and mcguinnessite

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Abstract. The crystal structure of rosasite, $(\text{Cu}, \text{Zn})_2(\text{CO}_3)(\text{OH})_2$, and mcguinnessite, $(\text{Mg}, \text{Cu})_2(\text{CO}_3)(\text{OH})_2$ have been determined from powder data. The two minerals are isostructural, with space group $P2_1/a$ and cell constants $a=12.8976(3)$, $b=9.3705(1)$, $c=3.1623(1)$ Å, $\beta=110.262(3)^\circ$, $V=358.54(2)$ Å³, for rosasite and $a=12.9181(4)$, $b=9.3923(2)$, $c=3.1622(1)$ Å, $\beta=111.233(3)^\circ$, $V=357.63(2)$ Å³ for mcguinnessite.

The crystal structure refinements were lead up to $R_p=7.51\%$, $wR_p=10.39\%$ for rosasite and $R_p=5.12\%$, $wR_p=6.22\%$ for mcguinnessite. In both the two structures, the Cu coordination octahedron is distorted towards an elongated tetragonal bipyramid, whereas the Zn (in rosasite) and Mg (in mcguinnessite) coordination octahedra display an almost regular shape, their distortion being due to a partial occupancy of Cu. The carbonate group was refined as a rigid body, with a regular triangular geometry. Metal coordination octahedra polymerize through edge sharing to form octahedral “columns” and “ribbons”, running along [001] and responsible for the acicular habit of these minerals. The structural relationships between rosasite and malachite are discussed.

Introduction

Rosasite, $(\text{Cu}, \text{Zn})_2(\text{CO}_3)(\text{OH})_2$ is a fairly common mineral, which belongs, together with the rare mineral mcguinnessite $(\text{Mg}, \text{Cu})_2(\text{CO}_3)(\text{OH})_2$ to the malachite-rosasite group, with general formula $\text{Me}^{2+}(\text{CO}_3)(\text{OH})_2$ also including glaukosphaerite ($\text{Me}^{2+}=\text{Cu}, \text{Ni}$), kolwezite (Cu,Co), malachite (Cu), nullaginite (Ni), pokrovskite (Mg). Apart from malachite and rosasite, complete single crystal studies are missing for the other phases, mainly because of their microcrystalline fibrous habit, and their symmetry and cell parameters were mainly deduced from powder pattern indexing, resulting in a fair degree of uncertainty on their crystallography.

As pointed out in [1] for the rosasite series, the “principal unknown in these minerals is the value of $c \sin \beta$ ”, whereas the $hk0$ reflections in these powder patterns are remarkably similar. In [1], a value of $c=3.2 \pm 0.3$ Å was measured through single-crystal photographs of rosasite

fibres from Widgiemooltha, Australia, moreover observing the a^*b^* net is dimensionally similar to malachite, with $h00$ and $0k0=2n$ as in malachite. Mcguinnessite, $(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2$ was firstly described in [2], through a detailed set of physical, optical and chemical data. Given the very fine grain and the fibrous habit of mcguinnessite, a single crystal study of the mineral could not be performed, its x-ray powder pattern being indexed on the basis of a malachite-like cell and space group. Anyway, in [2] the conflicting presence of some reflections, forbidden by the space group of malachite is pointed out.

A complete single-crystal study of rosasite from Tsumeb, Namibia, was presented in [3], reporting it is monoclinic, $P2_1/a$ with $a = 12.873$, $b = 9.354$, $c = 3.156 \text{ \AA}$, $\beta = 110.36^\circ$. A detailed X-ray powder pattern is also reported, together with new electron microprobe data pointing to the chemical formula $(\text{Cu}_{1.18}\text{Zn}_{0.82})(\text{CO}_3)(\text{OH})_2$. In the same work it is moreover stated that "A crystal structure determination is presently being undertaken by J.T. Szymansky, CANMET".

The results of this last study, the crystal structure being refined up to $R=11\%$, were briefly reported in an abstract [4]. These authors highlighted the strict similarity between the crystal structures of malachite and rosasite, but unfortunately details of the rosasite structure such as atomic coordinates and bond distances were not given.

Apart from malachite [5], no other structural determinations are available for the minerals of the malachite group. We therefore undertook the crystal structure determination of rosasite and of mcguinnessite, with the aim of clarifying the structural relationships between the various phases of the malachite group. A comprehensive Rietveld structural study of the malachite-rosasite group phases is presently in progress in our laboratory.

Experimental

A sample of rosasite from Ojuela mine, Durango, Mexico (Natural History Museum of Pisa University catalog number #17092) and a sample of mcguinnessite from the type locality of Red Mountain, Arizona, USA, were used in the present study. Both rosasite and mcguinnessite were present in the above samples as spheroidal aggregates of extremely thin fibrous crystals. The material was carefully hand picked under the binocular microscope to avoid contamination from unwanted phases, and gently hand milled in an agate mortar under acetone, to fill with the resulting powder a 0.5 mm Lindemann capillary.

Powder diffraction data for both phases were collected with primary $\text{Ge}(111)$ monochromated $\text{CuK}\alpha_1$ radiation on a D8 Bruker Vario diffractometer equipped with a PSD detector, working in rotary capillary geometry, so to use a low, carefully selected, amount of material, as well as to reduce the strong preferred orientation due to the $[001]$ fibrous habit of rosasite and mcguinnessite. For both rosasite and mcguinnessite, two datasets were collected, $11-50^\circ$ and $50-100^\circ 2\theta$, with step size $0.0156^\circ 2\theta$ and counting times 24s (16s mcguinnessite) and 48s (32s mcguinnessite).

Structure solution and Rietveld refinement

For the structural study of rosasite we assumed the space group $P2_1/a$, and initially the cell constants given in [3]. Refined cell parameters were $a = 12.8976(3)$, $b = 9.3705(1)$,

$c = 3.1623(1) \text{ \AA}$, $\beta = 110.262(3)^\circ$, $V = 358.54(2) \text{ \AA}^3$, for rosasite and $a = 12.9181(4)$, $b = 9.3923(2)$, $c = 3.1622(1) \text{ \AA}$, $\beta = 111.233(3)^\circ$, $V = 357.63(2) \text{ \AA}^3$ for mcguinnessite.

The crystal structure of rosasite was solved through the EXPO [6] program, which allowed us to identify the position of the two metals and of two oxygen atoms. This uncomplete model was used as a starting one for the subsequent Rietveld refinement, which was performed through the GSAS/EXPGUI suite of programs [7,8].

The missing oxygens and the carbon atom were located examining the Fourier difference maps, the displacement parameters and the distances and angles listing. The two hydroxyl groups were clearly identified through a bond valence balance and are henceforth denoted as O4 and O5. Zn was assumed to be in the more regular metal coordination polyhedron, and the occupancy of this site was fixed to the value $\text{Zn}_{0.8}\text{Cu}_{0.2}$, indicated by the microprobe data [3].

Both the malachite-like and the rosasite-like starting models were tested in the structure solution of mcguinnessite. Any effort to refine its crystal structure in a malachite-like model failed, whereas fairly promising results were obtained using a rosasite-like structure, assumed in the subsequent Rietveld refinement.

In mcguinnessite, a mixed occupancy of Mg and Cu was assumed for both the two independent octahedral sites, as indicated by the scrutiny of the displacement factors, assuming, as indicated by the microprobe data [2], a Mg/Cu ratio~1.12. The refined occupancies were $\text{Cu1} = 0.79\text{Cu} + 0.21\text{Mg}$, and $\text{Mg2} = 0.85\text{Mg} + 0.15\text{Cu}$.

In the early stages of both the two refinements, constraints on the Me-O bonds were introduced, initially with high statistical weights, which were progressively reduced in the course of the refinement, finally removing all the constraints. The carbonate group was refined as a rigid body, imposing a C-O distance of 1.284 \AA [9]. Isotropic displacement parameters were refined for all the atoms. The Rietveld refinement finally converged to $R_{\text{wp}} = 10.39\%$ $R_{\text{p}} = 7.51\%$ for rosasite and $R_{\text{wp}} = 4.45\%$ $R_{\text{p}} = 6.22\%$ for mcguinnessite.

Structure description

The final refined atomic coordinates, and isotropic displacement parameters for the two structures are reported in Table 1, whereas selected interatomic distances and angles are presented in Table 2. Partial occupancies were refined for the site $\text{Zn2} = 0.8\text{Zn} + 0.2\text{Cu}$ in rosasite, and for $\text{Cu1} = 0.79\text{Cu} + 0.21\text{Mg}$, $\text{Mg2} = 0.85\text{Mg} + 0.15\text{Cu}$ in mcguinnessite. The geometry of the coordination polyhedra of the two independent metals allows a clear distinction between the positioning of Cu^{2+} and of $\text{Zn}^{2+}/\text{Mg}^{2+}$ cations. As shown in Table 2, the Cu octahedron, due to the Jahn-Teller effect, is strongly distorted towards an elongated bipyramidal coordination both in rosasite and in mcguinnessite. Two oxygens and two hydroxyls, with Cu-O distances clustering close to 2 \AA , are arranged in a nearly planar square coordination, with two additional longer bonds to complete its sixfold coordination. As expected, the polyhedron hosting Zn in rosasite and Mg in mcguinnessite is a more regular one, the former polyhedron being slightly larger than the latter. Zn-O distances range from 2.01 to 2.26 \AA in rosasite and Mg-O distances are in the range 2.00 - 2.22 \AA for mcguinnessite, with mean values $\langle\text{Zn-O}\rangle 2.13 \text{ \AA}$ and $\langle\text{Mg-O}\rangle 2.12 \text{ \AA}$. The distortion from a regular shape can be attributed to the partial occupancy by Cu in these sites.

Table 1. Final refined coordinates and isotropic displacement parameters (\AA^2) for roasite and mcguinnessite. Me2 is the Zn-Mg site in roasite and mcguinnessite respectively.

Rosasite					Mcguinnessite			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
Cu1	0.2103(2)	0.0007(3)	0.449(1)	0.0129(5)	0.2117(2)	-0.0043(4)	0.446(1)	0.0147(4)
Me2	0.3945(2)	0.2302(2)	0.1730(9)	0.0163(5)	0.3920(2)	0.2283(3)	0.179(1)	0.0196(8)
C	0.1414	0.2745	0.6654	0.011(5)	0.1374	0.2705	0.6614	0.083(5)
O1	0.1353(1)	0.1420(3)	0.760(3)	0.009(3)	0.1311(1)	0.1360(1)	0.724(2)	0.042(2)
O2	0.2312(1)	0.3433(3)	0.863(1)	0.014(3)	0.2289(1)	0.3361(2)	0.8708(8)	0.027(2)
O3	0.0520(1)	0.3447(3)	0.471(2)	0.017(3)	0.0477(1)	0.3431(1)	0.490(2)	0.033(2)
O4	0.3543(7)	0.0946(9)	0.648(4)	0.012(3)	0.3518(5)	0.0907(7)	0.614(3)	0.033(2)
O5	0.4187(9)	0.385(1)	-0.256(6)	0.049(4)	0.4235(4)	0.3769(6)	-0.257(2)	0.012(2)

Table 2. Bond distances (\AA) and angles ($^\circ$) in the coordination polyhedra of roasite and mcguinnessite. Symmetry transformations used to generate equivalent atoms $i = \frac{1}{2}\text{-}x, y\text{-}\frac{1}{2}, \text{-}z$; $ii = \frac{1}{2}\text{-}x, y\text{-}\frac{1}{2}, 1\text{-}z$; $iii = x, y, z\text{-}1$; $iv = \frac{1}{2}\text{-}x, y\text{-}\frac{1}{2}, 2\text{-}z$; $v = x+\frac{1}{2}, \frac{1}{2}\text{-}y, z$; $vi = x, y, z+1$; $vii = x+\frac{1}{2}, \frac{1}{2}\text{-}y, z\text{-}1$.

Rosasite					Mcguinnessite						
Cu1	-O5 ⁱ	1.89(1)	Zn2	-O4 ⁱⁱⁱ	2.01(1)	Cu1	-O4	1.909(7)	Mg2	-O3 ^v	2.007(3)
	-O4	1.952(9)		-O3 ^v	2.046(3)		-O5 ⁱ	1.977(6)		-O4 ⁱⁱⁱ	2.087(9)
	-O2 ⁱⁱ	2.057(5)		-O5	2.07(1)		-O1	2.076(6)		-O5	2.104(8)
	-O1	2.078(8)		-O4	2.16(1)		-O2 ⁱⁱ	2.084(4)		-O4	2.110(9)
	mean	1.995		-O2 ⁱⁱⁱ	2.256(3)		mean	2.011		-O5 ^{vii}	2.183(8)
	-O1 ⁱⁱⁱ	2.443(7)		-O5 ^{vi}	2.251(1)		-O1 ⁱⁱⁱ	2.499(6)		-O2 ⁱⁱⁱ	2.220(4)
	-O2 ^{iv}	2.519(3)		mean	2.134		-O2 ^{iv}	2.524(3)		mean	2.119
	O1-CU1-O4 96.0(3)					O1-CU1-O4 98.6(3)					
	O1-CU1-O5 ⁱ 91.3(5)					O1-CU1-O5 ⁱ 87.4(2)					
	O2 ⁱⁱ -CU1-O4 90.8(3)					O2 ⁱⁱ -CU1-O4 90.1(3)					
	O2 ⁱⁱ -CU1-O5 ⁱ 81.7(4)					O2 ⁱⁱ -Cu1-O5 ⁱ 83.9(2)					

An hydrogen bonding scheme was derived for both the two structures by looking at those distances shorter than 3.1 \AA , between oxygen atoms not belonging to the same polyhedron. The two OH⁻ groups, O4 and O5, engage as acceptors the oxygen atoms O3 and O1 respectively, with O4...O3 of 2.721(9) and 2.742(7) \AA (rosasite and mcguinnessite, respectively) and O5...O1 of 2.80(1) and 2.706(7) \AA (rosasite, mcguinnessite). The bond valence balance, computed according to [10,11], is satisfactory for both minerals, with deviations less than 15% from the ideal anion sums, thus confirming the soundness of these crystal-chemical models.

In the following description of the polyhedral connections, we shall refer to roasite only, given its isostructurality with mcguinnessite. Both the Zn and the Cu octahedra connect by edge-sharing to form Cu-based and Zn-based octahedral "columns", and two columns large "ribbons" (Figure 1), running along [001], and responsible for the acicular habit of the mineral.

As already pointed out in [4] there is a close resemblance between the crystal structures of roasite (mcguinnessite) and of malachite, when seen projected along *c* (Figure 1).

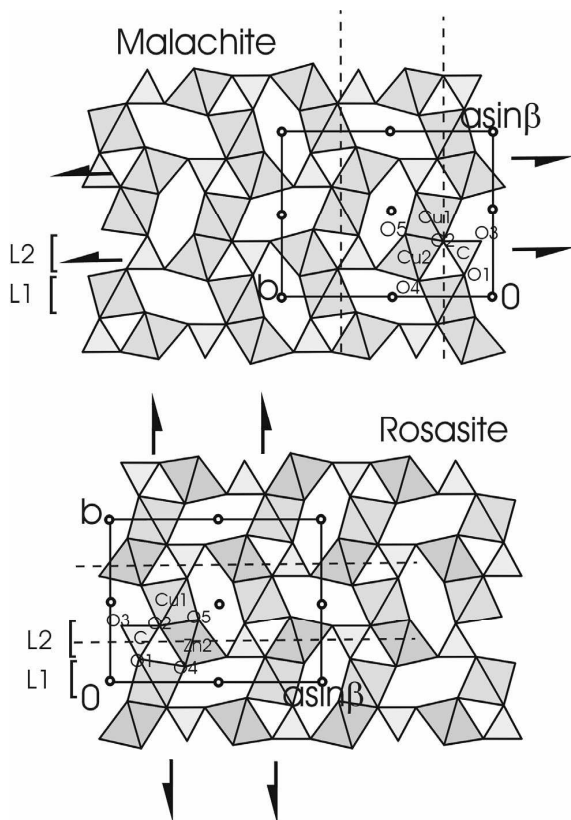


Figure 1. The close relationships between the crystal structures of rosasite and malachite, when seen along [001]. In both the two structures the same two kind of layers, denoted as L1 and L2, regularly alternate along the $\approx 9.5 \text{ \AA}$ axis.

One can identify, in both the two structures, two kinds of “layers”, regularly stacked along the $\approx 9.5 \text{ \AA}$ axis, and with thickness $\approx 1/4$ of the stacking periodicity. Referring to rosasite, a first layer (L1) is made up by Cu polyhedra only, and is placed nearly centered at $y \approx 0$, the Cu polyhedra inside this layer being related by the inversion centers. A second layer (L2), hosting Zn and C polyhedra, is placed centered at $1/4b$, with the polyhedra of the layer related by the a glide present at $y = 1/4$. Comparing the structure of rosasite (mcguinnessite) and of malachite in terms of the above “layers” one can remark that in both the two minerals the Cu-only (L1) layer hosts the more distorted metal polyhedron, whereas the L2 layer is made up by carbonate groups and by the more regular metal coordination polyhedron. Although the two structures are quite similar in [001] projection, the different orientation of the space group symmetry operators respect to the layers, leads anyway to the distinct crystal structures of these two phases.

Conclusions

The crystal structure of rosasite and mcguinnessite have been determined and refined from powder data. The two minerals are isostructural, crystallizing in the space group $P2_1/a$. Their structure host Cu in distorted octahedra, whereas almost regular octahedra are formed by Zn in rosasite and by Mg in mcguinnessite. Both the hydrogen bonding scheme and the valence balance confirm the reliability of the presented structural models. A comparison between the structures of rosasite and of malachite shows their close resemblance in [001] projection. These two structures are described in terms of layers, stacked along the ≈ 9.5 Å axis, remarking how the different orientation of the space group operators respect to these layers leads anyway to the different structures of malachite and rosasite.

References

1. Jambor, J., 1976, *Can. Mineral.*, **14**, 574.
2. Erd, R.C., Cesbron, F.P., Goff, F.E., Clark, J.R., (1981), *Mineral. Rec.*, **12**, 143.
3. Roberts, A. C., Jambor, J. L., Grice, J. D., (1986), *Powd. Diff.*, **1**, 56.
4. Szimansky, J.T., Le Page, Y., (1986), Program with Abstracts – Geol. Ass. Canada, Mineral. Ass. Canada, **11**, 133.
5. Zigan, F., Joswig, W., Schuster, H.D., Mason, S.A., (1977), *Zeit. Krist.*, **145**, 412.
6. Altomare, A., Burla, M.C., Cavalli, M., Carrozzini, B., Cascarano, G.L., Giacovazzo, C., Gagliardi, A., Moliterni, G. G., Polidori, G., & Rizzi, R., (1999), *J. Appl. Cryst.*, **32**, 339.
7. Larson, A.C., Von Dreele, R.B., (2000), Los Alamos National Laboratory Report LAUR 86.
8. Toby, B.H., (2001), *J. Appl. Cryst.*, **34**, 210.
9. Zemann, J., (1981), *Fortschr. Mineral.* **59**, 95.
10. Brese, N.E., O'Keeffe, M., (1991), *Acta Cryst.*, **B47**, 192.
11. Ferraris, G., Ivaldi, G., (1988), *Acta Cryst.*, **B44**, 341.

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