

MOZARTITE, $\text{CaMn}(\text{OH})\text{SiO}_4$, A NEW MINERAL SPECIES FROM THE CERCHIARA MINE, NORTHERN APENNINES, ITALY

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ABSTRACT

Mozartite occurs at the Cerchiara mine, Val di Vara, northern Apennines, Italy. Associated minerals are pectolite, calcite, quartz and hausmannite. Mozartite and the associated minerals fill wide veins in ophiolitic metacherts. Mozartite usually appears as minute anhedral crystals, but some subhedral prismatic [100] crystals have been found. It is transparent, deep red, strongly pleochroic and biaxial positive, with $2V_{\text{obs}} = 50(2)^\circ$, α 1.840(5), β 1.855(5), γ 1.920(5). The mean chemical composition leads to the empirical formula $\text{Ca}_{0.98}(\text{Mn}_{1.00}\text{Al}_{0.02})(\text{OH})_{1.00}\text{Si}_{0.99}\text{O}_{4.00}$. It crystallizes in space group $P2_12_12_1$, with a 5.838(1), b 7.224(1), c 8.690(1) Å and $Z = 4$. The strongest lines in the X-ray powder pattern [d in Å(hkl)] are 2.584(211), 2.687(013), 3.070(120) and 5.558(011). Mozartite is isostructural with the silicate vuagnatite, the vanadate tangeite (calciovolborthite) and the arsenates austinite, conichalcite and nickelaustinite. The crystal structure was refined to $R = 0.027$. The name honors Wolfgang Amadeus Mozart (1756–1791); the mineral was found in the year marking the 200th anniversary of his death.

Keywords: mozartite, occurrence, physical properties, chemical composition, powder pattern, structure refinement, Cerchiara mine, Italy.

SOMMAIRE

Nous avons découvert la mozartite, nouvelle espèce minérale, à la mine Cerchiara, dans la partie nord des Apennins, en Italie. Lui sont associés pectolite, calcite, quartz et hausmannite, en veines qui recoupent des métacherts ophiolitiques. La mozartite se présente normalement sous forme de très petits cristaux xénomorphes, quoique nous avons trouvé des cristaux sub-idiomorphes [100]. Elle est transparente, rouge foncé, fortement pléochroïque et biaxe positive, $2V_{\text{obs}} 50(2)^\circ$, α 1.840(5), β 1.855(5), γ 1.920(5). Les données chimiques moyennes mènent à la formule empirique $\text{Ca}_{0.98}(\text{Mn}_{1.00}\text{Al}_{0.02})(\text{OH})_{1.00}\text{Si}_{0.99}\text{O}_{4.00}$. Elle répond à la symétrie du groupe spatial $P2_12_12_1$, a 5.838(1), b 7.224(1), c 8.690(1) Å, $Z = 4$. Les quatre raies les plus intenses du cliché de diffraction [d en Å(hkl)] sont 2.584(211), 2.687(013), 3.070(120), 5.558(011). La mozartite possède la même structure que le silicate vuagnatite, le vanadate tangéite (calciovolborthite), et les arsenates austinite, conichalcite et nickelaustinite. Nous avons affiné la structure cristalline jusqu'à un résidu R de 0.027. La mozartite ayant été découverte en 1991, le nom choisi souligne l'anniversaire de la mort de Wolfgang Amadeus Mozart (1756–1791).

(Traduit par la Rédaction)

Mots-clés: mozartite, nouvelle espèce minérale, propriétés physiques, composition chimique, cliché de diffraction X, affinement de la structure, mine Cerchiara, Italie.

INTRODUCTION

Continuing studies of occurrences of manganese mineralization in ophiolitic sequences of the northern Apennines have led to the identification of a new silicate mineral species, mozartite, in the Cerchiara manganese mine, located in Val di Vara, in eastern Liguria, Italy. Assemblages of silicate and carbonate minerals from this mine have been described by Lucchetti *et al.* (1988), Basso *et al.* (1989a, b) and Cabella *et al.* (1990).

The new mineral is a basic calcium manganese nesosilicate closely related to minerals of the adelite and descloizite groups. It represents the Mn analogue of vuagnatite $\text{CaAl}(\text{OH})\text{SiO}_4$ (Sarp *et al.* 1976, McNear *et al.* 1976, Pabst *et al.* 1977). The name has been chosen in honor of Wolfgang Amadeus Mozart (1756–1791), since the mineral was identified as a new species during the 1991, year marking the 200th anniversary of his death. This unconventional choice is justified by the close association of geological and mineralogical sci-

ences with Mozart's music, and especially with his last opera "The Magic Flute" (Whittaker 1991). The mineral and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Type material is deposited in the collection of the Dipartimento di Scienze della Terra, Sezione di Mineralogia, Università di Genova.

OCCURRENCE AND PHYSICAL PROPERTIES

Mozartite forms reddish brown aggregates of minute anhedral crystals intergrown with pectolite and minor amounts of calcite, quartz and hausmannite. Mozartite and the associated minerals fill large veins that cross-cut massive braunite interbedded within the ophiolitic metacherts at the Cerchiara mine, near Faggiona, Val di Vara, La Spezia, eastern Liguria, Italy. The size of the individual grains of mozartite ranges from 0.1 to 0.5 mm, and some subhedral single crystals, included in calcite or pectolite, develop with stocky prismatic habit, elongate parallel to [100]; the dominant prism is terminated by a bisphenoid. Neither twinning nor cleavage was observed, and the fracture is conchoidal. The hardness could not be determined owing to the small grain-size; micro-indentation measurements were unsuccessful because of the brittleness of the mineral. The measured density, using Clerici solution and a Westphal balance, is 3.63(4) g/cm³; the calculated density is 3.68 g/cm³. The indices of refraction were determined by Cargille oil-immersion liquids at 25°C for 589 nm; the optical axial angle was obtained with a five-axis universal stage. The optical properties are summarized in Table 1.

CHEMICAL COMPOSITION

Sixteen spot chemical analyses were carried out by means of a PHILIPS SEM 515 scanning electron microscope equipped with an EDAX PV9100 spectrometer in energy-dispersion mode, with an accelerating voltage of 15 kV and a beam current of about 2 nA.

Diopside (Mg, Ca), rhodonite (Mn) and anorthoclase (Al, Si) were used as reference standards for the only elements having atomic number greater than 10 that are present. The H₂O content could not be determined owing to the paucity of material, but was calculated by

TABLE 1. OPTICAL PROPERTIES OF MOZARTITE

Transparent	Biaxial positive
Lustre: vitreous	Elongation: positive
Colour: deep red	Orientation: Z = a
Streak: red	$\alpha = 1.840(5)$
Non-fluorescent	$\beta = 1.855(5)$
	$\gamma = 1.920(5)$
Pleochroism: strong	$2V_{obs} = 50(2)^\circ$
X = yellow-brown	$2V_{calc} = 52.8^\circ$
Y = yellow	
Z = orange-red	

TABLE 2. ELECTRON-MICROPROBE DATA FOR MOZARTITE

	Range (wt%)	Mean (wt%)
MgO	0.00 - 0.15	0.05
CaO	26.78 - 27.20	27.08
Al ₂ O ₃	0.40 - 0.70	0.49
Mn ₂ O ₃	38.46 - 39.01	38.72
SiO ₂	28.75 - 29.66	29.25
Total		95.59

difference, after a microprobe check indicated the absence of detectable F. The calculated amount of H₂O agrees with the value inferred from the structural analysis. Spot analyses show neither significant variations of composition nor compositional zoning in individual crystals. The mean chemical composition is reported in Table 2, along with an indication of variability. The empirical formula, based on five oxygen atoms, is: Ca_{0.98}(Mn_{1.00}Al_{0.02})(OH)_{1.00}Si_{0.99}O_{4.00}.

X-RAY POWDER-DIFFRACTION DATA

The X-ray powder-diffraction analysis was performed by a Guinier STOE camera using CuK α radiation (graphite monochromator) and silicon as an internal standard. Relative intensities were assigned visually, and the reflections were indexed on the basis of the pattern calculated by the Lazy Pulverix program (Yvon *et al.* 1977) using the results of the single-crystal structure analysis. The cell parameters refined from powder data are *a* 5.837(1), *b* 7.229(1), *c* 8.690(2) Å. Measured and calculated powder-diffraction data are reported in Table 3.

REFINEMENT OF THE CRYSTAL STRUCTURE

An anhedral crystal, measuring approximately 128 × 102 × 26 µm, was mounted on an ENRAF-NONIUS

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR MOZARTITE

h k l	Calculated		Measured		h k l	Calculated		Measured	
	d	I	d	I		d	I	d	I
0 1 1	5.555	96	5.558	S	0 1 4	2.081	10	2.081	VW
1 1 1	4.024	23	4.025	W	2 2 2	2.012	26	2.013	VW
0 2 0	3.612	37	3.613	W	1 3 2	1.981	3	1.980	VW
1 2 0	3.072	73	3.070	S	1 1 4	1.960	5	1.959	VW
0 2 2	2.778	20	2.776	VW	0 2 4	1.862	11	1.862	W
0 1 3	2.689	73	2.687	S	3 1 1	1.837	6	1.836	VW
2 1 1	2.584	100	2.584	VS	2 3 1	1.817	20	1.817	W
1 2 2	2.508	36	2.509	W	0 4 0	1.806	3	1.806	VW
1 1 3	2.442	35	2.441	W	3 0 2	1.776	2	1.775	VWV
2 0 2	2.423	10	2.422	VW	1 3 3	1.765	18	1.766	W
0 3 1	2.321	9	2.320	VW	2 0 4	1.743	19	1.743	W
2 1 2	2.297	5	2.296	VW	3 2 0	1.713	9	1.713	VW
2 2 0	2.270	26	2.269	W	0 4 2	1.668	30	1.669	W
0 2 3	2.260	19	2.260	W	3 1 3	1.576	9	1.577	VW
2 2 1	2.197	28	2.197	W	2 2 4	1.570	13	1.570	VW
0 0 4	2.173	8	2.173	VW	2 3 3	1.564	51	1.565	M
0 3 2	2.106	4	2.106	VWV	2 4 0	1.536	18	1.538	VW

d values are in Å.

TABLE 4. CRYSTAL STRUCTURE DATA FOR MOZARTITE

Idealized formula	CaMn(OH)SiO ₄
Formula from structure refinement	Ca(Mn _{0.94} Al _{0.06})(OH)SiO ₄
Z	4
Space group	P2 ₁ 2 ₁ 2 ₁
a (Å)*	5.838(1)
b (Å)	7.224(1)
c (Å)	8.690(1)
V (Å ³)	366.5
μ (MoKα, mm ⁻¹)	4.86
Measured reflections (including Friedel pairs)	1930
Independent reflections	1056
Observed reflections (I > 3σ)	660
Extinction correction	4.9(5) × 10 ⁻⁴
R _w (observed)	0.024
R (observed)	0.027
R (all)	0.068

*Labeling of axes according to Parthé & Gelato (1984)

TABLE 5. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS (HAMILTON 1959) FOR MOZARTITE

Atom*	Site occupancy	x/a	y/b	z/c	B _u (Å ²)
Ca	1.	0.0216(2)	0.3748(2)	0.6741(1)	0.72
Mn/Al	0.94(5)/0.06	0.7488(2)	0.2570(2)	0.9964(1)	0.43
Si	1.	0.5103(3)	0.6307(2)	0.8164(1)	0.54
O1	1.	0.4913(7)	0.4534(4)	0.9336(3)	0.60
O2	1.	0.5716(6)	0.7995(4)	0.9397(4)	0.85
O3	1.	0.2729(7)	0.6586(5)	0.7218(4)	0.62
O4	1.	0.7388(7)	0.6234(5)	0.7068(4)	0.70
O5	1.	0.0033(7)	0.3943(4)	0.9414(3)	0.56

*Numbering of atoms according to McNear et al. (1976)

TABLE 6. INTERATOMIC DISTANCES (Å) FOR THE COORDINATION POLYHEDRA IN MOZARTITE

Si - O1	1.640(3)	Ca - O1	2.432(3)
- O2	1.662(3)	- O2	2.629(3)
- O3	1.624(4)	- O2'	2.456(3)
- O4	1.640(4)	- O3	2.493(4)
Average	1.642	- O3'	2.555(4)
		- O4	2.515(4)
Mn - O1	2.130(3)	- O4'	2.456(4)
- O1'	2.171(3)	- O5	2.329(3)
- O3	2.029(4)	Average	2.483
- O4	2.024(4)		
- O5	1.873(3)		
- O5'	1.858(3)		
Average	2.014		

TABLE 7. EDGE LENGTHS (Å) AND ANGLES (°) FOR THE COORDINATION POLYHEDRA IN MOZARTITE

O1 - Si - O2	2.545(4)	100.80(15)	O1 - Ca - O2	3.225(5)	79.07(11)
- O3	2.685(5)	110.68(21)	- O2'	2.545(4)	62.75(10)
- O4	2.735(5)	113.01(21)	- O3'	3.051(5)	75.40(12)
O2 - Si - O3	2.768(5)	114.77(18)	- O4'	2.903(5)	72.87(12)
- O4	2.582(5)	102.89(17)	O2 - Ca - O3'	3.086(5)	73.05(12)
O3 - Si - O4	2.735(4)	113.83(15)	- O4	2.582(5)	60.20(11)
Average	2.675	109.33	O2' - Ca - O2	3.183(2)	77.41(7)
			- O3	3.182(5)	80.01(11)
O1 - Mn - O3	2.873(5)	87.36(13)	- O4	3.877(5)	95.41(12)
- O4	2.903(5)	88.63(14)	- O4'	3.993(5)	108.78(13)
- O5	2.737(4)	86.03(14)	O3 - Ca - O4	3.131(4)	77.39(10)
- O5'	3.020(5)	98.21(13)	- O4'	3.418(6)	87.28(13)
O1' - Mn - O3	3.051(5)	93.10(15)	- O5	2.741(5)	69.17(12)
- O4	2.996(5)	91.06(14)	O3' - Ca - O4	3.916(6)	101.13(12)
- O5	2.881(5)	90.56(14)	- O4'	3.131(4)	77.33(9)
- O5'	2.737(4)	85.20(14)	- O5	3.124(5)	79.40(13)
O3 - Mn - O5	2.792(4)	91.27(14)	O4 - Ca - O5	2.785(5)	70.05(13)
- O5'	2.741(5)	89.56(14)	O4' - Ca - O5	3.046(5)	79.03(13)
O4 - Mn - O5	2.785(5)	91.14(14)	Average	3.151	79.21
- O5'	2.708(5)	88.35(14)			
Average	2.852	90.04			

CAD-4 automatic single-crystal diffractometer. The cell parameters were determined and refined, using 25 reflections within the angular range $18^\circ < \theta < 21^\circ$. Diffraction intensities were measured up to $\theta = 30^\circ$ using graphite-monochromated MoK α radiation and operating in the $\omega - 2\theta$ scan mode. An absorption correction was applied using the ψ scan method (North *et al.* 1968). The Laue symmetry of the reciprocal lattice is *mmm*, and systematic extinctions are present for $h00: h = 2n + 1, 0k0: k = 2n + 1, \text{ and } 00l: l = 2n + 1$. The space group is therefore $P2_12_12_1$.

The structure, solved using the Patterson map, confirmed the isotypy with vuagnatite suggested by chemical formula, unit cell and space group. The structural model was refined through eight cycles of least-squares refinement, carried out by a modified version of the ORFLS program (Busing *et al.* 1962). The scattering factors for neutral atoms, including corrections for anomalous dispersion, were taken from the International Tables for X-ray Crystallography, vol. IV (1974). Total occupancy was fixed for Ca and Si in their respective sites. Scale factor, coefficient of secondary extinction, occupancy of Mn versus Al in the octahedral site, coordinates and temperature factors were simultaneously derived. Anisotropic temperature-factors were introduced after the fourth cycle. Experimental details and refinement results are summarized in Tables 4, 5, 6 and 7.

A second refinement, under the same conditions, was performed using the antipodal coordinates $1 - x, 1 - y, 1 - z$ and led to the final values $R(\text{obs}) = 0.032$ and $R_w(\text{obs}) = 0.026$. The Hamilton test (Hamilton 1965) favors the first configuration at the 0.05 level of statistical significance.

Finally, geometrical considerations and formula balance suggest the presence of a hydrogen bond, in view of the short distance O5-O2 [2.474(4) Å]. The hydrogen atom, located on a difference Fourier map at 0.014, 0.529, 0.983, is involved in a strong hydrogen bond, whose geometry is characterized by the distances O5-H = 1.04 Å, H...O2 = 1.45 Å and the angle O5-H...O2 = 167.2°.

Tables of F_o , $\sigma(F_o)$ and anisotropic thermal parameters are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

Among the compounds with the general formula $\text{CaM}(\text{OH})\text{TO}_4$, five minerals whose structures have been described in the space group $P2_12_12_1$ are isostructural with mozartite. In addition to vuagnatite $\text{CaAl}(\text{OH})\text{SiO}_4$ (McNear *et al.* 1976), four members of the adelite group with pentavalent As and V in the *T* site and divalent cations Zn, Cu and Ni in the *M* site are involved: austinite $\text{CaZn}(\text{OH})\text{AsO}_4$ (Giuseppetti & Tadini 1988), conchal-

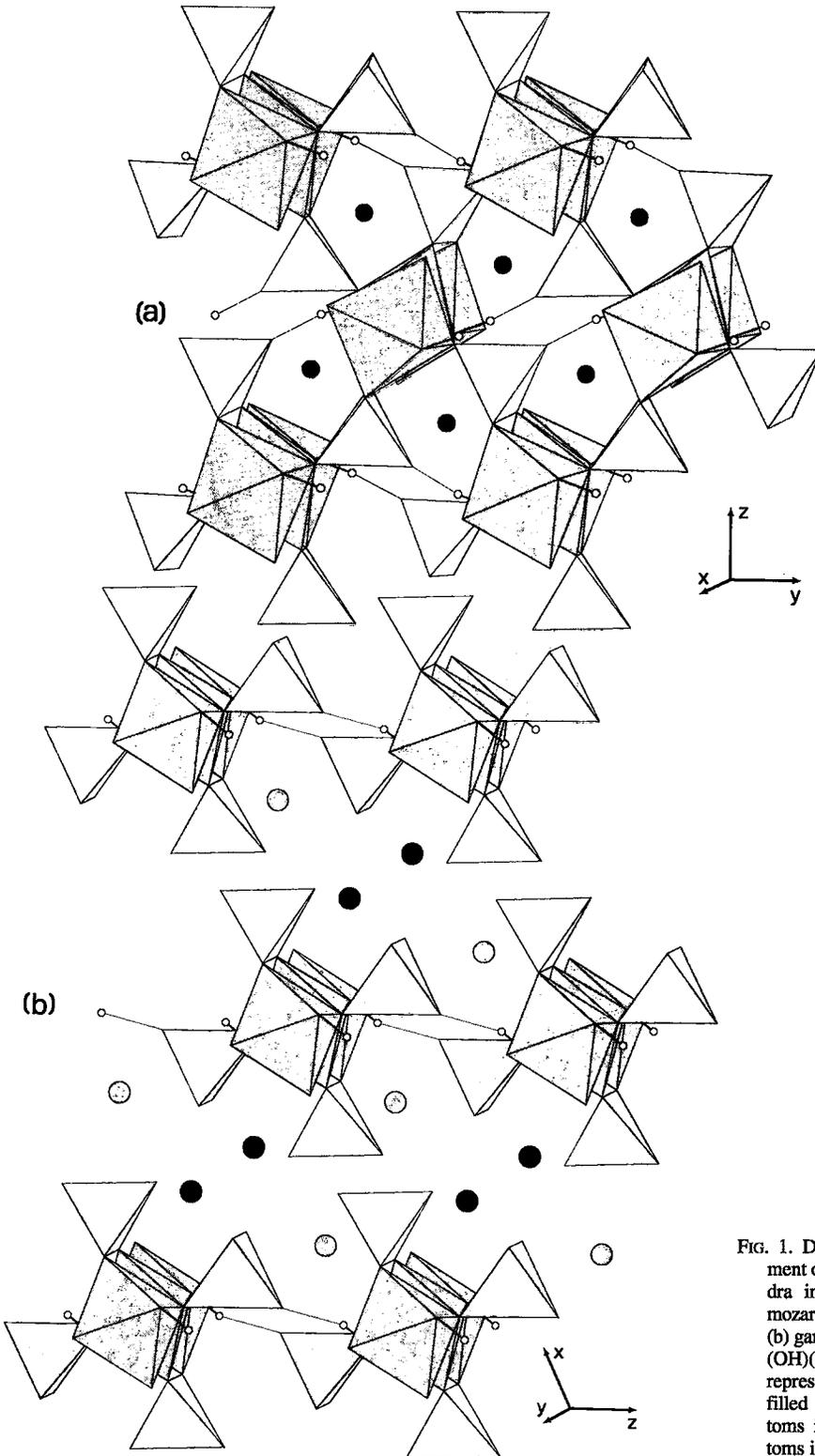


FIG. 1. Drawing of the arrangement of octahedra and tetrahedra in the structures of (a) mozartite CaMn(OH)SiO_4 and (b) gamagarite $\text{Ba}_2(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{OH})(\text{VO}_4)_2$. Empty circles represent hydrogen atoms, and filled circles represent Ca atoms in mozartite and Ba atoms in gamagarite.

cite $\text{CaCu}(\text{OH})\text{AsO}_4$ (Qurashi & Barnes 1963), nickelaustinite $\text{Ca}(\text{Ni,Zn})(\text{OH})\text{AsO}_4$ (Cesbron *et al.* 1987) and tangeite (calciovolborthite) $\text{CaCu}(\text{OH})\text{VO}_4$ (Basso *et al.* 1989c).

A comparison between the structures of vuagnatite and mozartite shows that the small rearrangement of the atomic positions, related to the different octahedrally coordinated cations, modifies slightly the geometry of the polyhedra. The mean Ca–O distance is affected by the change of the octahedrally coordinated cation, resulting in an elongation of about 0.04 Å in mozartite. The replacement of Al by Mn leads to a change in the variance of the bond angles from 20.64 to 11.99 for the octahedron and from 25.50 to 36.00 for the tetrahedron, whereas the mean quadratic elongation (Robinson *et al.* 1971) does not vary appreciably for both polyhedra. The two minerals exhibit very similar mean Si–O distances but rather different individual Si–O distances, except for Si–O4. The distance between the vertices O3 and O4 of contiguous octahedra, bridged by the tetrahedron, is slightly longer in mozartite, leading to a wider O3–Si–O4 angle, together with an unchanged Si–O4 distance and a shorter Si–O3 distance; Si–O1 undergoes a contraction balanced by a lengthening of the Si–O2 distance.

The amount of aluminum incorporated in the crystals studied is too small to ascertain its presence in tetrahedral coordination. Hence, Al has been assigned to the octahedral site, as in vuagnatite. The mean Mn–O distance and the electroneutrality of the formula suggest that manganese occupies the octahedral site as Mn^{3+} .

From a topological point of view, mozartite provides a new example of the occurrence of a structural motif representing the "backbone" common to several compounds (Shen & Moore 1982). Such a motif, consisting of a linear chain of edge-sharing octahedra with connected tetrahedra developed along a 2-fold screw axis, involves octahedrally coordinated Mn along with tetrahedrally coordinated Si in mozartite. Figure 1 points out the two different types of stacking sequence of the layers, built up of "backbones" joined by hydrogen bonds, in the structures of mozartite and gamagarite $\text{Ba}_2(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{OH})(\text{VO}_4)_2$ (Basso *et al.* 1987), members respectively of the third and first of the three structural categories proposed by Shen & Moore. The stacking sequence for the structures of the third category, solved in space groups $P2_12_12_1$ or $Pnma$, is fixed by the two 2-fold screw axes orthogonal to the "backbone". In the resulting arrangement of octahedra and tetrahedra (Fig. 1a), the unique tetrahedron in mozartite assumes the different roles played by the two independent tetrahedra in gamagarite (Fig. 1b), providing both intra- and interchain links.

The chains of octahedra, the connected tetrahedra and the large cations are mutually differently displaced in the three categories, but their topology is sufficiently similar to allow for the following structural relations. The structures of the first and second category can be

described as recombinations (Lima-de-Faria *et al.* 1990) of the structural type represented by the third category. The first two categories contain layers cut out from the archetypal structure (third category) by omitting, in every second layer (Fig. 1), the octahedrally coordinated cations and the OH groups; therefore, half of the octahedral chains are missing, as compared with the third category, and the derivative structures result.

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