Carraraite and zaccagnaite, two new minerals from the Carrara marble quarries: their chemical compositions, physical properties, and structural features

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ABSTRACT

Two new mineral species, carraraite and zaccagnaite, were found in cavities in calcite veins in marble quarries of the Carrara basin (Apuan Alps, Italy). Carraraite, $Ca_3Ge(OH)_6(SO_4)_{1.08}$ $(CO_3)_{0.92} \cdot 12H_2O$, occurs as submillimetric crystals, tabular on {001}. The cell dimensions are $a = 11.056$ (3), $c = 10.629$ (6) Å, and the space group is $P6_3/m$. Carraraite is optically uniaxial (–), $\omega = 1.509$, $\varepsilon = 1.479$. The strongest lines of the X-ray diffraction pattern are at d-spacings (Å): 9.57 (vs) (100), 5.53 (s) (110), 3.83 (s) (112), 3.56 (ms) (202), 2.74 (ms) (302). Carraraite is a new member of the ettringite-thaumasite group, which is characterized by columns of composition $[Ca_3Ge(OH)_6 \cdot 12H_2O]^{4+}$ running along **c** and interconnected through hydrogen bonding to $(SO_4)^{2-}$ and $(CO_3)^{2-}$ groups.

Zaccagnaite, $Zn_4Al_2(OH)_{12}(CO_3) \cdot 3H_2O$, occurs as minute hexagonal crystals, elongated parallel to [001]. The cell dimensions are $a = 3.0725$ (3), $c = 15.114$ (4) Å and the space group is $P6_3/mmc$. The crystals are always covered by a thin crust of fraipontite. The strongest lines of the X-ray diffraction pattern are at d-spacings (Å): 7.51 (vs) (002), 3.794 (m) (004), 1.542 (ms) (108), 1.539 (ms) (110). Zaccagnaite is a new member of the hydrotalcite-manasseite family; its structure is characterized by a regular alternation of brucite-like layers with composition $(Zn_{2/3}Al_{1/3})(OH)_2$ and an interlayer composed of carbonate groups and water molecules.

INTRODUCTION

Carrara marble is a very pure metamorphic limestone, Liassic in age, that outcrops in the Apuan Alps, a tertiary mountain chain in the north of Tuscany, Italy. It has been quarried in the Apuan Alps for more than 2000 years and has been appreciated worldwide since the Roman conquest of the Apuan territories. "The popularity of Carrara marble was due in part to the wide range of varieties available (statuary, flowered, veined, brecciated, bardiglio, etc.), to the constancy of its quality, scarcity of defects, large size of single blocks that could be extracted, excellent physical and mechanical characteristics, and long-lasting strength and beauty. The Romans were masters at selecting the finest and more durable marbles. Many Roman monuments still preserve their delicate bas-reliefs while the marble decorations on medieval cathedrals a thousands years younger show major deterioration" (Franzini et al. 1987).

From a mineralogical point of view Carrara marble is also known for the numerous fine and rare minerals that occur within small cavities hosted by typical metamorphic structures, such as boudins or tension gashes. The cavities lie within definite levels, generally dolomitic horizons that underwent brittle deformation during Tertiary metamorphism (Orlandi and Franzini 1994). Metamorphic solutions circulating within the cavities were responsible for a small and sporadic mineralization characterized by many rare mineralogical species, present as minute and well-defined crystals. Approximately 100 mineral species have been identified for this occurrence. The most common are quartz, gypsum, fluorite, and dolomite but most of the species are sulfides and sulfosalts; among these colusite, sulvanite, sphalerite, and wurtzite are well known to mineral collectors worldwide for the beauty and perfection of the crystals and for epitaxial overgrowths (Orlandi 2000). The minerals were deposited over a range of temperatures from about 350 °C to room temperature.

In this paper we present chemical, physical, crystallographic, and structural data for two new mineral species, carraraite and zaccagnaite. These minerals crystallized within the cavities of the marble during a late stage of deposition and were formed through hydrothermal alteration of sulfides and sulfosalts in the presence of aluminum-rich hydrothermal fluids (crystals of nordstrandite and dawsonite frequently occur within the cavities).

The minerals and their names were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material of the two new species has been deposited at Museo di Storia Naturale e del Territorio, University of Pisa, Via Roma 103, I-56011 Calci (PI), Italy.

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OCCURRENCE AND PHYSICAL PROPERTIES

Carraraite was found at the Gioia quarry in the Colonnata valley, where it occurs in calcite vein cavities within the marble, together with azurite and volborthite, as hydrothermal alteration product of copper-vanadium sulfides such as sulvanite and colusite; in fact colusite crystals with germanium contents of 1.3 wt% were found in the Carrara area (Orlandi et al. 1981). Carraraite occurs as milky or transparent, vitreous submillimetric hexagonal crystals, prismatic {100}, tabular {001}; the largest are 0.05 to 0.06 mm across with a thickness of 0.02 mm (Fig. 1). No cleavage was observed. Optically the mineral is (λ = 5890 Å) uniaxial (–), ω = 1.509 (1), ε = 1.479 (1). On the basis of the unit-cell contents and the calculated density (see below) Gladstone-Dale calculations (Mandarino 1976, 1979) gave K_p = 0.2514 and K_c = 0.2520, indicating superior compatibility. The name is from the Carrara region.

Zaccagnaite was found at the Calagio quarry in the Colonnata valley where it occurs in cavities in calcite veins, associated with hydrozincite and fraipontite. It formed as an alteration product of sphalerite by reaction with aluminum-rich hydrothermal fluids. Zaccagnaite occurs as minute hexagonal crystals, elongated on [001], less than 0.2 mm long and 0.02 to 0.03 mm thick, with perfect (001) cleavage. The mineral is transparent to milky, with subvitreous lustre and white color and streak. The crystals are always covered by a thin crust of another phase which gives them a very peculiar aspect (Fig. 2), resembling that of the so-called "Brugola" screws. Optical properties could not be measured due to the very small dimensions of the crystals, their fragility, and the presence of the encrusting material. The name is in memory of the late scholar Domenico Zaccagna (Carrara 1851-Rome 1940). Zaccagna published the first geological map of the Apuan Alps and was also a competent collector of minerals from the Carrara marble. His collection is still preserved in the "Museo di Storia Naturale e del Territorio" of the University of Pisa.
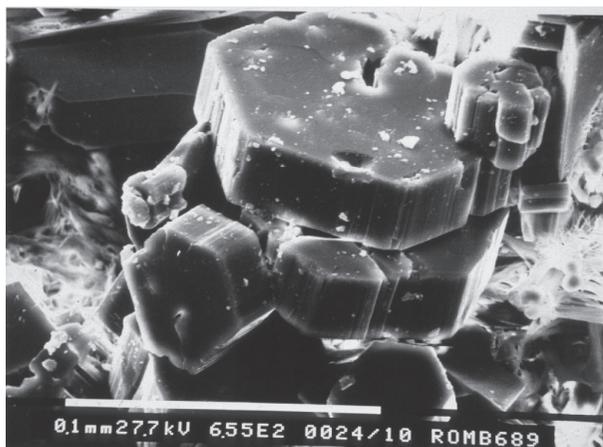

FIGURE 1. SEM image of carraraite crystals.

FIGURE 2. SEM image of zaccagnaite crystals, covered by a thin crust of fraipontite.

X-RAY CRYSTALLOGRAPHY AND CHEMICAL DATA

Carraraite

Rotation and Weissenberg photographs showed that carraraite has space group $P6_3$ or $P6_3/m$, with cell dimensions a ~ 11.0, c ~ 10.6 Å. Powder diffraction data collected with a Gandolfi camera (diameter 114.6 mm, CuKα radiation) gave a pattern very similar to that of thaumasite (Knill 1960; Table 1). Preliminary qualitative chemical analyses were carried out by means of an energy-dispersive (ED) spectrometer attached to a Philips 515 scanning electron microscope (SEM), working at an accelerating voltage of 20 kV and a beam current of 10 nA. The analyses indicated the presence of Ca, Ge, and S, and no other element with atomic number higher than 11. These preliminary data strongly supported the hypothesis that the mineral under investigation was a new member of the ettringite group, closely related to thaumasite and containing Ge. The crystal chemical formula of thaumasite $Ca_3Si(OH)_6(SO_4)(CO_3)\cdot12H_2O$ was used as a guide for interpreting and discussing the results of the chemical and structural studies.

Due to the small quantity of the material at our disposal we had to rely on microprobe data alone. However, the assumed relationship with thaumasite pointed to a high water content and possible decomposition under the electron beam. In fact the results of the preliminary runs, carried out on a ARL-SEMQ apparatus at operating conditions of 15 kV, 10 nA, with a defocused beam of 20 μm in diameter, indicated that the oxide values were not reliable (the sum of CaO, SO_3, and GeO_2 gave totals from 63 to 83 wt%) and that the atomic ratios were not fully acceptable. We therefore carried out additional microprobe analyses (standards: gypsum for Ca and S, metallic germanium for Ge) on crystals of both carraraite and schaurteite, $Ca_3Ge(OH)_6(SO_4)_2\cdot3H_2O$, which has a structure related to that of thaumasite, although with a lower water content. The analytical results are reported in Table 2. The measured cationic ratios S:Ca:Ge in schaurteite are 1.70:3:0.82, whereas the actual ratios are 2:3:1. This suggests that the cationic ratios for carraraite are S:Ca:Ge = 1.12:3:1. The missing anionic coun-

TABLE 1. X-ray powder diffraction pattern (Gandolfi camera, 114.6 mm diameter, Cu$K\alpha$ radiation) of carraraite, compared with the pattern thaumasite (Knill 1960)

thaumasite			carraraite			
d_{obs}(Å)	Intensity	hkl	hkl	Intensity	d_{calc}(Å)	d_{obs}(Å)
9.56	100	100	100	vs	9.605	9.57
7.04	2	101	101	w	7.121	7.11
5.51	40	110	110	s	5.545	5.53
4.88	5	111	111	w	4.915	4.90
4.76	5	200				
4.56	6	102	102	vw	4.645	4.66
4.34	4	201	201	vw	4.375	4.41
3.78	16	112	112	s	3.834	3.83
3.61	1	210				
3.51	6	202	202	ms	3.561	3.56
3.41	20	211	211,212	m	3.435	3.44
3.18	16	300	300	mw	3.202	3.20
3.04	<1	301				
2.935	<1	113	113	w	2.996	2.99
2.755	2	220				
2.713	14	302	302	ms	2.741	2.74
2.649	4	310	310,130	w	2.664	2.66
2.599	<1	004				
2.565	10	311	311,131	vw	2.584	2.58
2.499	10	213	213,123	m	2.534	2.53
			222	vw	2.457	2.46
2.357	4	312	312,132	m	2.381	2.38
2.282	<1	204				
2.191	6	320				
2.155	13	223	223	m	2.182	2.18
			321,231	mw	2.157	2.16
2.106	5	313	313,133	m	2.128	2.13
2.086	2	410	410,140	vw	2.096	2.095
2.045	4	411				
2.019	3	322	322,232	mw	2.035	2.036
1.934	3	412	403	vw	1.987	1.985
			115		1.982	
1.911	10	500	500	mw	1.921	1.919
			314,134	w	1.880	1.881
1.809	3	331	331	vw	1.821	1.817
1.778	3	421	421,241	vw	1.789	1.782
1.733	3	332	332	vw	1.746	1.744
1.692	2	511	510,150	vw	1.725	1.718
			422,242		1.717	
			116	w	1.685	1.686
			315,135	vw	1.660	1.661
			206		1.660	
1.626	4	414	414,144	w	1.645	1.643
1.592	4	600	600	vw	1.596	1.601

Notes: The d_{calc} values of carraraite have been obtained on the basis of the parameters a = 11.056, c = 10.629 Å. For carraraite the indices have been assigned taking into account also the values of the intensities collected for the structural study. The intensities are given as follows: vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak. Both *hkl* and *khl* indices, corresponding to non equivalent reflections with the same *d* value, are explicitly indicated.

TABLE 2. Results of the electron microprobe analyses carried out on crystals of carraraite and schaurteite

carraraite

Oxide	wt%							Average
SO$_3$	17.02	17.63	15.86	12.97	15.63	17.11	17.11	16.19
CaO	37.58	37.45	34.23	30.82	37.10	36.43	36.32	35.70
GeO$_2$	18.85	18.78	17.38	16.06	18.64	19.01	18.32	18.15
Total	73.45	73.86	67.47	59.85	71.37	72.55	71.44	70.04

schaurteite

Oxide	wt%						Average
SO$_3$	24.25	23.83	23.84	22.45	24.56	24.36	23.88
CaO	30.42	30.21	29.21	27.60	29.81	29.87	29.52
GeO$_2$	15.46	14.66	15.54	13.47	15.62	15.61	15.06
Total	70.13	68.71	68.60	63.52	69.98	69.84	68.46

terpart should be provided by $(CO_3)^{2-}$ groups as suggested by the chemical formula of thaumasite. This hypothesis was confirmed by a new qualitative analysis carried out by means of an ED DX4-I spectrometer attached to a Philips XL30 SEM, working at an accelerating voltage of 20 kV and beam current of 10 nA, which clearly showed a C peak. The C content was also semiquantitatively evaluated through an ion probe analysis (data collected on a polished, uncoated sample), yielding a C/Ca atomic ratio of 0.21(2).

Zaccagnaite

The single-crystal X-ray diffraction study, carried out with preliminary rotation, Weissenberg and precession photographs, followed by data collection with a Siemens *P*4 four-circle diffractometer, showed that the crystals are hexagonal, space group $P6_3/mmc$ (or $P6_3mc$, $P\bar{6}2c$), with unit-cell dimensions a = 3.0725 (3), c = 15.114 (4) Å.

Due to the encrusting material the preliminary qualitative chemical analyses, carried out by means of an ED spectrometer attached to a Philips 515 SEM, were highly misleading, in that they indicated the presence of Si as well as Al and Zn. Successive microprobe analyses showed that the Si peak is due to the encrusting material. Microprobe analyses were carried out with an ARL-SEMQ instrument, with operating conditions 20 kV, 10 nA, beam diameter 5 µm (standards were sphalerite for Zn, chalcopyrite for Cu, and spessartine for Si and Al). Due to the presence of weakly bonded interlayers with carbonate groups and water molecules, some volatile loss was expected, but this turned out to be minor. The analytical results are given in Table 3. The presence of carbonate groups was confirmed by means of an ED DX4-I spectrometer attached to a Philips XL30 SEM, working at accelerating voltage of 20 kV and beam current of 10 nA, which clearly showed the presence of the C peak.

The unit-cell parameters and space group $P6_3/mmc$, together with the results of the EMP analyses, suggested a new mineral of the hydrotalcite-manasseite family. The crystal chemistry and structural features of the natural phases in this group (Table 4) were discussed by Taylor (1973). In these phases all the structures are based on alternating brucite-like layers and interlayers, composed of carbonate groups and water molecules; the octahedral sites of the brucite-like layer are occupied by both di- and trivalent cations. The M^{2+}/M^{3+} ratio is generally 3:1, but in the case of hydrotalcite the ratios 2:1 as well as 3:1 have been found. The carbonate content in the interlayer is obviously related to the value of this ratio. The results presented in Table 3 unequivocally point to a (Zn+Cu)/Al ratio of 2:1 as found in some samples of hydrotalcite. Consequently the corresponding crystal chemical formula, on the basis of Zn + Cu + Al = 6,

TABLE 3. Results of the electron microprobe analyses carried out on a crystal of zaccagnaite

Oxide	wt%				Average	Standard
CuO	0.25	0.30	0.19	0.21	0.24	chalcopyrite
ZnO	58.22	55.63	56.27	53.91	56.01	sphalerite
Al$_2$O$_3$	18.25	18.57	18.71	18.22	18.44	spessartine
(SiO$_2$)*	0.00	0.18	0.06	0.13	0.09	spessartine
Total	76.72	74.68	75.22	72.48	74.78	

* The low content of SiO$_2$ is given by the encrusting material.

TABLE 4. Selected natural phases of the hydrotalcite-manasseite group

Composition	3R-polytype $a \approx 3.1$ $c \approx 23.4$ Å $R\overline{3}m$	2H-polytype $a \approx 3.1$ $c \approx 15.6$ Å $P6_3/mmc$
$Mg_{4.5}$ $Al_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	hydrotalcite	manasseite
$Mg_{4.0}$ $Al_{2.0}$ $(OH)_{12}$ $(CO_3)_{0.50}$ 3 H_2O	(some specimens have this composition)	
$Mg_{4.5}$ $Fe^{3+}_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	pyroaurite	sjögrenite
$Mg_{4.5}$ $Cr_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	stichtite	barbertonite
$Mg_{4.5}$ $Mn^{3+}_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	desautelsite	———
$Ni_{4.5}$ $Fe^{3+}_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	reevesite	———
$Ni_{4.5}$ $Al_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	takovite	———
$Ni_{4.5}$ $Co^{3+}_{1.5}$ $(OH)_{12}$ $(CO_3)_{0.75}$ 3 H_2O	comblainite	———
$(Mg,Fe^{2+})_{4.0}$ $Al_{2.0}$ $(OH)_{12}$ (Cl_2,CO_3) 2 H_2O	———	chlormagaluminite
$Mg_{4.5}$ $Fe^{3+}_{1.5}$ $(OH)_{12}$ $Cl_{1.5}$ 3 H_2O	iowaite	———
$Zn_{4.0}$ $Al_{2.0}$ $(OH)_{12}$ $(CO_3)_{0.50}$ 3 H_2O	———	zaccagnaite

is $[(Zn_{3.92}Cu_{0.02}Al_{2.06})(OH)_{12}][(CO_3)\cdot 3H_2O]$, or, in simplified formula, $Zn_4Al_2(OH)_{12}(CO_3)\cdot 3H_2O$.

CRYSTAL STRUCTURE OF CARRARAITE

The chemical composition of carraraite was confirmed through a complete structure determination. The crystals appeared generally not suitable for single-crystal study because most are composed of several slightly rotated or misaligned individuals. After testing various specimens with rotation and Weissenberg photographs, a fragment composed of two slightly misaligned individuals, with dimensions, $0.12 \times 0.10 \times 0.015$ mm^3, was selected for single-crystal X-ray diffraction study. Precise cell parameters were determined by least-squares refinement, using 15 reflections in the 2θ range $15–21°$, collected on a Siemens $P4$ four circle diffractometer operating at 50 kV and 40 mA with graphite monochromatized Mo$K\alpha$ radiation. The refined cell parameters are: $a = 11.056$ (3), $c = 10.629$ (6) Å. The data collection was performed up to $2\theta = 50°$, in ω-scan mode, scan width $2°$ in θ, scan speed $1.5°$/min.

The structure refinement was carried out using the SHELX-97 (Sheldrick 1997) program, in space group $P6_3/m$ using 329 independent reflections with $F_o > 5 \sigma(F_o)$, with starting parameters as derived from the structural results of Edge and Taylor (1971) for thaumasite. No absorption correction was applied. We first introduced $(SO_4)^{2-}$ anions with full occupancy, but in the first refinement cycles the values of the thermal parameters indicated that, whereas the site of the basal oxygen atom OB was fully occupied, the sulfur and apical oxygen sites S and OA were incompletely filled. The results suggested a $(SO_4)^{2-}$–$(CO_3)^{2-}$ substitution, with the C atom in the centre of the basal triangular face. The chemical data suggested a S:C ratio higher than 1 and in subsequent refinement cycles the occupancies p of the S, C and OA sites were refined with the constraints: $p(S) = p(OA) = 1 - p(C)$. The final values were $p(S) = 0.54$ and $p(C) = 0.46$.

Due to the close similarity with the structure of thaumasite (Edge and Taylor 1971; Zemann and Zobetz 1981; Effenberger et al. 1983), the H atoms were placed in positions corresponding to those reported by Edge and Taylor (1971) for thaumasite and the refinement was completed with fixed isotropic thermal parameters for the H atoms. The final R_1 [$R_1 = (\Sigma \mid |F_o| - |F_c| \mid)/\Sigma|F_o|$] value was 0.094, quite acceptable considering the bad quality of the crystal. We also tried to refine the structure in the acentric space group $P6_3$, ordering the $(SO_4)^{2-}$ and $(CO_3)^{2-}$ groups as in thaumasite (Effenberger et al. 1983) but the results were poor. The final atomic coordinates and isotropic thermal parameters are given in Table 5.

The crystal chemical formula obtained from the structural analysis is $Ca_3Ge(OH)_6(SO_4)_{1.08}(CO_3)_{0.92}\cdot 12H_2O$, in keeping with the chemical data; with $Z = 2$, the calculated density is 1.979 g/cm^3.

Description of the crystal structure

The crystal structure as seen along **c** is shown in Figure 3. It is composed of columns of composition $[Ca_3Ge(OH)_6\cdot 12H_2O]^{4+}$ parallel to **c** and interconnected through hydrogen bonding to $(SO_4)^{2-}$ and $(CO_3)^{2-}$ groups placed along the threefold axes at $z \sim 0$ and $z \sim 0.5$.

The structure of a single column, which is the common structural feature in the thaumasite-ettringite family, is shown in

TABLE 5. Atomic coordinates, occupancy (p) and thermal parameters in carraraite

Atom	Wyckoff notation	x	y	z	p	U_{iso} or U_{eq}
Ca	6(h)	0.1976 (6)	−0.0122 (7)	1/4	1.0	0.023 (2)
Ge	2(b)	0	0	0	1.0	0.018 (2)
O1	6(h)	0.3985 (25)	0.2348 (25)	1/4	1.0	0.041 (6)
O2	6(h)	0.2593 (31)	0.4054 (26)	1/4	1.0	0.037 (7)
O3	12(i)	0.0153 (20)	0.3461 (20)	0.0705 (19)	1.0	0.044 (5)
O4	12(i)	0.1349 (16)	0.1269 (16)	0.1110 (13)	1.0	0.023 (4)
S	4(f)	1/3	2/3	−0.0110 (21)	0.54 (6)	0.026 (7)
C	4(f)	1/3	2/3	0.0379 (15)	0.46 (6)	0.033 (12)
OA	4(f)	1/3	2/3	−0.1473 (45)	0.54 (6)	0.031 (14)
OB	12(i)	0.1960 (16)	0.6224 (18)	0.0379 (15)	1.0	0.039 (5)
H11	6(h)	0.326 (29)	0.253 (28)	1/4	1.0	0.03
H12	6(h)	0.503 (27)	0.229 (26)	1/4	1.0	0.03
H2	12(i)	0.276 (20)	0.424 (19)	0.178 (15)	1.0	0.03
H31	12(i)	−0.068 (21)	0.292 (19)	0.055 (16)	1.0	0.03
H32	12(i)	0.108 (20)	0.465 (20)	0.070 (15)	1.0	0.03
H4	12(i)	0.191 (22)	0.179 (22)	0.084 (17)	1.0	0.03

Notes: The e.s.d. are given in parentheses; where they are absent, the corresponding parameter has been kept fixed in the refinement.
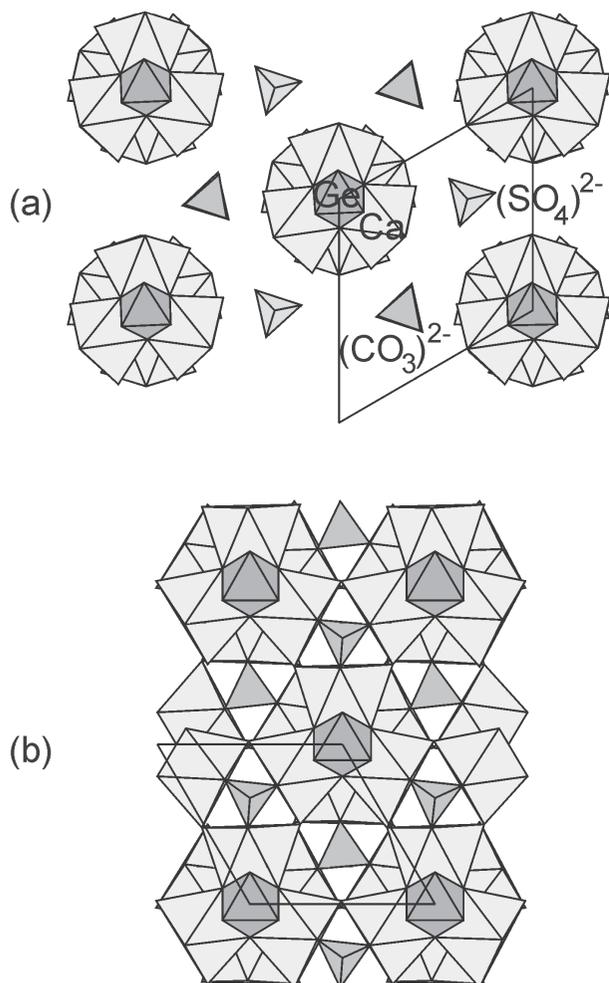
FIGURE 3. (a) Crystal structure of carraraite, as seen along c. The sulfate and carbonate groups are represented as orderly distributed in space group $P6_3$. Actually the distribution is disordered, with sulfate groups pointing up and down, in space group $P6_3/m$. Germanium octahedra are located at $z = 0$ and 1/2, calcium polyhedra are located at $z = 1/4$ and 3/4. (b) The structure type of fleischerite (from Otto 1975) and schaurteite as seen along c.

FIGURE 4. Structure of the columns $[Ca_3Ge(OH)_6 \cdot 12H_2O]^{4+}$ running along c in carraraite. Small circles correspond to cations (black for Ge and grey for Ca), whereas large circles correspond to hydroxyl anions (pale grey) and water molecules (dark grey).

Figure 4. $Ge(OH)_6$ octahedra alternate with groups of three Ca atoms in a square antiprismatic coordination; each Ca atom is linked to four hydroxyl groups of $Ge(OH)_6$ octahedra above and below it; these four OH⁻ groups form a square toward the axis of the column, and the opposite square is made up of water molecules. The infinite column, which displays "rod" symmetry $p\bar{6}2m$, has a nearly cylindrical shape with an external surface entirely composed of water molecules. Similar columns are present in the structure of schaurteite, $Ca_3Ge(OH)_6$ $(SO_4)_2 \cdot 3H_2O$, which is isostructural with fleischerite, $Pb_3Ge(OH)_6(SO_4)_2 \cdot 3H_2O$, and despujolsite, $Ca_3Mn(OH)_6$ $(SO_4)_2 \cdot 3H_2O$. In schaurteite, fleischerite, and despujolsite the columns are more tightly bound through the basal oxygen atoms of the $(SO_4)^{2-}$ groups and through shared water molecules (Fig. 3b).

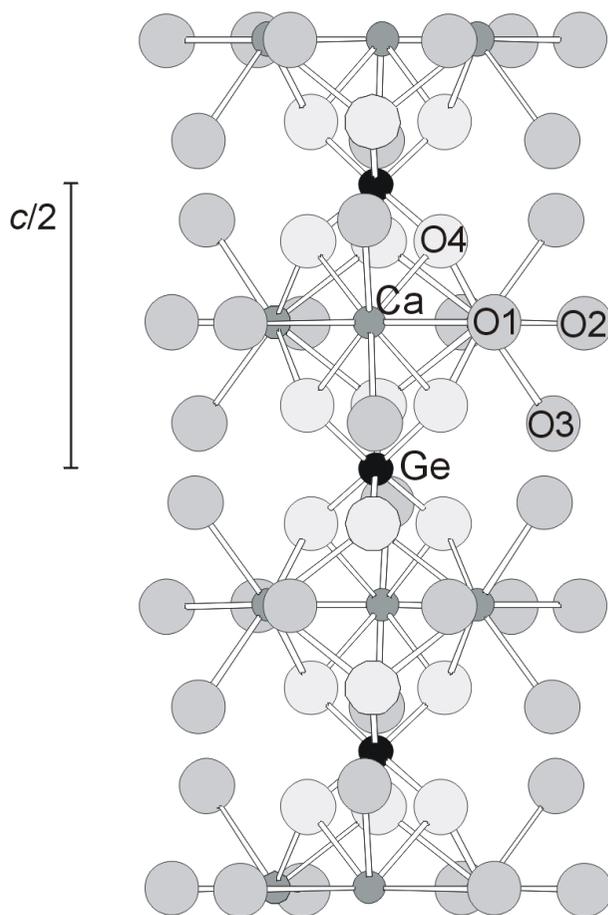## Bond distances and polyhedral coordination

Selected bond distances are given in Table 6 and are compared with the corresponding distances in jouravskite. Ge^{4+} is octahedrally coordinated by six crystallographically equivalent OH⁻ groups, with Ge-OH distances of 1.869(14) Å, comparable to the Ge-OH distance of 1.900(20) Å reported by Otto (1975) for the crystal structure of fleischerite. A similar bond distance has been found in jouravskite $Ca_3Mn(OH)_6$ $(SO_4)(CO_3) \cdot 12H_2O$ (Granger and Protas 1969) where the average Mn^{4+}-OH bond distance is 1.88 Å. The Ca-O bond distances in the square antiprism range between 2.42 and 2.52 Å; the corresponding ranges are 2.40–2.51 Å in thaumasite (Effenberger et al. 1983) and 2.39–2.55 Å in jouravskite (Granger and Protas 1969). The sulfate and carbonate groups give acceptable distances, comparable with those found in thaumasite and jouravskite.

As the corresponding polyhedra in carraraite and jouravskite have similar dimensions, the difference in the cell volumes, 1125.2 Å³ for carraraite and 1113.9 Å³ for jouravskite is most probably dependent on the different $(SO_4)^{2-}/(CO_3)^{2-}$ ratios (1 in

TABLE 6. Selected bond distances (in Å) in carraraite (e.s.d. in parentheses), as compared with the corresponding distances in jouravskite

		carraraite $Ca_3Ge(OH)_6(SO_4)_{1.08}(CO_3)_{0.92}\cdot12H_2O$		jouravskite $Ca_3Mn(OH)_6(SO_4)(CO_3)\cdot12H_2O$	
Ge-OH	[O4]	1.869 (14) (×6)	Mn-OH	1.83	
			-OH	1.93	
Ca-OH	[O4]	2.470 (17) (×2)	Ca-OH	2.46	
			-OH	2.49	
Ca-OH	[O4']	2.471 (18) (×2)	-OH	2.47	
			-OH	2.50	
Ca-H$_2$O	[O3]	2.421 (19) (×2)	-H$_2$O	2.39	
			-H$_2$O	2.47	
Ca-H$_2$O	[O2]	2.495 (29)	-H$_2$O	2.55	
Ca-H$_2$O	[O1]	2.516 (23)	-H$_2$O	2.46	
S-O	[OB]	1.439 (17) (×3)	S-O	1.41 (×3)	
-O	[OA]	1.448 (49)	-O	1.55	
C-O	[OB]	1.342 (16) (×3)	C-O	1.30	

jouravskite and 1.17 in carraraite). This also explains why only the *c* parameter is different (10.629 Å in carraraite and 10.540 Å in jouravskite), whereas the *a* parameters are similar, because of the similar lateral dimensions of the $(SO_4)^{2-}$ and $(CO_3)^{2-}$ groups. The high $(SO_4)^{2-}/(CO_3)^{2-}$ ratio may explain the space group symmetry $P6_3/m$, corresponding to a disordered distribution of $(SO_4)^{2-}$ and $(CO_3)^{2-}$ groups, relative to space group $P6_3$ in thaumasite and jouravskite. In fact the ordered alternation of $(SO_4)^{2-}$ and $(CO_3)^{2-}$ anions, corresponding to space group $P6_3$, may be destroyed by the insertion of additional $(SO_4)^{2-}$ groups.

Bond valence balance and hydrogen bond scheme

A reliable hydrogen bonding scheme was obtained by examining O···O distances less than or equal to 3.00 Å and connecting oxygen atoms not bonded to the same cation. The scheme is given in Table 7 with indication of the donor (D) or acceptor (A) character of the oxygen atoms; the bond strengths have been calculated according to Ferraris and Ivaldi (1988).

The chemical character (water molecules or hydroxyl anions) of the oxygen atoms O1 to O4 can be confirmed by calculating for each of them the corresponding bond valence sum (Brese and O'Keeffe 1991), with hydrogen bond contributions negative for donor and positive for acceptor oxygen atoms. The results reported in Table 7 indicate that O4 is an hydroxyl anion (valence bond sum about 1) and O1 to O3 are water molecules (valence bond sum about 0).

TABLE 7. Hydrogen bonds with D··A distances ≤3.0 Å and bond valence sums for O1 to O4 atoms in carraraite

D-H	A	d(D··A)	symmetry relationships	bond strength
O1-H11	O2	2.97		0.14
O1-H12	OA^i	2.82	[i = −x+1, −y+1, z+1/2]	0.18
O2-H2	OB^{ii}	2.80	[ii = −y+1, x−y+1, z]	0.18
O3-H31	OB^{iii}	2.78	[iii = −x, −y+1, −z]	0.19
O3-H32	OB	2.71		0.22
O4-H4	O3^{iv}	3.00	[iv = y, −x+y, −z]	0.13

Bond valence sums for O1 to O4 oxygen atoms

	Ca	Ge	Hydrogen bond contributions	sum
O1	0.23	−0.14	−0.18	−0.09
O2	0.24	+0.14	−0.18 x 2	0.02
O3	0.29	−0.22	−0.19	−0.12
O4	0.25 x 2	0.72	−0.13	1.09

STRUCTURAL STUDY OF ZACCAGNAITE

The 2:1 metal ratio and the crystal chemical formula of zaccagnaite were confirmed with a structure refinement carried out with the SHELX-97 (Sheldrick 1997) program, in space group $P6_3/mmc$ using 89 independent reflections with $F_o > 4\sigma(F_o)$ collected with a Siemens $P4$ four-circle diffractometer (operating conditions: 50 kV and 40 mA; graphite monochromatized Mo$K\alpha$ radiation; $2\theta_{max} = 50°$, ω-scan mode, scan speed 1.5°/min). No absorption correction was applied. The starting parameters were derived from the structural results of Ingram and Taylor (1967) for sjögrenite and the refinement was carried out with anisotropic thermal parameters for the metal and oxygen atoms of the brucite-like layer and isotropic thermal parameters for the atoms of the interlayer, O2 and C; both are characterized by partial occupancies, 1/3 and 1/6, respectively. The final R_1 value was 0.037. The atomic coordinates are given in Table 8.

The crystal structure of zaccagnaite is shown in Figure 5 which shows alternation of brucite-like layers and interlayers, interconnected through hydrogen bonding. In Figure 6a the structure is projected down **c** with the brucite-like layer represented by Zn and Al polyhedra; the (Zn,Al)-OH bond distance of 2.031 (3) Å is in keeping with the assumed site occupancy $Zn_{2/3}Al_{1/3}$; the interlayer oxygen atoms are distributed over three symmetry related positions with a geometry which permits not only the distribution of water molecules but also the formation of carbonate groups with C-O bond distances of 1.28 (2) Å: water molecules and carbonate groups (their number is related to the number of trivalent cations in the brucite-like layer) are statistically distributed in the interlayer.

Cation ordering and diffuse streaks

All the zaccagnaite crystals showed, besides sharp reflections corresponding to the *a* and *c* parameters (*a* = 3.07, *c* = 15.11 Å), diffuse streaks parallel to **c*** at positions defining a supercell with $a' = \sqrt{3} a$, which suggests that ordering of the metal atoms occurs, according to the model illustrated in Figure 6b; the diffuseness of the reflections indicates that whereas there is perfect two-dimensional long range ordering, the ordering schemes of subsequent brucite-like layers are not related. It is important to note that the two-dimensional ordering and the consequent trebling of the unit cell just described are in keeping with the metal ratio Zn/Al equal to 2:1 obtained from the microprobe analyses and confirmed by the structure refinement.

TABLE 8. Atomic coordinates, occupancy (*p*), and thermal parameters in zaccagnaite

Atom	Wyckoff notation	x	y	z	p	U_{iso} or U_{eq}
M (Zn$_{2/3}$Al$_{1/3}$)	2(a)	0	0	0	1.0	0.011 (1)
O1	4(f)	1/3	2/3	0.0655 (4)	1.0	0.017 (1)
O2	6(h)	0.241 (3)	−x	1/4	1/3	0.040 (4)
C	2(b)	0	0	1/4	1/6	0.019 (15)
H	4(f)	1/3	2/3	0.099 (6)	1.0	0.01 (2)

Note: The e.s.d. values are given in parentheses; where they are absent, the corresponding parameter has been kept fixed in the refinement.
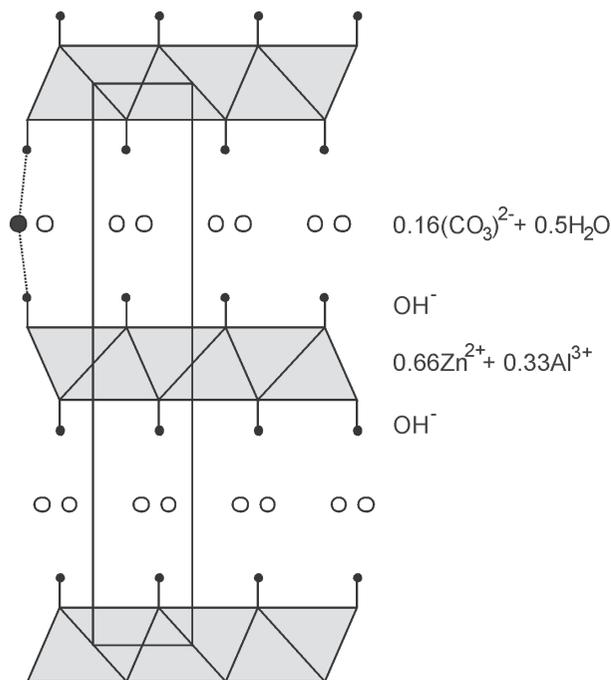
0.16$(CO_3)^{2-}$ + 0.5H_2O

OH^-

0.66Zn^{2+} + 0.33Al^{3+}

OH^-

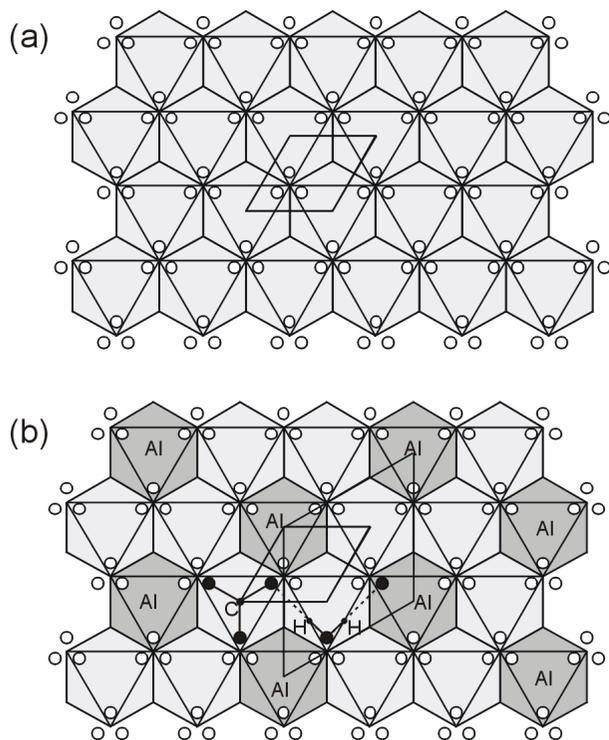**FIGURE 5.** The crystal structure of zaccagnaite represented down a (c vertical).

FIGURE 6. (**a**) The structure of zaccagnaite seen down c, with the brucite-like layer represented in terms of polyhedra and the interlayer oxygen atoms distributed on three symmetry related positions. (**b**) Ordering of the metal atoms in the brucite layer. The supercell (a' = $\sqrt{3}a$) is indicated.

Powder pattern interpretation and indexing

Continuous streaks along **c*** were clearly visible in rotation photographs of zaccagnaite. In the photograph three types of reflections were displayed: (1) sharp spots corresponding to the unit cell with $a = 3.07$, $c = 15.11$ Å; (2) a faint powder pattern of the phase coating the zaccagnaite crystals; (3) continuous streaks which follow the Bernal ξ-constant curves, clearly distinct from the powder pattern mentioned in (2); three such streaks were clearly visible, parallel to **c*** and passing through the following reciprocal lattice points (indices are referred to the cell with $a' = \sqrt{3}\ a$): 100 (d = 4.62 Å), 200 (d = 2.31 Å), 210 (d = 1.75 Å).

In Table 9 the reflections corresponding to the encrusting material are indicated in italics. They appear as wide bands in the Gandolfi pattern and they correspond to powder lines in the aforementioned rotation photograph. Their values and intensities closely correspond to those of the strongest diffractions of a 1M 1:1 trioctahedral layer silicate (Bailey 1969). On the basis of the powder pattern and the chemical content indicated by the SEM-EDS analyses, we suggest that the material corresponds to fraipontite $(Zn,Al)_3(Si,Al)_2O_5(OH)_4$.

The anisotropic thermal parameters of carraraite and zaccagnaite and the list of F_o and F_c for the two structures can be found in Table 10[1].

DISCUSSION

Among the numerous fine and rare minerals occurring within cavities in marble of the Carrara basin, the two minerals described here are the first new species. Carraraite and zaccagnaite present interesting structural arrangements which place them

TABLE 9. X-ray powder pattern of zaccagnaite (Gandolfi camera, diameter 114.6 mm, Fe$K\alpha$ radiation)

hkl	d_{calc} (Å)	d_{obs} (Å)	Int	d_{obs} (Å)	hkl
0 0 2	7.56	7.51	vs		
				7.151	0 0 1
				4.610	0 2 0
0 0 4	3.782	3.794	m		
				3.560	0 0 2
				2.655	2 0 1
1 0 0	2.663	2.65	w		
1 0 2	2.512	2.511	mw		
				2.392	2 0 2
1 0 3	2.355	2.354	vw		
				2.275	2 0 1
1 0 4	2.177	2.175	mw		
				2.020	2 0 3
1 0 5	1.999	2.003	vw		
0 0 8	1.891	1.890	w		
1 0 6	1.831	1.830	mw		
				1.666	2 0 4
1 0 8	1.542	1.542	ms		
1 1 0	1.537	1.539	ms		

Notes: Intensities are given as follows: vs = very strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak. The reflections corresponding to fraipontite are given in italics.

TABLE 11. Natural phases of the thaumasite-ettringite group

Name	Composition	S. G.	a	c	ω	ε
thaumasite*	$[Ca_6Si_2(OH)_{12}.24H_2O][(SO_4)_2(CO_3)_2]$	$P6_3$	11.030	10.396	1.504	1.470
jouravskite†	$[Ca_6(Mn^{4+})_2(OH)_{12}.24H_2O][(SO_4)_2(CO_3)_2]$	$P6_3$	11.047	10.540	1.556	1.540
carraraite‡	$[Ca_6Ge_2(OH)_{12}.24H_2O][(SO_4)_{2.16}(CO_3)_{1.84}]$	$P6_3/m$	11.056	10.629	1.509	1.479
ettringite§	$[Ca_6Al_2(OH)_{12}.24H_2O][(SO_4)_3.2H_2O]$	$P31c$	11.23	21.44	1.466	1.462
bentorite‖	$[Ca_6(Cr,Al)_2(OH)_{12}.24H_2O][(SO_4)_3.2H_2O]$	——	22.35	21.41	1.478	1.484
sturmanite#	$[Ca_6(Fe^{3+},Al)_2(OH)_{12}.24H_2O]\{(SO_4)_2[B(OH)_4].2H_2O\}$	$P31c$	11.16	21.79	1.500	1.505
charlesite**	$[Ca_6(Al,Si)_2(OH)_{12}.24H_2O]\{(SO_4)_2[B(OH)_4].2H_2O\}$	$P31c$	11.16	21.21	1.492	1.475

Notes: Name, crystal chemical formula, space group symmetry, unit-cell parameters (in Å) and refraction indices of the various natural phases in thaumasite-ettringite group.
* Cell parameters from Effenberger et al. (1983), refraction indices from Edge and Taylor (1971).
† Cell parameters calculated through least-squares refinement from the powder data given by Gaudefroy and Permingeat (1965), refraction indices from Gaudefroy and Permingeat (1965).
‡ This paper.
§ Cell parameters from Moore and Taylor (1970), refractive indices from Bannister (1936).
‖ Gross (1980).
\# Peacor et al. (1983).
** Dunn et al. (1983).

in two distinct groups of minerals, the thaumasite-ettringite and the hydrotalcite-manasseite groups, respectively. The groups were discussed by Taylor (1973) in his Hallimond lecture, where the common structural features of the various natural and synthetic phases were presented. At that time only three natural phases were known in the first group: thaumasite, ettringite, and jouravskite. Since then bentorite (Gross 1980), sturmanite (Peacor et al. 1983), charlesite (Dunn et al. 1983), and now carraraite have been discovered in nature and an updated list is given in Table 11. The crystal chemical formulas given in Table 11 present, in the first part, the composition of the structural columns running along **c** and, in the second part, the anionic groups and water molecules placed between the columns. Two distinct subgroups exist, one with tetravalent cations, the other with trivalent cations in octahedral coordination within the columns; as a consequence four divalent anionic groups—tetrahedral $(SO_4)^{2-}$ and trigonal $(CO_3)^{0-}$—are present in the minerals of the first subgroup, whereas only three anionic groups—tetrahedral $(SO_4)^{2-}$ and $[B(OH)_4]^{2-}$—are present in the minerals of the second subgroup. The high birefringence, negative optical character, and the relatively short c parameter support the presence of trigonal carbonate groups, with atomic plane normal to the **c** axis, in the structures of thaumasite, jouravskite, and carraraite; as regards the minerals of the second subgroup, the optical and metrical features suggest that in charlesite, which contains a substantial amount of Si substituting for Al in octahedral coordination, at least some of the B may be present in trigonal coordination, with the atomic plane normal to the **c** axis.

In his lecture Taylor (1973) not only presented the main structural features of the phases in the hydrotalcite-manasseite group (he called it the "pyroaurite-sjögrenite group") but also discussed the evidence for cation ordering and segregation into regions of different chemical composition. In particular he reported the results of studies carried out on a series of hydrotalcites of differing chemical composition by Gastuche et al. (1967), who noted the occurrence of an X-ray powder reflection that could be attributed to a superlattice with an a-axial length $\sqrt{3}$ times the basic value of about 3.1 Å. Taylor also reported on his own study (Taylor 1969) where he found superlattice reflections in crystals of pyroaurite and sjögrenite, corresponding to a-axial lengths of both $\sqrt{3}$ and $\sqrt{13}$ times the

basic value, the first probably indicating "the existence of regions in which the Mg and Fe are ordered and in the ratio 2:1" (Taylor 1973). It is therefore understandable that in zaccagnaite, which has an M^{2+}/M^{3+} ratio of 2:1, a substantial ordering occurs, corresponding to a supercell with $a = 5.322$ Å. The long range ordering in the brucite sheet is likely compatible with various ordering schemes of carbonate groups and water molecules in the interlayer; the absence of correlations between the ordering in subsequent brucite layers prevents the possibility of long range ordering in the **c** direction. It seems interesting to recall that Arakcheeva et al. (1996) recently found evidence for substantial ordering in a mineral from the Jacupiranga alkaline-ultrabasic carbonatite massif (Sao Paulo, Brasil) with composition $Mg_4Al_2(OH)_{12}(CO_3)\cdot3H_2O$. This mineral is a member of the hydrotalcite-manasseite group with Mg:Al ratio 2:1, space group symmetry $P\bar{6}2m$, unit-cell dimensions $a = 5.283$, $c = 15.150$ Å. They found a perfect ordering both in the brucite layers and in the interlayers where sheets occupied by carbonate groups regularly alternate with sheets occupied by water molecules. It is therefore possible that a similar ordered alternation of carbonate and water sheets occurs also in zaccagnaite.

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