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## A CONTRIBUTION TO THE MINERALOGY OF THE LARDERELLO GEOTHERMAL FIELD. X-RAY CRYSTALLOGRAPHIC STUDIES ON BORATE MINERALS “BECHILITE” AND “LAGONITE” AND CRYSTAL STRUCTURE DETERMINATION OF GINORITE

**Abstract** - *A contribution to the mineralogy of the Larderello geothermal field. X-ray crystallographic studies on borate minerals “bechilite” and “lagonite” and crystal structure determination of ginorite.* This work reports the results of mineralogical studies on some borate minerals from the Larderello geothermal field. XRD patterns of “bechilite” and “lagonite” confirmed they actually are respectively admixtures of sassolite and ammonioborite, and of sassolite with minor santite, gypsum and larderellite. Single crystal structural study of ginorite from the type locality, Sasso Pisano (Castelnuovo val di Cecina, Pisa) confirmed its isotypism with strontioGINORITE. Ginorite is monoclinic, space group  $P2_1/a$ , with unit cell parameters  $a = 12.7673(1) \text{ \AA}$ ,  $b = 14.3112(11)$ ,  $c = 12.7298(9)$ ,  $\beta = 101.055(5)^\circ$ ,  $V = 2282.8(2) \text{ \AA}^3$ . The refinement of its crystal structure converged to  $R_1 = 0.058$  on the basis of 3387 reflections with  $F_o > 4\sigma(F_o)$ . Analogously to strontioGINORITE, ginorite crystal structure can be described in terms of complex “sheets” parallel to (010), made up by borate groups and Ca coordination polyhedra, with interlayer linkage assured by Ca cations and hydrogen bonds. The cell volume contraction of ginorite respect to strontioGINORITE is related to the shrinkage of Ca coordination polyhedra present in the complex Me-borate sheets.

**Key-words** - Larderello, borates, “bechilite”, “lagonite”, ginorite crystal structure.

**Riassunto** - *Contributo alla mineralogia del campo geotermico di Larderello. Studi cristallografici a raggi X dei borati “bechilite” e “lagonite” e determinazione strutturale della ginorite.* Vengono riportati in questo lavoro i risultati degli studi mineralogici condotti su alcuni borati rinvenuti nell’area geotermica di Larderello. Studi in diffrazione da polveri ai raggi-X mostrano come “bechilite” e “lagonite” siano miscele rispettivamente di sassolite e ammonioborite, e di sassolite con minori quantità di santite, gesso e larderellite. La ginorite è monoclinica, gruppo spaziale  $P2_1/a$ , con parametri di cella  $a = 12.7673(1)$ ,  $b = 14.3112(11)$ ,  $c = 12.7298(9) \text{ \AA}$ ,  $\beta = 101.055(5)^\circ$ ,  $V = 2282.8(2) \text{ \AA}^3$ . Il raffinamento strutturale condotto utilizzando un campione dalla sua località-tipo, Sasso Pisano (Castelnuovo Val di Cecina, Pisa), converge ad un fattore di accordo  $R_1 = 0.058$  sulla base di 3387 riflessi con  $F_o > 4\sigma(F_o)$  e conferma l’isostrutturalità fra ginorite e strontioGINORITE. La struttura cristallina della ginorite, come quella della strontioGINORITE, può essere descritta in termini di “strati”, paralleli a (010), composti da poliedri di coordinazione del boro e del calcio. I legami tra stati successivi sono assicurati dai cationi Ca e da legami idrogeno. La contrazione del volume di cella della ginorite rispetto al suo analogo di Sr risulta legata alla contrazione del volume dei poliedri Ca presenti nei complessi strati paralleli a (010).

**Parole-chiave** - Larderello, borati, “bechilite”, “lagonite”, ginorite struttura cristallina.

## INTRODUCTION

The Larderello geothermal field is located in the southernmost part of Pisa province, southern Tuscany. Southern Tuscany is an inner part of the northern Apennines, its geological setting being related to the building of Apennines, due to the continental collision between Corsica-Sardinia block and Adriatic microplates, and to the subsequent extensional tectonic phase acting from early Miocene (Carmignani *et al.*, 1994; Brunet *et al.*, 2000; Molli, 2008).

Magmatism derived from crustal and mantle sources (Dini *et al.*, 2005; Peccerillo, 2003) is coeval with the extensional phase, with the formation of crustal granitoids, generating hydrothermalism and relevant thermal anomalies such that of the Larderello geothermal field, where the heat flow reach  $500 \text{ mW/m}^2$  (Bellani *et al.*, 2004).

A remarkable set of borate minerals was firstly discovered (Tab. 1) in the Larderello “lagoons”, and in the neighbouring locality of Sasso Pisano, associated to other borates such as borax, sassolite, and tinalconite. With the exception of ginorite, all these phases were subsequently object of crystal structural studies. Besides these well characterized species, “bechilite” and “lagonite” are presently considered as admixtures of minerals, and only their early wet chemical and optical studies are available, modern X-ray and chemical data being absent.

A noticeable set of Larderello area borate specimens is presently preserved in the mineralogical collections of the Natural history museum of Pisa University. To contribute to the knowledge of the mineralogy of Larderello geothermal area, X-ray crystallographic studies were undertaken on ginorite, whose crystal structure is still undetermined, and to confirm, on the basis of sound X-ray diffraction studies, the true nature of the uncertain phases “bechilite” and “lagonite”.

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## PREVIOUS STUDIES ON “BECHILITE”, “LAGONITE” AND GINORITE

The existence of calcium borates in the Larderello area was firstly hypothesized by Beudant (1832), who described their occurrence as white incrustations on limestone, without giving for them any quantitative chemical or optical data. Following Beudant's observations Bechi (1853) reports the existence of a mineral with chemical formula  $\text{CaB}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , subsequently named in his honour “bechilite” (Dana, 1868). “Bechilite” was subsequently studied by D'Achiardi (1900, 1932) examining specimens of the mineralogical collections of the Natural History Museum of Pisa University. D'Achiardi (1900) describes “bechilite” as a mixture of sassolite, gypsum and larderellite, whereas in D'Achiardi (1932) “bechilite”, on the basis of optical observations, is described as a mixture of sassolite, larderellite and ammonioborite.

The existence of iron borate (*Borate de Fer*) at Larderello was firstly mentioned by Beudant (1832), and Omalius d'Halloy (1833). The chemical composition of “lagonite” is given by Bechi (1853) as  $\text{B}_2\text{O}_3$  49.5%,  $\text{Fe}_2\text{O}_3$  37.8%,  $\text{H}_2\text{O}$  12.7%. D'Achiardi (1932, 1934) describes “lagonite”, as a mixture of sassolite and “yellow ochre”. After D'Achiardi observations no other studies were subsequently performed on “bechilite” and “lagonite”.

D'Achiardi (1934) discovers ginorite in veins within sandstones at Sasso Pisano, associated to calcite, occurring in stubby fibrous or granular massive powdery

aggregates. In this study, detailed chemical and optical data for the new phase, together with specific gravity and Mohs hardness measurements.

Literature chemical data for ginorite are reported in Tab. 2, recalculated to 100 after the deduction of their insoluble residues.

Chemical formulae for ginorite from Sasso Pisano (mean of the three analyses of Tab. 2) and from the Death Valley, recalculated on the basis of O = 31 are  $\text{Ca}_{2.13}\text{Na}_{0.01}\text{B}_{13.77}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$  and  $(\text{Ca}_{1.94}\text{Sr}_{0.08})_{2.02}\text{B}_{14.02}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$  respectively. Both the two formulae are close to the ideal formula for ginorite,  $\text{Ca}_2\text{B}_{14}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ , with ginorite from Death Valley showing a quite limited substitution of Sr for Ca. After its discovery at Sasso Pisano, ginorite was subsequently found in several localities worldwide, Tincalayu mine, Argentina (Helvaci & Alonso, 2000), Lena-Angara salt Basin, Russia (Garrett, 1998), East Coleman Mine, Inyo Co., California, USA (Pember-ton, 1983). However a detailed description of ginorite is reported only for the Death Valley occurrence (Allen & Kramer, 1957). Strontiojinorite,  $\text{SrCaB}_{14}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$  is the Sr-analogue of ginorite, discovered by Braitsch (1959) within salt beds in Konigshall-Hindenburg mine, Germany.

Ginorite is guessed to be isostructural with strontiojinorite  $\text{CaSrB}_{14}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ , whose structure was solved by Konnert *et al.* (1970) and subsequently refined by Grice (2005) as monoclinic,  $P2_1/a$ ,  $a = 12.8171(4)$ ,  $b = 14.4576(4)$ ,  $c = 12.8008(4)$  Å,  $\beta = 101.327(1)^\circ$ ,  $V = 2325.8(2)$  Å<sup>3</sup>,  $Z = 4$ .

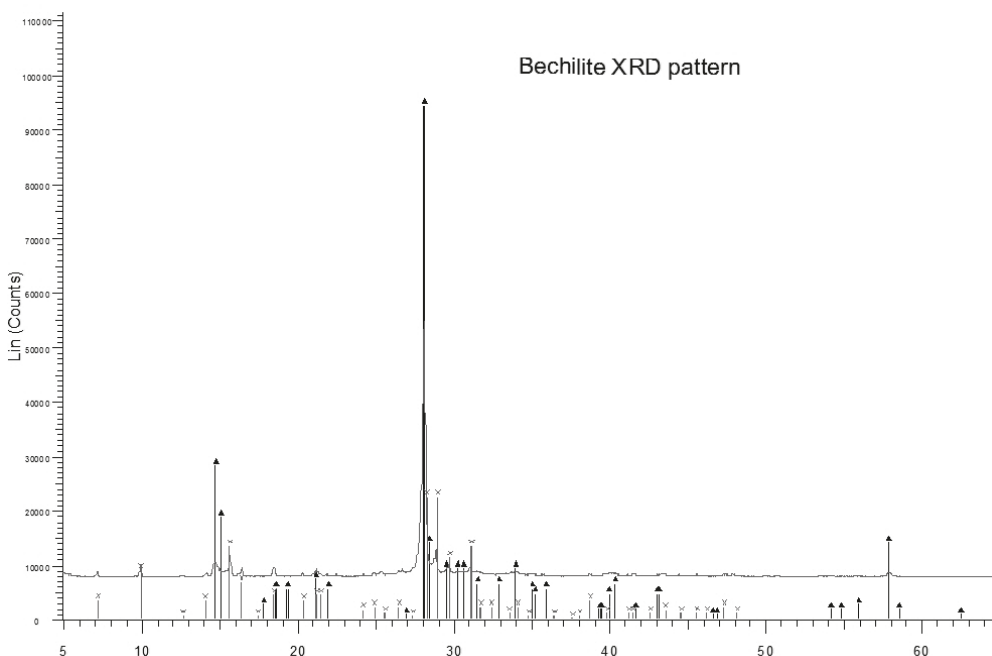


Fig. 1 - XRD pattern of “bechilite” #7137, showing it is a mixture of sassolite (bars with upper triangle) and ammonioborite (bars with upper cross).

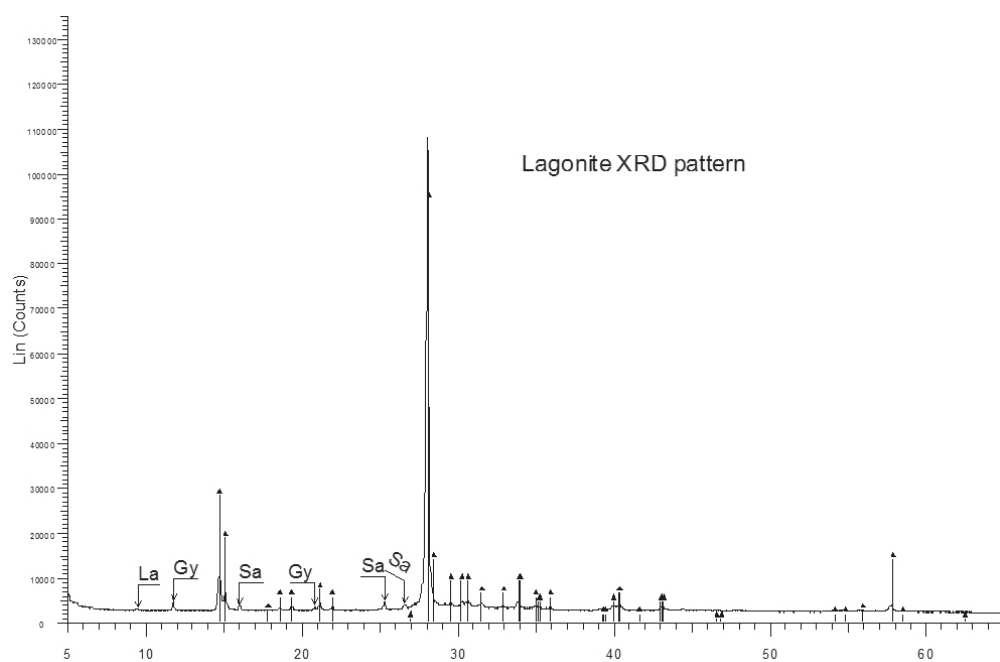


Fig. 2 - XRD pattern of “lagonite” #7138. It can be seen “lagonite” is actually a mixture of major sassolite (bars with upper triangle), with minor gypsum, larderellite and santite, indicated by arrows with labels “Gy”, “La” and “Sa” respectively.

Tab. 1 - Borate mineral species firstly discovered in the Larderello geothermal field.

MINERAL SPECIES	CHEMICAL FORMULA	SPECIES DEFINITION	STRUCTURAL STUDY
Ammonioborite	$(\text{NH}_4)_2[\text{B}_5\text{O}_6(\text{OH})_4]_2 \cdot \text{H}_2\text{O}$	Schaller, 1933	Merlino & Sartori, 1971
Biringuccite	$\text{Na}_2\text{B}_5\text{O}_8(\text{OH}) \cdot \text{H}_2\text{O}$	Cipriani & Vannuccini, 1961a	Corazza et al, 1974
Ginorite	$\text{Ca}_2\text{B}_{14}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$	D’Achiardi, 1934	This study
Larderellite	$(\text{NH}_4)\text{B}_5\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$	Bechi, 1854	Merlino & Sartori, 1969
Nasinite	$\text{Na}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot 2\text{H}_2\text{O}$	Cipriani & Vannuccini, 1961b	Corazza <i>et al.</i> , 1975
Santite	$\text{K}[\text{B}_3\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$	Merlino & Sartori, 1970	Zachariassen, 1937
Sassolite	$\text{H}_3\text{BO}_3$	Mascagni, 1779	Zachariassen, 1934
Sborgite	$\text{Na}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$	Cipriani, 1957	Merlino & Sartori, 1972

### X-RAY STUDY OF “BECHILITE” AND “LAGONITE”

“Bechilite” and “lagonite” specimens from the mineralogical collections of the Natural History Museum of Pisa University, inventory number #7137 and #7138 respectively, were investigated through X-ray powder diffraction. “Bechilite” occurs in massive microcrystalline powdery masses, “lagonite” in fine grained powdery whitish masses explicitly including iron oxides rich zones. Powder X-ray diffraction patterns (Fig. 1, 2) were collected through a Bruker D2 PHASER equipped with a Lynxeye 1D detector and Ni-filtered Cu K $\alpha$  radiation from 4 to 65° 2 $\phi$ , step

size 0.02° counting time 0.3s/step.

As it can be seen from Fig. 1, examined “bechilite” is actually a mixture of sassolite and ammonioborite, whereas “lagonite” (Fig. 2) is a mixture of sassolite with minor santite, gypsum and larderellite. Iron rust-like phases were clearly present in the “lagonite” hand specimen, but they are not represented in the diffraction pattern, because they are below the detection limit or possibly amorphous.

Our observations are in agreement with D’Achiardi observations reported above, taking into account the possible compositional variability typical of these borate massive specimens.

Tab. 2 - Chemical composition of ginorite. (1, 2, 3) Sasso Pisano (4) Death Valley.

	1	2	3	4
B <sub>2</sub> O <sub>3</sub>	64.42	64.49	63.64	65.21
CaO	15.75	16.11	16.03	14.56
Na <sub>2</sub> O/SrO			0.17	1.10
H <sub>2</sub> O	19.83	19.40	20.16	19.13

1: analyst Gallori, in D'Achiardi, 1934; 2: analyst Rossoni, in D'Achiardi, 1934; 3: analyst Hey, in Hey & Bannister, 1952; 4: Allen & Kramer, 1957

Tab. 3 - Experimental details for ginorite crystal structural study.

X-ray formula Ca <sub>2</sub> B <sub>14</sub> O <sub>20</sub> (OH) <sub>6</sub> ·5H <sub>2</sub> O	Data collection Bruker SMART Breeze
Crystal size 0.15x0.07x0.02 mm	Radiation type MoK $\alpha$
Space group $P2_1/a$	Collected reflections 23718
$a = 12.7673(1)$ Å	Unique reflections 5632
$b = 14.3112(11)$	Observed reflections > $4\sigma(F_o)$ 3387, $R_{int}$ 0.0735
$c = 12.7298(9)$	$R[F^2 > 4\sigma(F^2)]$ , $wR(F^2)$ , $S$ 0.058, 0.128, 1.002
$\beta = 101.055(5)^\circ$	No. of parameters, restraints 471, 16
$V = 2282.8(2)$ Å <sup>3</sup> , $Z = 4$ , $\mu = 0.647$	$\Delta\rho_{max}$ , $\Delta\rho_{min}$ ( $e\text{-}\text{Å}^3$ ) 0.66, -0.68

Tab. 4 - Atomic fractional coordinates and equivalent isotropic displacement parameters (in Å<sup>2</sup>) for ginorite.

	X	Y	Z	U <sub>EQ</sub>		X	Y	Z	U <sub>EQ</sub>
CA1	0.61065(6)	0.16763(5)	0.72937(7)	0.01612(21)	O17	0.50787(17)	0.30670(17)	0.38506(20)	0.01177(58)
CA2	0.13032(5)	0.21840(5)	0.24890(7)	0.01322(20)	O18	0.53817(17)	0.21234(17)	0.54311	0.01102(57)
B1	0.39571(30)	0.19997(28)	-0.11983(36)	0.01060(92)	OH19	0.27537	0.55271	0.39991(21)	0.02652(75)
B2	0.43672(31)	0.30266(29)	0.05372(38)	0.01278(96)	O20	0.38202(18)	0.11496(16)	0.49148(21)	0.01252(58)
B3	0.26759(30)	0.19451(28)	0.01662(37)	0.01113(93)	OH21	0.37616(21)	-0.02316(18)	0.38922(23)	0.01872(65)
B4	0.58030(29)	0.25411(29)	-0.04063(37)	0.01106(91)	O22	0.47824(20)	0.10461(18)	0.34854(23)	0.01853(64)
B5	0.34608(29)	0.25856(28)	0.19814(38)	0.01200(96)	OH23	0.50079(22)	-0.02534(19)	0.23897(25)	0.02360(71)
B6	0.30532(33)	0.05362(30)	-0.07673(41)	0.0166(10)	OH24	0.59843(21)	0.11701(18)	0.23460(24)	0.02054(66)
B7	0.39427(29)	0.32139(28)	0.38287(35)	0.00915(88)	O25	0.17634(17)	0.25184(17)	0.44616(21)	0.01224(57)
B8	0.42446(30)	0.20219(28)	0.54236(37)	0.00983(91)	O26	0.33364(19)	0.25749(17)	0.79710(21)	0.01376(59)
B9	0.25783(30)	0.31241(27)	0.50988(37)	0.01007(92)	OW27	0.11223(23)	0.16176(21)	0.72336(26)	0.02582(72)
B10	0.57348(29)	0.25402(28)	0.46051(36)	0.01019(90)	OW28	0.15941(26)	0.06034(21)	0.27322(30)	0.03487(85)
B11	0.33792(30)	0.25303(28)	0.69247(37)	0.01032(90)	OW29	0.22987(22)	0.43822(20)	0.84233(25)	0.02217(68)
B12	0.29526(31)	0.46003(30)	0.41859(39)	0.01362(96)	OW30	0.01960(28)	0.04198(24)	0.86697(29)	0.03850(78)
B13	0.41135(32)	0.06561(29)	0.41118(38)	0.01278(95)	OW31	0.04906(25)	-0.02894(24)	0.39432(32)	0.04090(91)
B14	0.52577(32)	0.06240(28)	0.27442(37)	0.01363(97)	H8	0.2446(31)	-0.0646(33)	-0.0676(38)	0.05
O1	0.37269(18)	0.22756(29)	-0.01163(39)	0.00910(55)	H9	0.4267(35)	0.4351(27)	0.0574(34)	0.05
O2	0.43633(18)	0.28992(18)	0.16675(21)	0.01502(61)	H19	0.2359(36)	0.5733(34)	0.4426(35)	0.05
O3	0.26651(18)	0.21492(18)	0.12777(21)	0.01439(60)	H21	0.3354(34)	-0.0454(32)	0.4324(34)	0.05
O4	0.26142(20)	0.09371(18)	0.00047(23)	0.01904(65)	H23	0.5387(35)	-0.0485(33)	0.1919(33)	0.05
O5	0.36668(19)	0.10094(17)	-0.13462(22)	0.01555(61)	H24	0.6309(37)	0.0887(33)	0.1855(32)	0.05
O6	0.50981(17)	0.20893(18)	-0.11910(20)	0.01278(58)	H27A	0.1233(40)	0.1542(37)	0.7907(16)	0.05
O7	0.54842(18)	0.29441(18)	0.04503(22)	0.01518(61)	H27B	0.1540(33)	0.1260(30)	0.6917(35)	0.05
OH8	0.29444(25)	-0.04035(20)	-0.09772(28)	0.03195(82)	H28A	0.1297(37)	0.0315(30)	0.3239(32)	0.05
OH9	0.38961(20)	0.39183(18)	0.01475(24)	0.02063(68)	H28B	0.1956(35)	0.0158(25)	0.2509(38)	0.05
O10	0.18278(18)	0.24391(19)	-0.05326(22)	0.01748(62)	H29A	0.2756(33)	0.4082(32)	0.8944(31)	0.05
O11	0.32602(18)	0.26873(17)	0.29731(21)	0.01250(58)	H29B	0.2190(40)	0.4821(28)	0.8879(34)	0.05
O12	0.36594(17)	0.28574(16)	0.48649(20)	0.00883(54)	H30A	0.0081(40)	0.0052(29)	0.8065(27)	0.05
O13	0.41373(18)	0.20317(16)	0.65371(21)	0.01074(56)	H30B	0.0602(34)	0.0779(29)	0.8291(35)	0.05
O14	0.26033(18)	0.30253(17)	0.62392(21)	0.01176(58)	H31A	0.0068(27)	0.0116(26)	0.3879(41)	0.05
O15	0.23786(18)	0.40960(17)	0.47918(21)	0.01285(59)	H31B	0.0106(33)	-0.0827(20)	0.3888(42)	0.05
O16	0.37111(18)	0.42007(17)	0.37231(21)	0.01391(60)					



Tab. 5 - Selected bond distances (Å) and angles (°) for gonorite coordination polyhedra.

		Ca1		Ca2			
		OW29	2.417(3)	OW28	2.304(3)		
		OW27	2.443(4)	O2	2.500 (2)		
		O18	2.459(3)	O25	2.513(3)		
		OH23	2.560(3)	O3	2.536(3)		
		O13	2.565(2)	O11	2.559(2)		
		O14	2.573(2)	O17	2.572(3)		
		OH21	2.584(3)	O7	2.612(3)		
		O6	2.584(3)				
		O26	3.009(2)				
		O10	3.022(3)				
		MEAN	2.622	MEAN	2.516		
<b>Tetrahedral B coordination</b>							
		<b>B1</b>				<b>B2</b>	
O26	1.450(5)	O1-O5	106.3(3)	O2	1.451(5)	O1-O2	110.8(3)
O6	1.461(4)	O1-O6	109.8(3)	O7	1.456(5)	O1-O7	109.7(3)
O5	1.468(5)	O1-O26	109.9(3)	OH9	1.457(5)	O1-OH9	107.0(3)
O1	1.515(5)	O5-O6	108.2(3)	O1	1.502(5)	O2-O7	104.8(3)
MEAN	1.474	O5-O26	111.4(3)		1.467	O2-OH9	111.6(3)
		O6-O26	111.1(3)			O1-O2	110.8(3)
		MEAN	109.5				109.1
		<b>B3</b>				<b>B7</b>	
O3	1.447(5)	O1-O3	109.9(3)	O16	1.444(5)	O11-O12	105.4(3)
O10	1.447(5)	O1-O4	107.4(3)	O17	1.460(4)	O11-O16	110.6(3)
O4	1.457(5)	O1-O10	106.9(3)	O11	1.466(5)	O11-O17	112.8(3)
O1	1.529(5)	O3-O4	109.1(3)	O12	1.521(5)	O12-O16	109.3(3)
	1.471	O3-O10	110.9(3)		1.473	O12-O17	109.6(3)
		O4-O10	112.5(3)			O16-O17	109.1(3)
			109.5				109.5
		<b>B8</b>				<b>B9</b>	
O12	1.513(5)	O12-O13	108.7(3)	O14	1.453(5)	O12-O14	108.9(3)
O13	1.450(5)	O12-O18	109.0(3)	O15	1.454(5)	O12-O15	107.9(3)
O18	1.457(4)	O12-O20	111.0(3)	O25	1.472(5)	O12-O25	108.5(3)
O20	1.462(5)	O13-O18	105.9(3)	O12	1.516(4)	O14-O15	109.3(3)
	1.471	O13-O20	110.2(3)		1.474	O14-O25	111.7(3)
		O18-O20	111.9(3)			O15-O25	110.2(3)
			109.5				109.5
<b>Triangular B coordination</b>							
		<b>B4</b>				<b>B5</b>	
O10	1.349(4)	O6-O7	121.8(3)	O11	1.343(5)	O2-O3	121.3(4)
O7	1.363(5)	O6-O10	116.0(4)	O2	1.366(5)	O2-O11	124.3(4)

O6	1.372(5) 1.362	O7-O10	122.1(4) 116.3	O3	1.369(5) 1.360	O3-O11	114.4(3) 116.0
		<b>B6</b>				<b>B10</b>	
O4	1.349(6)	O4-O5	123.2(4)	O18	1.359(5)	O17-O18	122.3(3)
O5	1.355(5)	O4-OH8	121.2(4)	O25	1.363(4)	O17-O25	114.5(3)
OH8	1.373(5) 1.359	O5-OH8 119.1	115.5(4)	O17	1.373(47) 1.362	O18-O25	123.2(3) 119.1
		<b>B11</b>				<b>B12</b>	
O26	1.345(5)	O13-O14	120.7(4)	O16	1.353(5)	O15-O16	121.9(4)
O13	1.368(5)	O13-O26	123.2(4)	OH19	1.363(5)	O15-OH19	120.7(3)
O14	1.383(5) 1.366	O14-O26	116.1(3) 119.0	O15	1.367(5) 1.362	O16-OH19	117.4(4) 120.5
		<b>B13</b>				<b>B14</b>	
O20	1.353(5)	O20-OH21	121.0(4)	OH23	1.352(5)	O22-OH23	122.5(4)
OH21	1.359(5)	O20-O22	120.8(3)	O22	1.358(5)	O22-OH24	115.1(3)
O22	1.392(5) 1.363	OH21-O22	118.2(4) 119.0	OH24	1.382(5) 1.364	OH23-OH24	122.4(4) 119.6

## CRYSTAL STRUCTURAL STUDY OF GINORITE

A tiny single crystal of ginorite, with  $0.15 \times 0.07 \times 0.02$  mm dimensions, was luckily found in specimen number #7678 after a close scrutiny of all the available ginorite specimens. Preliminary chemical SEM/EDAX analyses performed on ginorite from this specimen, indicate Sr in ginorite from the type locality is below the detection limit, in agreement with the literature chemical data.

For the X-ray single-crystal study, the intensity data were collected using a Bruker SMART Breeze diffractometer equipped with an air-cooled CCD detector, with Mo  $K\alpha$  radiation. The detector-to-crystal distance was 50 mm. and 1607 frames were collected using  $\omega$  and  $\phi$  scan modes, in  $0.5^\circ$  slices, with an exposure time of 20 s per frame. The data were corrected for the Lorentz and polarization factors, and absorption using the software package APEX2 (Bruker, 2012). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson, 1992). Crystal data and details of the intensity data collection and refinement are reported in Tab. 3.

All calculations were done with SHELX/WINGX software package (Sheldrick, 2015; Farrugia, 2012), assuming the structural model of strontioGINORITE given by Grice (2005) as a starting model. Crystal structure

drawings were performed with CrystalMaker software (Palmer, 2014).

Following the indications of chemical data, the occupancies of the two independent Ca sites were fixed to full Ca occupancy. A trial to free the Ca sites occupancies did not give significant results, with the refined occupancies quite close to the full occupancy. About the hydrogen atoms, their positions were refined imposing soft constraints on the O <sup>$\delta$</sup> -H distances, expressed with an ideal distance O-H = 0.9(0.05) Å.

Final positional and equivalent displacement isotropic parameters are reported in Tab. 4, whereas in Tab. 5 and 6 are reported bond distances and angles, and the ginorite hydrogen bonding respectively.

## STRUCTURE DESCRIPTION

As expected, ginorite is isostructural with strontioGINORITE (Konnert *et al.* 1970; Grice, 2005). We find in ginorite (Fig. 3) the same complex “sheets” parallel to (010), made up by borate groups and Ca coordination polyhedra. Moreover, by comparing the bond distances of the two phases, one can notice that the borate frame of ginorite is quite similar to that of strontioGINORITE, and one can refer to Grice (2005) for a full description of the relationships between the fourteen distinct B coordi-

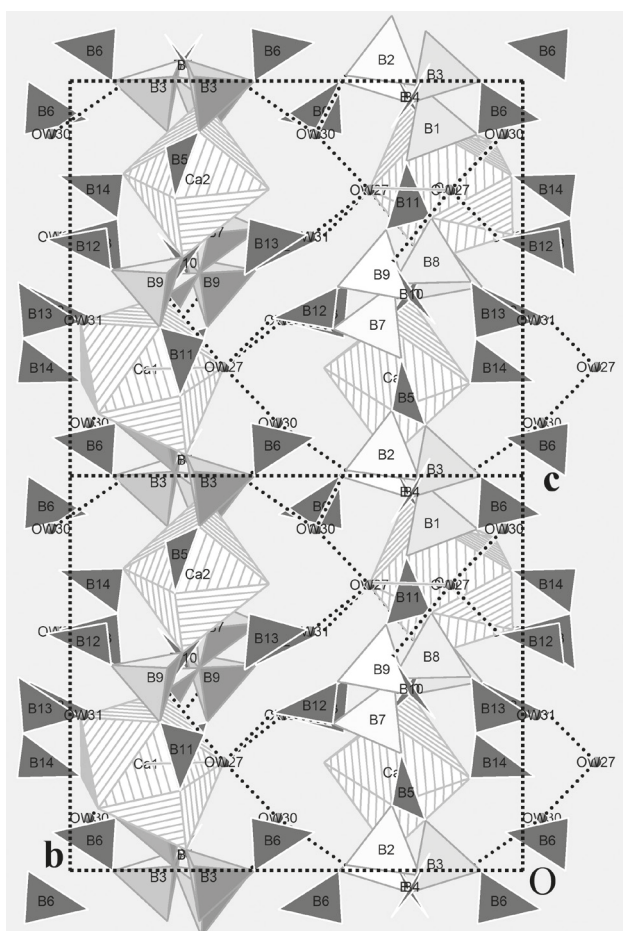


Fig. 3 - Ginatorite crystal structure as seen along [100]. Complex sheets made up by  $[BO_3]$  and  $[BO_4]$  groups, together with Ca coordination polyhedra link together along [010] by hydrogen bonds and Ca bridging bonds. Ca polyhedra are represented as plain solids,  $[BO_3]$  and  $[BO_4]$  groups as plain and stripe filled solids respectively.

nation polyhedra and for the topology of borate sheets. As it can be seen from Table 5, similarly to strontioginorite, the two independent Ca1 and Ca2 coordination polyhedra display ten and eight coordination number respectively. Ca1 polyhedron, analogous to Sr coordination polyhedron in strontioginorite, displays a definitely larger volume ( $37.1 \text{ \AA}^3$ ) respect to the Ca<sub>2</sub> polyhedron ( $25.9 \text{ \AA}^3$ ). These values compare with  $40.2$  and  $26.1 \text{ \AA}^3$ , the volume of the Sr and Ca polyhedra in strontioginorite. Whereas the contraction of Ca<sub>2</sub> polyhedron is quite limited, a relevant shrinkage of Ca<sub>1</sub> polyhedron in ginatorite can be noticed. In Fig. 4 the Ca1 coordination polyhedron is represented, and the its bond lengths directed nearly parallel to the *b* direction are reported and compared with the corresponding values for strontioginorite. It can be noticed the relevant shortening of these bond distances

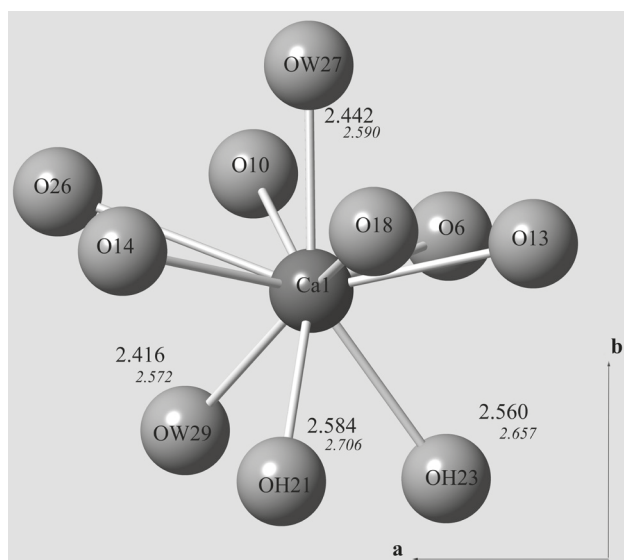


Fig. 4 - Ca1 coordination polyhedron in ginatorite structure viewed along [001] direction. Bond distances directed nearly parallel to the *b* axis are reported, and compared with the corresponding values for strontioginorite (*italic*, smaller size).

in ginatorite, whereas the mean value of the six bond lengths lying nearly parallel to (010) is quite similar for ginatorite and strontioginorite,  $2.702$  and  $2.708 \text{ \AA}$  respectively. This is in agreement with the strong contraction of the *b* parameter in ginatorite,  $14.3112 \text{ \AA}$  compared to  $14.4576 \text{ \AA}$  in strontioginorite, which is the main responsible for the cell volume contraction of ginatorite  $2282.8(2) \text{ \AA}^3$ , when compared to the value of  $2325.8(2) \text{ \AA}^3$  found in strontioginorite. Analogously to strontioginorite, Ca coordination polyhedra form bonds both within and between adjacent borate layers, which are linked through the Ca1-OH23 e Ca2-OH24 bonds. Linking between adjacent borate layers is moreover assured by a complex system of hydrogen bonds (Tab. 6a). Hydrogen bonding, reported in Table 6a, was taken into account examining the O...O distances distances less than or equal to  $3.00 \text{ \AA}$  and connecting oxygen atoms not bonded to the same cation. The bond strengths have been calculated according to Ferraris & Ivaldi (1988), and the indication of the donor (D) or acceptor (A) character of the oxygen atoms is reported.

All the six independent hydroxyl groups and the five water molecules are involved in hydrogen bonding. Three of the five  $H_2O$  molecules are linked to Ca coordination polyhedra: OW29 is bonded to Ca1, whereas OW27 and OW28 make part of the smaller Ca2 coordination sphere. The two remaining water molecules OW30 and OW31 are not linked to Ca, being involved in hydrogen bonds only. As it can be seen from Tab. 6, OW30 forms two bonds as donor with

Table 6a. Hydrogen bonding in ginorite structure (distances in Å, angles in °). D and A indicate donor and acceptor oxygen atoms respectively.

	D-H	H...A	D...A	D...H...A
OH8-H8...OH9	0.88(2)	2.05(2)	2.921(4)	170(5)
OH9-H9...OW30	0.90(2)	1.87(2)	2.749(4)	168(5)
OH19-H19...O20	0.86(2)	1.95(2)	2.794(4)	166(5)
OH21-H21...O15	0.89(2)	1.72(2)	2.605(4)	177(5)
OH23-H23...O5	0.90(2)	1.70(2)	2.581(4)	164(5)
OH24-H24...OH8	0.90(2)	1.75(2)	2.650(4)	174(5)
OW27-H27A...OW30	0.85(2)	2.40(5)	2.917(5)	120(4)
OW27-H27B...OH19	0.89(2)	1.92(2)	2.797(4)	169(5)
OW28-H28A...OW31	0.91(2)	1.72(2)	2.613(5)	166(5)
OW28-H28B...OW29	0.87(2)	1.99(2)	2.831(4)	162(5)
OW29-H29A...OH9	0.90(2)	1.91(3)	2.775(4)	159(5)
OW29-H29B...O4	0.88(2)	2.12(2)	2.981(4)	164(5)
OW30-H30B...OW27	0.93(2)	2.01(2)	2.917(5)	166(5)
OW31-H31A...O16	0.91(2)	1.82(2)	2.725(4)	173(4)
OW31-H31B...OW27	0.91(2)	2.22(4)	2.986(5)	142(4)

Table 6b. Bond-strength sums, expressed in valence units, for anions involved in hydrogen bonding, ignoring (Ss\*) and including (Ss\*\*) hydrogen bonds contributions.

ANION	Ss*	Ss**
O4	1.85	1.99
O5	1.81	2.11
OH8	0.99	1.10
OH9	0.79	0.93
O15	1.81	2.10
O16	1.87	2.09
OH19	1.02	1.02
O20	1.83	2.02
OH21	1.03	0.75
OH23	1.05	0.75
OH24	0.97	0.72
OW27	-	0.10
OW28	0.40	0.07
OW29	0.30	0.14
OW30	-	0.06
OW31	-	-0.07

OW27 and OW28, and one bond as acceptor with OH9. OW31 forms two bonds as donor with O16 and OW27, and as an acceptor with OW27 and OW28. In Tab. 6b the bond valence balance of anions involved in hydrogen bonding is reported, also taking into account the contributions of the hydrogen bonding. The chemical character of oxygen atoms, water molecules or hydroxyl anions resulting from the structural model is fully confirmed. It can be noticed that the three hydroxyl groups OH21, OH23, OH24 show the largest deviations (0.75-0.72 *v.u.*) from the expected value of 1 *v.u.*, a feature present also in strontiojinorite. Grice (2005) remarks as the above mentioned OH groups are H-donors only, and play a peculiar crystal chemical role, being linked in the triangular borate groups B13 and B14 groups (Tab. 5), which are the “decorations” of the borate fundamental building block (FBB) of strontiojinorite structure.

## CONCLUSIONS

X-ray diffraction study of “bechilite” and “lagonite” from Larderello (type locality) show they actually are admixtures of sassolite and ammonioborite (“bechilite”), and of sassolite with minor santite, gypsum and larderellite (“lagonite”). Single crystal structural study of ginorite confirmed its guessed isostructurality with strontiojinorite. The shrinking of cell volume in ginorite if compared with strontiojinorite is neatly re-

lated to the volume contraction of the coordination polyhedron hosting Sr in strontiojinorite, Ca1 in ginorite. The complex sheets parallel to (010) made up by borate groups and Ca polyhedra are linked through *b* by Ca cations and by a complex hydrogen bonding scheme.

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