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The crystal structure of barrerite

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Abstract. — The crystal structure of the zeolite barrerite, $[(Ca_{1.7}Mg_{0.3}Na_{10.9}K_{2.1})(Al_{16.4}Si_{55.4})O_{144}]\cdot 51.6H_2O$, has been studied by X-ray methods : space group *Amma* with $a = 13.643$ (2), $b = 18.200$ (3), $c = 17.842$ (3) Å. The framework of barrerite is topologically identical to that of stilbite and stellerite. The lowering of the symmetry from *Fmmm* of stellerite to *Amma* of barrerite is due to the presence of cations in sites that are vacant in both stellerite and stilbite and which impose rotational displacements within the framework around the screw axes parallel to the *a* axis.

Structure cristalline de la barrérite.

Résumé. — La structure cristalline de la zéolite barrérite $[(Ca_{1,7}Mg_{0,3}Na_{10,9}K_{2,1})(Al_{16,4}Si_{55,4})O_{144}]\cdot 51,6H_2O$ a été étudiée au moyen des rayons X : le groupe spatial est *Amma* avec $a = 13,643$ (2), $b = 18,200$ (3), $c = 17,842$ (3) Å. La charpente de la barrérite est identique à celles de la stilbite et de la stellérite.

L'abaissement de la symétrie du groupe spatial *Fmmm* de la stellerite au groupe spatial *Amma* de la barrérite est une conséquence de la présence, dans des sites vacants, de cations soumis à des déplacements induits par des axes hélicoïdaux parallèles à *a*.

INTRODUCTION.

The new mineral name, Barrerite, in honour of R. M. Barrer, who has largely contributed to zeolite studies, was approved by the Commission for New Minerals and Mineral Names, of the I. M. A., for a mineral first described by Passaglia and Pongiluppi (1974 and 1975) as sodian stellerite. It was found at Capo Pula, Sardinia, Italy, and it is similar to stellerite in both its powder pattern and its Si/Al ratio, but it differs from stellerite in its symmetry and in its exchangeable cations, which are mainly alkalies. The aim of this research is to verify whether barrerite has the same framework of stilbite (Galli, 1971) and stellerite (Galli and Alberti, 1975) and to investigate the reasons for its different symmetry.

EXPERIMENTAL.

Barrerite from Capo Pula (Passaglia and Pongiluppi, 1974) used in the present work has space group *Amma*, with $a = 13.643$ (2), $b = 18.200$ (3), $c = 17.842$ (3) (all Å, errors in parentheses). The unit cell content is :

$$(Ca_{1.68}Mg_{0.34}Na_{10.90}K_{2.12})_{15.04}[(Al_{16.38}Fe_{0.02})_{16.40}Si_{55.44}O_{144}]\cdot 51.56H_2O$$

A single crystal ($\simeq 0.4 \times 0.35 \times 0.25$ mm) was X-rayed with Zr-filtered Mo-radiation in the θ-2 θ scan mode on a Philips PW 1100 four-circle computer-controlled diffractometer of the « Centro di Cristallografia Strutturale del C. N. R. di Pavia, Italy ». 3,543 diffraction intensities possible in space group *Ammm* were inspected. The systematically absent reflections of the type $hk0$ with $h = 2n + 1$, confirmed the space group to be *Amma*. Of the remaining 3,444 diffractions compatible with the correct space group, corresponding to 13.3 per cent of the possible diffractions in the molybdenum sphere, 2,483 diffractions (72 % of the measured reflections) were considered as observed having $I > 2\sigma(I)$. No absorption correction was applied

REFINEMENT.

Atomic scattering factors given by Hanson *et al.* (1964) for neutral atoms were used throughout ; for the exchangeable cations an average scattering curve was obtained considering all the elements detected by the chemical analysis, each with its own weight, as follows : Na : 72,4 %, K : 14.1 %, Ca : 11.1 %, Mg : 0.2 % ; for the Si atoms an average curve was obtained with 77.2 % of Si and 22.8 of Al.

The refinement was carried out on the CDC 6600 computer of the CINECA as an alternation of least square cycles and electron density maps, the last maps allowed the contents of the channels in the tetrahedral framework to be located. The atomic parameters of the framework atoms given by Galli and Alberti (1975) for stellerite were used to start

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the refinement. Due to the lower symmetry, some of the atomic positions of stellerite split into two positions in barrerite, and these are coded with a « P » in both tables and figures : so Si1 of the first one split into Si1 and Si1P in the second one, and so on. The good convergence in the first stages of the refinement confirmed that the barrerite framework is topologically the same as that of stilbite and stellerite. The final residual was R = 0.122 (including zeros) or R = 0.068 (excluding zeros); the final weighted residual was R = 0.067 (excluding zeros). Some of the water molecules have shown a poor convergence in the full-matrix refinement in the occupancy and temperature factors. For this reason the occupancy factors of four water molecules (W4, W4P, W8 and W8P) were fixed at a value of 50 % in the final cycles of refinement; some isotropic thermal parameters obtained according to this precedure resulted to be very high. Among the last mentioned water molecules, this is particularly true for the first three ones (W4, W4P and W8), and for W1 and W6P; all these molecules gave B-values above 10 Å². It is obvious that these high values depend in part on the high-mobility of water molecules in the zeolite channels, and in part on the choice of the parameters to be fixed during the least squares refinement.

TABLE I.

Atomic coordinates, thermal parameters and occupancy factors, with their e. s. d.'s on the last digit in parentheses (1).

The form of the anisotropic temperature factors (× 10)^4 is :

$$\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2\,hk\,\beta_{12} - 2\,hl\,\beta_{13} - 2\,kl\,\beta_{23})$$

Atom	x/a	y/b	z/c	β_{11} or B(Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy %
Si1	.1356(1)	.3037(1)	.1248(1)	13(1)	9(1)	11(1)	1(1)	-1(1)	0(1)	100
Si1P	.1363(1)	.3122(1)	.3724(1)	12(1)	11(1)	10(1)	0(1)	1(1)	0(1)	100
Si3	.0512(1)	.4110(1)	.2433(1)	16(1)	6(1)	13(1)	-1(1)	-1(1)	1(1)	100
Si4	.1386(1)	.1846(1)	.2541(1)	11(1)	8(1)	10(1)	-1(1)	0(1)	0(1)	100
Si5	0	.2399(1)	0	11(1)	15(1)	11(1)	0	0(1)	0	100
O1	.0699(3)	.2937(2)	.0495(2)	35(3)	23(1)	23(1)	-11(2)	-9(2)	4(1)	100
O1P	.0664(3)	.3136(2)	.4475(2)	30(3)	21(1)	25(1)	-8(1)	15(2)	-6(1)	100
O3	.1195(3)	.2338(2)	.1806(2)	42(3)	22(1)	22(1)	-3(2)	-4(2)	12(1)	100
O3P	.1247(3)	.2331(2)	.3299(2)	29(2)	18(1)	19(1)	-2(1)	4(1)	-5(1)	100
O4	.1062(3)	.3806(2)	.1677(2)	48(3)	17(1)	28(2)	0(2)	18(2)	-6(1)	100
O4P	.1060(3)	.3810(2)	.3188(2)	43(3)	19(1)	26(2)	1(2)	-5(2)	5(1)	100
O7	1/4	.3104(3)	.0971(3)	15(3)	31(2)	24(2)	0	0	0(2)	100
O7P	1/4	.3219(3)	.4007(3)	26(3)	21(2)	15(2)	0	0	0(1)	100
O8	.0656(2)	.1142(2)	.2550(2)	21(2)	15(1)	32(2)	-5(1)	-5(2)	3(1)	100
O9	.0546(4)	1/2	.2435(3)	47(4)	8(1)	30(2)	0	-1(3)	0	100
O10	1/4	.1508(3)	.2540(3)	18(2)	17(2)	22(2)	0	0	-3(2)	100
C1	1/4	0	.0417(5)	243(18)	44(4)	49(4)	0	0	0	72(2)
C1P	1/4	0	.4558(3)	135(9)	1(1)	10(2)	0	0	0	61(2)
C2	.0482(24)	.0624(9)	.0446(18)	218(43)	10(4)	168(27)	10(10)	114(25)	-7(8)	14(2)
C2P	.0369(18)	.0634(15)	.4792(14)	206(30)	193(18)	109(16)	-80(18)	28(16)	-86(14)	25(3)
C3	.1611(26)	0	.2386(31)	276(41)	49(10)	157(24)	0	76(32)	0	25(2)
W1	.1911(22)	.1160(10)	.0519(9)	10.3(7)						49(3)
W1P	.0894(14)	.0824(11)	.4356(10)	8.1(7)						41(2)
W2	1/4	.1259(11)	.0557(10)	2.3(7)						32(4)
W2P	1/4	.1313(6)	.4421(6)	9.3(5)						91(2)
W3	.1750(22)	0	.1764(16)	7.4(9)						38(3)
W3P	.2177(14)	0	.3221(10)	6.0(6)						46(2)
W4	.0915(23)	0	.1217(17)	13.7(9)						50
W4P	.1479(23)	0	.3869(18)	14.2(9)						50
W5	.2174(21)	1/2	.0917(15)	2.9(8)						20(2)
W5P	.1966(19)	1/2	.4154(12)	8.0(9)						42(2)
W6	.1251(10)	1/2	.0607(7)	8.1(3)						83(4)
W6P	.0814(21)	1/2	.4349(13)	11.4(11)						50(3)
W8	1/4	1/2	.1615(34)	19.9(20)						50
W8P	1/4	1/2	.3615(7)	1.2(2)						50

(1) Final data of the refinement having the occupancy factor of W4, W4P, W8 and W8P fixed.

As an alternative we fixed at 10 Å² the thermal parameters for all those water molecules which in the previous refinement gave B-values larger than 10 Å². The new choice resulted in a small (less than 5 %) decrease in the occupancy factors of the water molecules with fixed B; all the positional parameters were affected by changes lower than the standard errors. As the results obtained with the two different refinements differ slightly, the data listed in all the tables refer only to the refinement with fixed occupancy of water molecules. The observed and calculated structure factors are available from the authors. The atomic and anisotropic thermal parameters are listed in Table I. Table II gives the analysis of the thermal parameters. Bond distances and angles within the framework atoms are listed in Table III. Table IV gives the cation, oxygen and water molecule distances less 3.30 Å. Part of the structure is projected along *b* in Figure 1.

The origin of the unit cell of barrerite is shifted by:

$$1/4\,a + 1/4\,c$$

in comparison with stellerite (Galli and Alberti, 1975) whereas it coincides with the origin used for stilbite (Galli, 1971).

The agreement between the crystallochemical results and the data of the chemical analysis is satisfactory; refinement revealed 58.56 water molecules and 13.56 exchangeable cations as compared to the 51.56 water molecules and a total of 15.04 exchangeable cations from the chemical analysis.

TABLE II.

Analysis of the anisotropic thermal parameters (1).

Atom	R.m.s.	$U_i a$	$U_i b$	$U_i c$	Atom	R.m.s.	$U_i a$	$U_i b$	$U_i c$
Si1	.11(1)	19°	106°	80°	O7	.12(1)	0°	90°	90°
	.13(1)	107	163	87		.20(1)	90	90	0
	.13(1)	99	85	10		.23(1)	90	0	90
Si1P	.10(1)	19	93	108	O7P	.16(1)	90	94	4
	.13(1)	109	98	159		.16(1)	0	90	90
	.14(1)	90	9	98		.19(1)	90	4	86
Si3	.10(1)	76	14	94	O8	.13(1)	30	60	85
	.12(1)	164	77	99		.17(1)	63	147	73
	.14(1)	98	84	10		.23(1)	102	78	17
Si4	.10(1)	24	66	92	O9	.12(1)	90	0	90
	.12(1)	67	151	74		.21(1)	172	90	98
	.13(1)	95	74	16		.22(1)	98	90	8
Si5	.10(1)	2	90	88	O10	.13(1)	0	90	90
	.13(1)	88	90	178		.16(1)	90	155	115
	.16(1)	90	0	90		.19(1)	90	115	25
O1	.14(1)	36	61	71	C1	.27(1)	90	0	90
	.17(1)	93	53	143		.28(1)	90	90	0
	.24(1)	126	51	59		.48(2)	0	90	90
O1P	.12(1)	34	84	124	C1P	.05(3)	90	0	90
	.17(1)	100	151	117		.13(1)	90	90	0
	.25(1)	58	118	45		.36(1)	0	90	90
O3	.13(1)	87	133	43	C2	.11(3)	99	12	82
	.19(1)	162	105	100		.31(3)	40	78	127
	.24(1)	108	47	49		.62(4)	52	90	38
O3P	.15(1)	111	53	45	C2P	.29(3)	74	55	39
	.16(1)	150	120	91		.40(3)	152	99	64
	.20(1)	70	128	45		.67(3)	112	36	117
O4	.14(1)	123	58	49	C3	.29(3)	90	0	90
	.18(1)	120	146	74		.40(4)	46	90	136
	.26(1)	47	100	45		.59(5)	44	90	46
O4P	.16(1)	105	35	121					
	.20(1)	146	118	108					
	.22(1)	120	70	37					

(1) Root mean square thermal vibrations (Å) along the ellipsoid axes (with e. s. d.'s in parentheses), and angles between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoids.

TABLE III.

Interatomic distances (Å) and angles (°) within the framework, with e. s. d.'s on the last digit in parentheses.

Interatomic distances and bond angles symmetrically equivalent are bracketed.

The superscripts refer to the symmetry code

None	x	y	z	IX	-x	-y	1-z
I	-x	1/2-y	1/2-z	X	-x	y	1-z
II	-x	y	-z	XI	x	1/2-y	1/2+z
III	x	1/2-y	z-1/2	XII	-x	1/2+y	1/2-z
IV	x	-y	z	XIII	x	1-y	z
V	1/2-x	y	z	XIV	x	1/2+y	1/2+z
VI	1/2-x	-y	z	XV	x	1/2+y	z-1/2
VII	1/2-x	1/2-y	z-1/2	XVI	1/2-x	1-y	z
VIII	-x	-y	-z				

Si1 tetrahedron		Si1P tetrahedron		Si3 tetrahedron	
Si1-O1	1.63(1)Å	Si1P-O1P	1.65(1)Å	Si3-O4	1.64(1)Å
Si1-O3	1.63(1)	Si1P-O3P	1.64(1)	Si3-O4P	1.63(1)
Si1-O4	1.64(1)	Si1P-O4P	1.63(1)	Si3-O8^{I}	1.66(1)
Si1-O7	1.64(1)	Si1P-O7P	1.64(1)	Si3-O9	1.62(1)
Average	1.635	Average	1.64	Average	1.64
O1-O3	2.67(1)	O1P-O3P	2.68(1)	O4-O4P	2.70(1)
O1-O4	2.68(1)	O1P-O4P	2.66(1)	O4-O8^{I}	2.72(1)
O1-O7	2.62(1)	O1P-O7P	2.65(1)	O4-O9	2.65(1)
O3-O4	2.69(1)	O3P-O4P	2.71(1)	O4P-O8^{I}	2.69(1)
O3-O7	2.71(1)	O3P-O7P	2.67(1)	O4P-O9	2.64(1)
O4-O7	2.66(1)	O4P-O7P	2.67(1)	O8^{I}-O9	2.65(1)
O1-Si1-O3	110.1(2)°	O1P-Si1P-O3P	109.6(2)°	O4-Si3-O4P	110.9(2)°
O1-Si1-O4	110.2(2)	O1P-Si1P-O4P	108.6(2)	O4-Si3-O8^{I}	111.2(2)
O1-Si1-O7	106.5(2)	O1P-Si1P-O7P	107.2(2)	O4-Si3-O9	109.0(3)
O3-Si1-O4	110.3(2)	O3P-Si1P-O4P	112.4(2)	O4P-Si3-O8^{I}	109.4(2)
O3-Si1-O7	111.7(3)	O3P-Si1P-O7P	109.2(2)	O4P-Si3-O9	108.6(3)
O4-Si1-O7	108.0(3)	O4P-Si1P-O7P	109.8(2)	O8^{I}-Si3-O9	107.7(2)

Si4 tetrahedron		Si5 tetrahedron			
Si4-O3	1.61(1)Å	Si5-O1 Si5-O1^{II}	1.63(1)Å	Si1-O7-Si1^{V}	143.9(4)°
Si4-O3P	1.63(1)	Si5-O1P^{I} Si5-O1P^{III}	1.63(1)	Si1-O4-Si3	141.4(3)
Si4-O8	1.62(1)			Si1-O3-Si4	155.5(3)
Si4-O10	1.64(1)			Si1-O1-Si5	147.0(3)
Average	1.625	Average	1.63	Si1P-O7-Si1P^{V}	141.9(3)
				Si1P-O4P-Si3	148.9(3)
				Si1P-O3P-Si4	148.4(3)
O3-O3P	2.66(1)	O1-O1^{II}	2.60(1)	Si1P-O1P-Si5^{XI}	141.5(2)
O3-O8	2.65(1)	O1-O1P^{I} O1^{II}-O1P^{I}	2.70(1)	Si3-O9-Si3^{XIII}	176.7(4)
O3-O10	2.68(1)			Si3^{I}-O8-Si4	144.0(2)
O3P-O8	2.67(1)	O1-O1P^{III} O1^{II}-O1P^{III}	2.67(1)	Si4-O10-Si4^{V}	136.0(3)
O3P-O10	2.65(1)				
O8-O10	2.60(1)	O1P^{I}-O1P^{III}	2.61(1)		
O3-Si4-O3P	110.9(2)°	O1-Si5-O1^{II}	105.9(3)°		
O3-Si4-O8	110.3(2)	O1-Si5-O1P^{I} O1^{II}-Si5-O1P^{III}	112.0(2)		
O3-Si4-O10	111.0(2)				
O3P-Si4-O8	110.4(2)	O1^{II}-Si5-O1P^{I} O1-Si5-O1P^{III}	110.3(2)		
O3P-Si4-O10	108.2(2)				
O8-Si4-O10	105.9(2)	O1P^{I}-Si5-O1P^{III}	106.5(3)		

TABLE IV.

Cation, oxygen and water molecule distances, less than 3.30 Å, with their e. s. d.'s in parentheses (¹).

C1 polyhedron	
C1-C2	2.98(3) Å
C1-C2$^{\mathrm{IV}}$	
C1-C2$^{\mathrm{V}}$	
C1-C2$^{\mathrm{VI}}$	
C1-W1	2.27(2)
C1-W1$^{\mathrm{IV}}$	
C1-W1$^{\mathrm{V}}$	
C1-W1$^{\mathrm{VI}}$	
C1-W2	2.30(2)
C1-W2$^{\mathrm{IV}}$	
C1-W3	2.61(3)
C1-W3$^{\mathrm{V}}$	
C1-W4	2.59(3)
C1-W4$^{\mathrm{V}}$	
C1-W5P$^{\mathrm{III}}$	2.37(2)
C1-W5P$^{\mathrm{VII}}$	
C1-W6P$^{\mathrm{III}}$	2.99(3)
C1-W6P$^{\mathrm{VII}}$	
C1-W8P$^{\mathrm{III}}$	3.22(2)

W1 polyhedron	
W1-C1	2.27(2)
W1-C2	2.18(4)
W1-O1P$^{\mathrm{III}}$	2.83(2)
W1-O3	3.29(2)
W1-O7P$^{\mathrm{III}}$	3.03(2)
W1-W1$^{\mathrm{V}}$	1.61(6)
W1-W2	0.83(3)
W1-W3	3.07(3)
W1-W4	2.80(3)
W1-W5P$^{\mathrm{III}}$	3.22(2)

W3P polyhedron	
W3P-C1P	2.43(2)
W3P-C3	1.68(3)
W3P-C3$^{\mathrm{V}}$	2.22(5)
W3P-O8	3.17(1)
W3P-O8$^{\mathrm{IV}}$	
W3P-O10	3.03(2)
W3P-O10$^{\mathrm{IV}}$	
W3P-W1P	3.07(2)
W3P-W1P$^{\mathrm{IV}}$	
W3P-W2P	3.24(2)
W3P-W2P$^{\mathrm{IV}}$	
W3P-W3	2.66(3)
W3P-W3$^{\mathrm{V}}$	2.98(3)
W3P-W3P$^{\mathrm{V}}$	0.88(4)
W3P-W4P	1.50(3)
W3P-W4P$^{\mathrm{V}}$	2.17(4)

C1P polyhedron	
C1P-C2P	3.16(3) Å
C1P-C2P$^{\mathrm{IV}}$	
C1P-C2P$^{\mathrm{V}}$	
C1P-C2P$^{\mathrm{VI}}$	
C1P-W1P	2.68(2)
C1P-W1P$^{\mathrm{IV}}$	
C1P-W1P$^{\mathrm{V}}$	
C1P-W1P$^{\mathrm{VI}}$	
C1P-W2P	2.40(1)
C1P-W2P$^{\mathrm{IV}}$	
C1P-W3P	2.43(2)
C1P-W3P$^{\mathrm{V}}$	
C1P-W4P	1.86(3)
C1P-W4P$^{\mathrm{V}}$	
C1P$^{\mathrm{III}}$-W5	2.47(3)
C1P$^{\mathrm{III}}$-W5$^{\mathrm{V}}$	
C1P$^{\mathrm{III}}$-W6	2.53(1)
C1P$^{\mathrm{III}}$-W6$^{\mathrm{V}}$	

W1P polyhedron	
W1P-C1P	2.68(2)
W1P-C2P	1.11(2)
W1P-C2P$^{\mathrm{IV}}$	2.86(3)
W1P-C2P$^{\mathrm{X}}$	2.32(3)
W1P-O1$^{\mathrm{I}}$	3.14(2)
W1P-O1$^{\mathrm{XI}}$	3.05(2)
W1P-O8	3.29(2)
W1P-W2P	2.37(2)
W1P-W3P	3.07(2)
W1P-W4P	1.91(3)
W1P-W6$^{\mathrm{I}}$	3.29(2)
W1P-W6$^{\mathrm{XI}}$	2.73(2)

W4 polyhedron	
W4-C1	2.59(3)
W4-C2	1.88(4)
W4-C2$^{\mathrm{IV}}$	
W4-C3	2.29(6)
W4-O8	3.18(2)
W4-O8$^{\mathrm{IV}}$	
W4-O9$^{\mathrm{I}}$	3.12(3)
W4-W1	2.80(3)
W4-W1$^{\mathrm{IV}}$	
W4-W3	1.50(4)
W4-W6P$^{\mathrm{I}}$	2.57(4)

W8P polyhedron	
W8P-C1$^{\mathrm{XI}}$	3.22(2)
W8P-O4P	3.02(1)
W8P-O4P$^{\mathrm{XIII}}$	
W8P-O4P$^{\mathrm{V}}$	
W8P-O4P$^{\mathrm{XVI}}$	
W8P-W5P	1.21(2)
W8P-W5P$^{\mathrm{V}}$	
W8P-W6P	2.65(3)
W8P-W6P$^{\mathrm{V}}$	

C2 polyhedron	
C2-C1	2.98(3) Å
C2-C2$^{\mathrm{II}}$	2.06(7)
C2-C2$^{\mathrm{IV}}$	2.27(3)
C2-C2$^{\mathrm{VIII}}$	3.07(5)
C2-O1P$^{\mathrm{III}}$	2.86(2)
C2-W1	2.18(4)
C2-W2	2.99(3)
C2-W3	3.13(4)
C2-W4	1.88(4)
C2-W5P$^{\mathrm{III}}$	3.27(3)
C2-W6P$^{\mathrm{I}}$	2.13(4)
C2-W6P$^{\mathrm{III}}$	2.31(3)

W2 polyhedron	
W2-C1	2.30(2)
W2-C2	2.99(3)
W2-C2$^{\mathrm{V}}$	
W2-O1P$^{\mathrm{III}}$	2.83(2)
W2-O1P$^{\mathrm{VII}}$	
W2-O7P$^{\mathrm{III}}$	2.92(2)
W2-W1	0.83(3)
W2-W1$^{\mathrm{V}}$	

W4P polyhedron	
W4P-C1P	1.86(3)
W4P-C2P	2.52(4)
W4P-C2P$^{\mathrm{IV}}$	
W4P-C3	2.65(6)
W4P-W1P	1.91(3)
W4P-W1P$^{\mathrm{IV}}$	
W4P-W2P	2.94(2)
W4P-W2P$^{\mathrm{IV}}$	
W4P-W3P	1.50(3)
W4P-W3P$^{\mathrm{V}}$	2.17(4)
W4P-W4P$^{\mathrm{V}}$	2.78(6)
W4P-W6$^{\mathrm{XI}}$	3.12(3)

W6 polyhedron	
W6-C1P$^{\mathrm{III}}$	2.53(1)
W6-C2P$^{\mathrm{I}}$	2.59(3)
W6-C2P$^{\mathrm{XII}}$	
W6-C2P$^{\mathrm{III}}$	2.21(3)
W6-C2P$^{\mathrm{XV}}$	
W6-O4	2.90(1)
W6-O4$^{\mathrm{XIII}}$	
W6-W1P$^{\mathrm{I}}$	3.29(2)
W6-W1P$^{\mathrm{XII}}$	
W6-W1P$^{\mathrm{III}}$	2.73(2)
W6-W1P$^{\mathrm{XV}}$	
W6-W4P$^{\mathrm{III}}$	3.12(3)
W6-W5	1.38(3)
W6-W5$^{\mathrm{V}}$	2.22(3)
W6-W8	2.48(5)

C2P polyhedron	
C2P-C1P	3.16(3) Å
C2P-C2P$^{\mathrm{IV}}$	2.31(5)
C2P-C2P$^{\mathrm{IX}}$	2.62(5)
C2P-C2P$^{\mathrm{X}}$	1.25(5)
C2P-O1$^{\mathrm{I}}$	3.02(3)
C2P-O1$^{\mathrm{XI}}$	2.92(2)
C2P-W1P	1.11(2)
C2P-W1P$^{\mathrm{IV}}$	2.86(3)
C2P-W1P$^{\mathrm{X}}$	2.32(3)
C2P-W2P	3.23(2)
C2P-W4P	2.52(4)
C2P-W6$^{\mathrm{I}}$	2.59(3)
C2P-W6$^{\mathrm{XI}}$	2.21(3)

W2P polyhedron	
W2P-C1P	2.40(1)
W2P-C2P	3.23(2)
W2P-C2P$^{\mathrm{V}}$	
W2P-O3P	3.22(1)
W2P-O3P$^{\mathrm{V}}$	
W2P$^{\mathrm{III}}$-O7	2.96(1)
W2P-W1P	2.37(2)
W2P-W1P$^{\mathrm{V}}$	
W2P-W3P	3.24(2)
W2P-W3P$^{\mathrm{V}}$	
W2P-W4P	2.94(2)
W2P-W4P$^{\mathrm{V}}$	

W5 polyhedron	
W5-C1P$^{\mathrm{III}}$	2.47(3)
W5-O4	2.98(2)
W5-O4$^{\mathrm{XIII}}$	
W5-W5$^{\mathrm{V}}$	0.89(6)
W5-W6	1.38(3)
W5-W6$^{\mathrm{V}}$	2.22(3)
W5-W8	1.32(6)

W6P polyhedron	
W6P-C1$^{\mathrm{XI}}$	2.99(3)
W6P-C2$^{\mathrm{I}}$	2.13(4)
W6P-C2$^{\mathrm{XII}}$	
W6P-C2$^{\mathrm{XI}}$	2.31(3)
W6P-C2$^{\mathrm{XIV}}$	
W6P-O4P	3.02(2)
W6P-O4P$^{\mathrm{XIII}}$	
W6P-W4$^{\mathrm{I}}$	2.57(4)
W6P-W5P	1.61(3)
W6P-W5P$^{\mathrm{V}}$	3.05(5)
W6P-W6P$^{\mathrm{X}}$	3.21(5)
W6P-W8P	2.65(3)

C3 polyhedron	
C3-C3$^{\mathrm{V}}$	2.43(7)
C3-O8	2.47(2)
C3-O8$^{\mathrm{IV}}$	
C3-O9$^{\mathrm{I}}$	2.96(3)
C3-O10	3.01(2)
C3-O10$^{\mathrm{IV}}$	
C3-W3	1.13(4)
C3-W3$^{\mathrm{V}}$	2.50(4)
C3-W3P	1.68(5)
C3-W3P$^{\mathrm{V}}$	2.22(5)
C3-W4	2.29(6)
C3-W4P	2.65(6)

W3 polyhedron	
W3-C1	2.61(3)
W3-C2	3.13(4)
W3-C2$^{\mathrm{IV}}$	
W3-C3	1.13(4)
W3-C3$^{\mathrm{V}}$	2.50(4)
W3-O8	2.92(2)
W3-O8$^{\mathrm{IV}}$	
W3-O10	3.24(2)
W3-O10$^{\mathrm{IV}}$	
W3-W1	3.07(3)
W3-W1$^{\mathrm{IV}}$	
W3-W3$^{\mathrm{V}}$	2.05(6)
W3-W3P	2.66(3)
W3-W3P$^{\mathrm{V}}$	2.98(3)
W3-W4	1.50(4)

W5P polyhedron	
W5P-C1$^{\mathrm{XI}}$	2.37(2)
W5P-C2$^{\mathrm{XI}}$	3.27(3)
W5P-C2$^{\mathrm{XIV}}$	
W5P-O4P	3.03(2)
W5P-O4P$^{\mathrm{XIII}}$	
W5P-W1$^{\mathrm{XI}}$	3.22(2)
W5P-W1$^{\mathrm{XIV}}$	
W5P-W5P$^{\mathrm{V}}$	1.46(5)
W5P-W6P	1.61(3)
W5P-W6P$^{\mathrm{V}}$	3.05(5)
W5P-W8P	1.21(2)

W8 polyhedron	
W8-O4	2.93(1)
W8-O4$^{\mathrm{XIII}}$	
W8-O4$^{\mathrm{V}}$	
W8-O4$^{\mathrm{XVI}}$	
W8-O9	3.04(3)
W8-O9$^{\mathrm{V}}$	
W8-W5	1.32(6)
W8-W5$^{\mathrm{V}}$	
W8-W6	2.48(5)
W8-W6$^{\mathrm{V}}$	

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(1) Distances too short for simultaneous occupation of both sites are also reported.

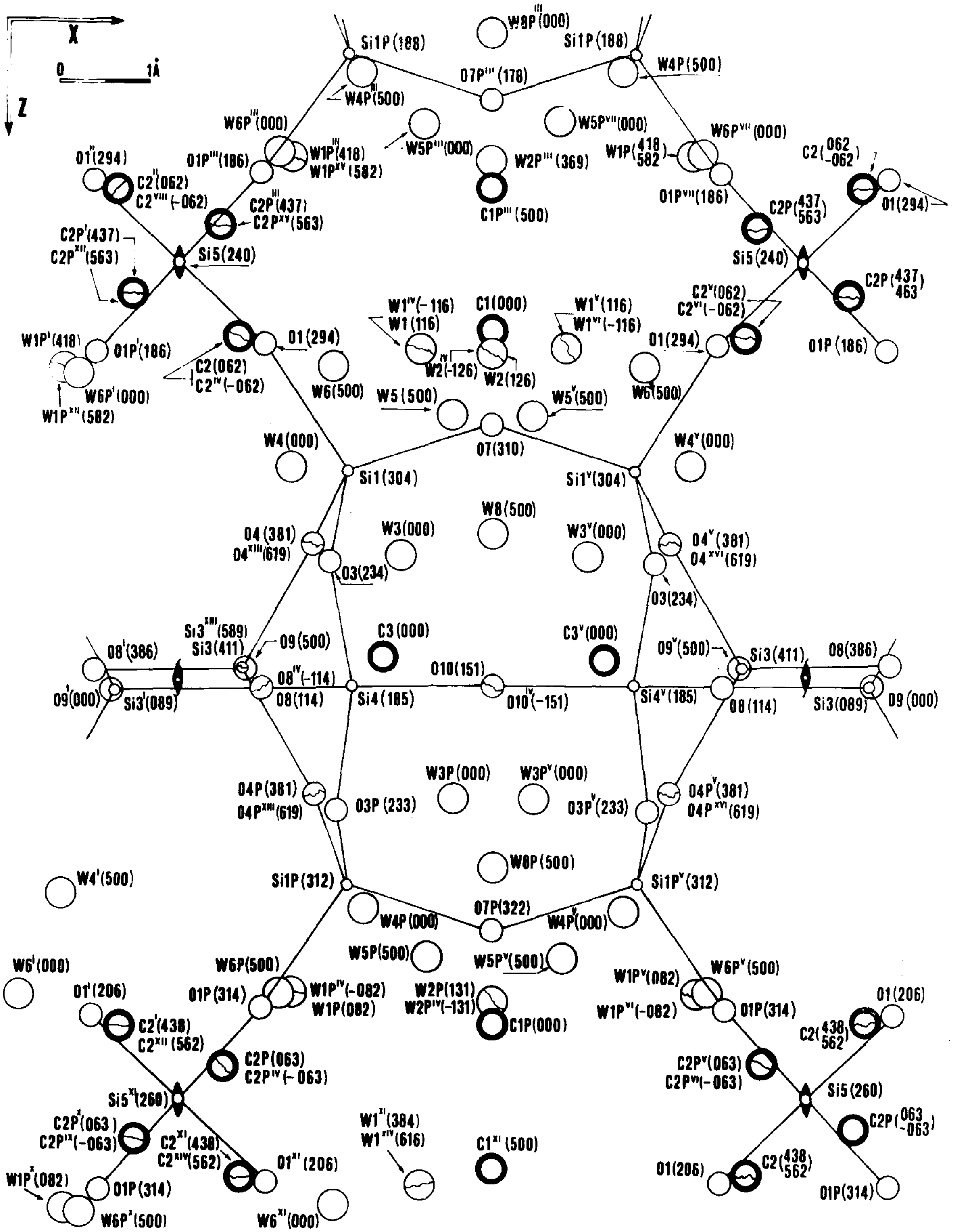

FIG. 1. — Part of the structure of barrerite projected along *b*. Codes of the atoms are those given in Table II, and three digit numbers in parentheses give the height above the plane $y = 0$. The part of the structure shown here corresponds to the part of the stellerite structure shown in Figure 1 of Galli and Alberti (1975).

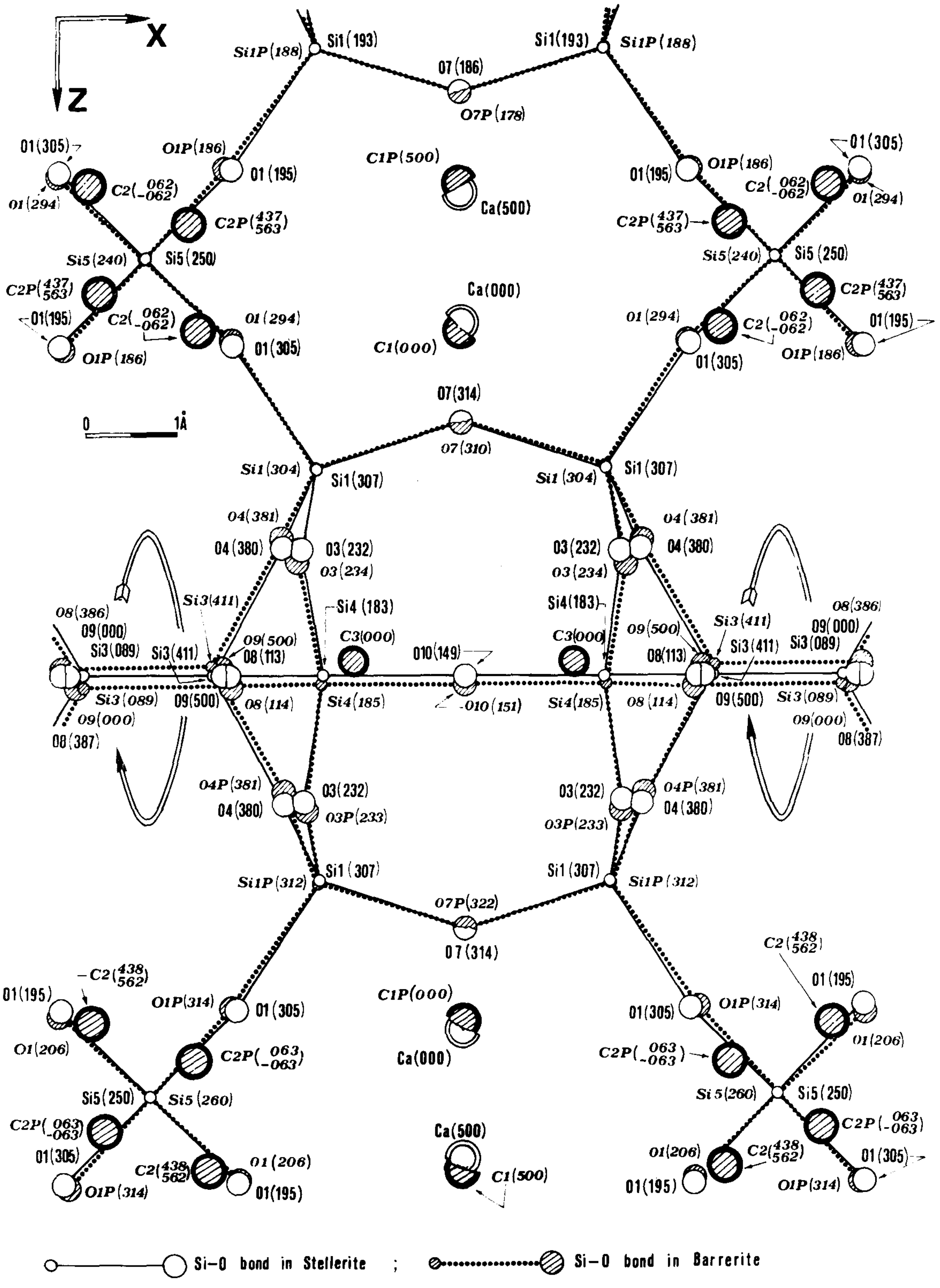

FIG. 2. — Comparison of the framework and the exchangeable cations of barrerite with those of stellerire. C2 and C3 cation sites are absent in stellerite. It is possible to transform the stellerite framework into the barrerite framework by a slight rotation around a screw diad parallel to *a* (see curved arrow). The direction of this rotation is reversed in nearby screw diads, so that (010) mirror planes are maintained, whereas (001) mirror planes disappear. In this and following figures dashed circles refer to barrerite, empty circles to stellerite.

DISCUSSION OF THE STRUCTURE OF BARRERITE AND COMPARISON WITH STELLERITE AND STILBITE

The most stricking difference between the three minerals is their total number of cations, which is ≃ 8 in stellerite, ≃ 12 in stilbite (considering its pseudo-orthorhombic cell), and ≃ 16 in barrerite. From the structural point of view this means that :

A) in stellerite all cations (mainly Ca) are located in one set of equivalent positions, in a widening of the main channel, without contact with the oxygens of the framework, because they are completely surrounded by water molecules ;

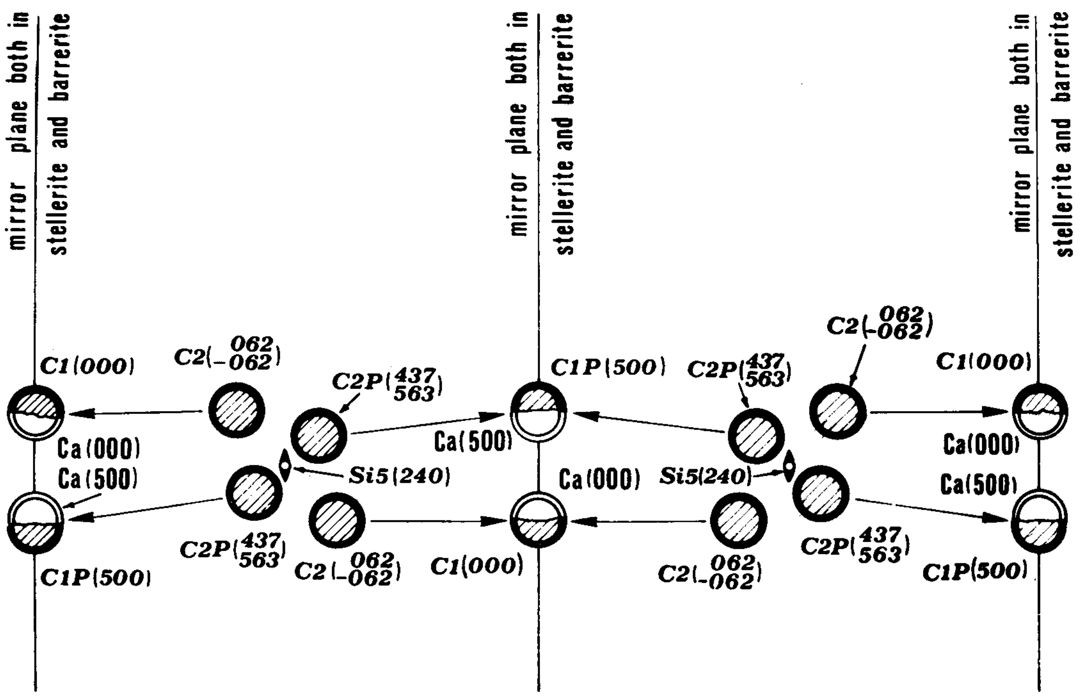

FIG. 3. — Detail of the C1 and C2 cation sites, showing the repulsion forces which are present on both sides of the mirror planes of stellerite, which therefore is maintained in barrerite (compare this drawing with Figure 4 of Galli and Alberti, 1975).

B) in stilbite 8Ca have the same location as in stellerite, whereas 4Na are located near Si (5), causing the lowering of the symmetry to the monoclinic system (see Galli and Alberti, 1975) ;

C) in barrerite nearly 16 cations (mainly Na and K) are distributed not only in the locations (C1 and C1P) which are characteristic for Ca in stellerite and stilbite, and in the locations (C2 and C2P) which are characteristic for Na in stilbite, but also in a third new location (C3).

When the number of cations is the lowest (8Ca), the symmetry is at its highest (*Fmmm*) ; in stilbite the cation number is 12 (= 8Ca + 4Na) and the symmetry is *C2/m* ; in barrerite the cation number is the highest (16Na) and the symmetry is *Amma*. Galli and Alberti (1975) (in particular Fig. 4) have shown how the presence of Na-cations in stilbite forces the framework to rotate (Fig. 3 of the same authors) and thus to reduce the symmetry. Something similar happens in the structure of barrerite. Figure 2 compares the actual frameworks of stellerite and barrerite, showing that here another rotation occurs in place of that of stilbite. Repulsions from cations C2, which cause rotation in stilbite, is here counteracted by position C2P, so that the stilbite rotation does not take place here, (see Fig. 3) but the cation site C3 forces the framework to rotate around the screw diads parallel to *a*. This barrerite rotation can be better perceived when the structure is viewed along *a* (Fig. 4). Figure 5 gives a summary of the two kinds of rotations, which differ not only for the different orientations of their axes, but also because of the direction of rotation, which is always the same in one case, and is alternated in the other one. Hence stellerite, stilbite and barrerite form a group of zeolites where the symmetry of the framework is differently lowered by different cation contents. This is not the only case of this phenomenon (lowerings of symmetry due to order-disorder phenomena are not considered here) the other one being present in the natrolite, mesolite and scolecite group, where the differences in cations result in two different space groups (*Fdd2*, *Fdd2*, *Cc*) and in mesolite a *b* axis (56.674 Å) which is three times the *b* axis of scolecite and natrolite.

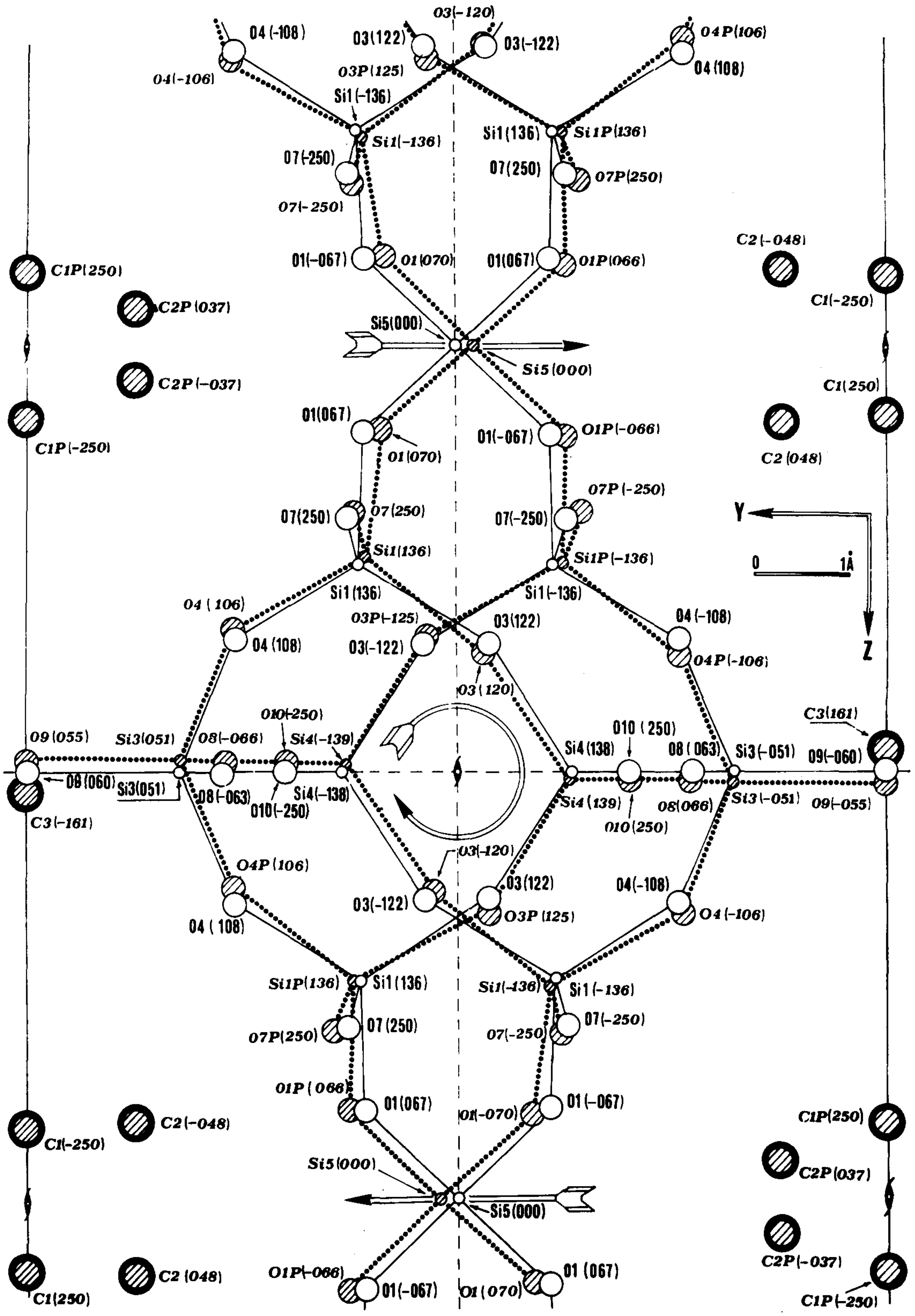

FIG. 4. — Comparison of the framework and exchangeable cations of both stellerite and barrerite, made in the same way as Figure 2, but projected along *a*. To superpose stellerite with barrerite, the necessary rotation is here clockwise, but it is counterclockwise on the next screw diad, both in the *b*- and *c*-direction.

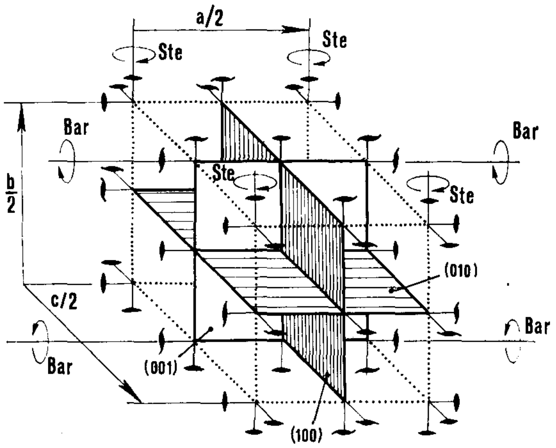

Fig. 5. — Symmetry elements of space group *Fmmm*, which is the highest possible symmetry for the framework of both stellerite-stilbite and barrerite, and coincides with the symmetry of stellerite. By a slight rotation around the diads coded Ste, the (100)- and (001)-mirrors disappear, and symmetry becomes *C2/m* (space group of stilbite); the rotation direction is always the same around all diads. By a slight rotation around the screw diads coded Bar, the (001)-mirrors disappear and the symmetry becomes *Amma* (space group of barrerite); the rotation direction changes alternatively, following a row of Bar-screw diads.

In other groups of zeolites with the same framework, such as heulandite-clinoptilolite or phillipsite-harmotome the different cation content is not associated with symmetry changes, although differences in other properties may be striking.

Similarly to the cases of stibilite and stellerite no indication of Si/Al ordering was found in barrerite.

The average value of the (Si, Al)-O distances (1.635) is in good agreement with the value expected on the basis of the Al content (Jones, 1968). While the cations exhibit very marked anisotropy, the vibrations of all of the framework atoms are not significantly anisotropic.

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