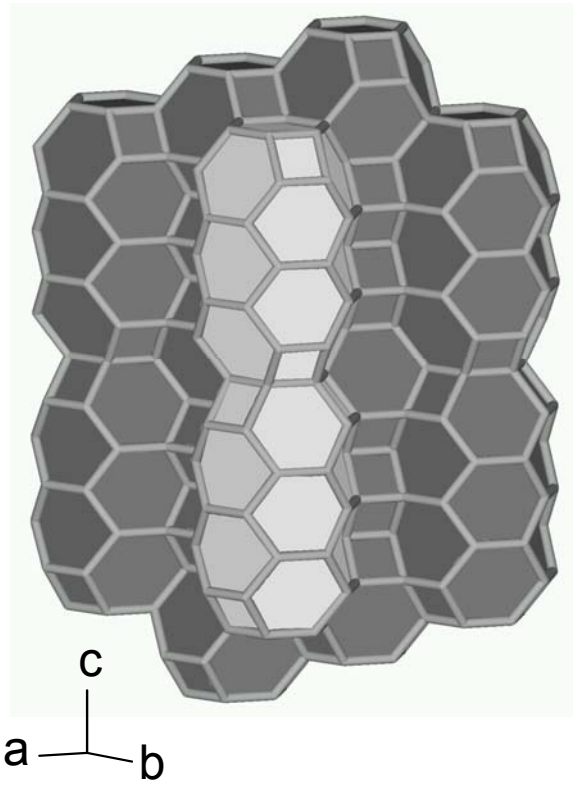
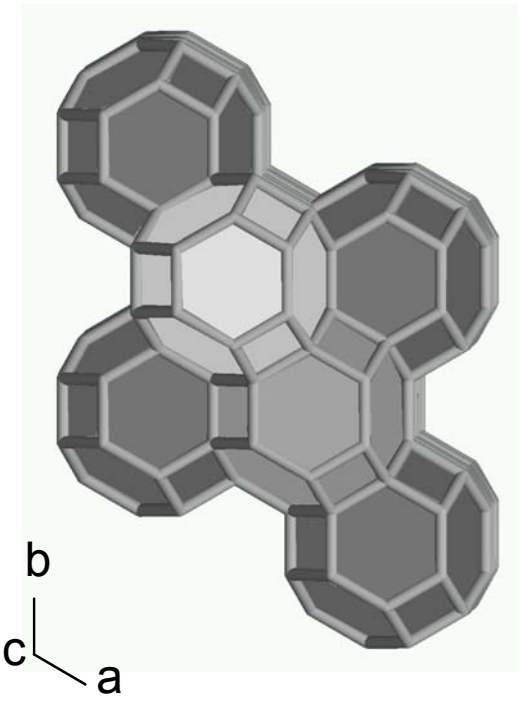
MAR

MAR.1 Zeolite framework type and topology

The framework type code is named after the mineral **MAR**inellite, $(Na,K)_{42}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4\,2Cl\,6H_2O$, first found in volcanic rocks at Sacrofano, Biacchella Valley, Latium (Italy), and described by Bonaccorsi and Orlandi [2003Bon1]. Marinellite belongs to the cancrinite family of minerals, thus representing a feldspathoid with an open framework closely related to zeolites.



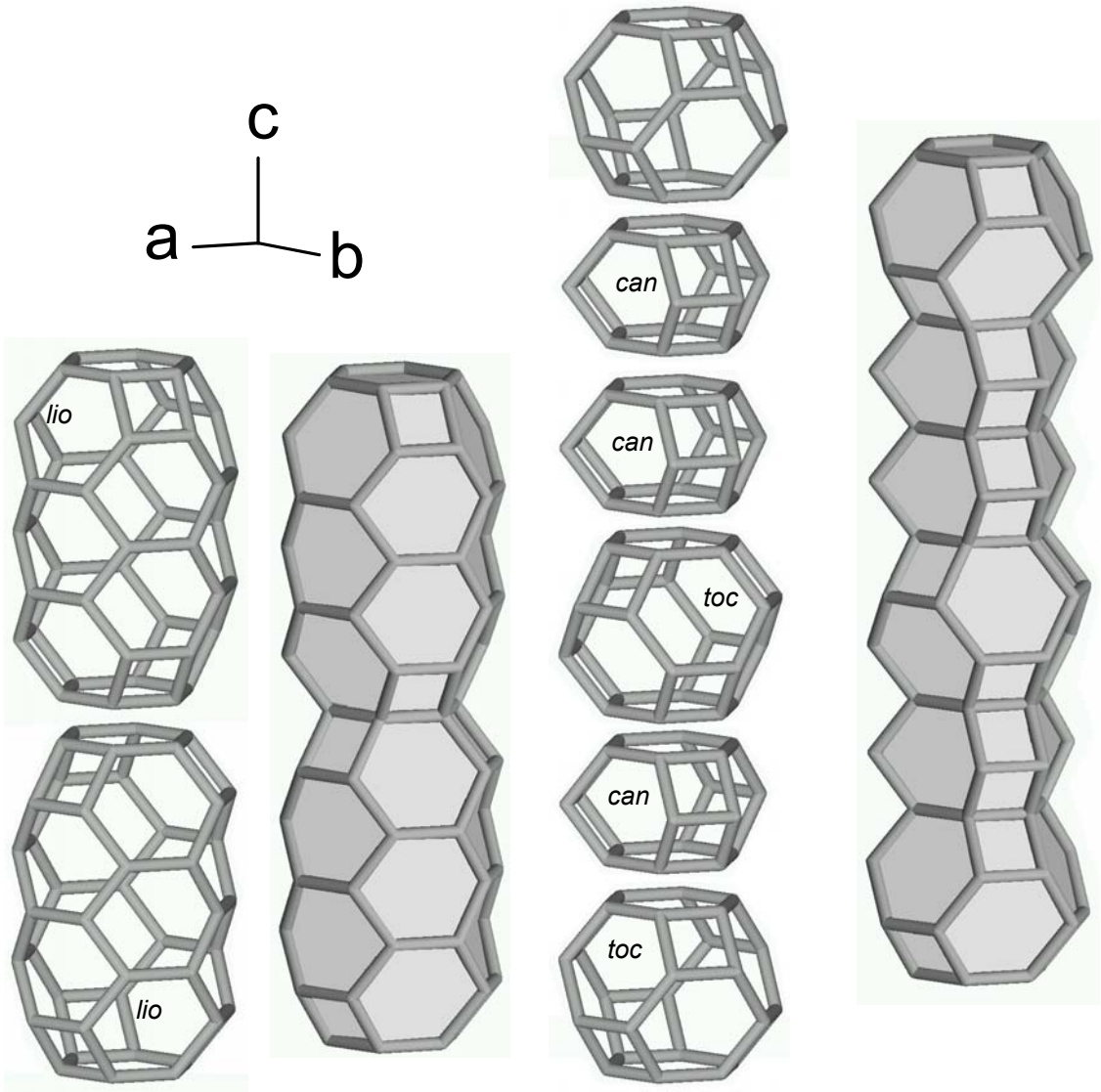
a View parallel [110] rotated by 10° about [$\bar{1}$ 10] and [001].



b View parallel [001] rotated by 1° about [210] and [010].

Fig. MAR.1.1. The framework structure of MAR-type compounds in the highest possible topological symmetry $P\,6_3/m\,m\,c$.

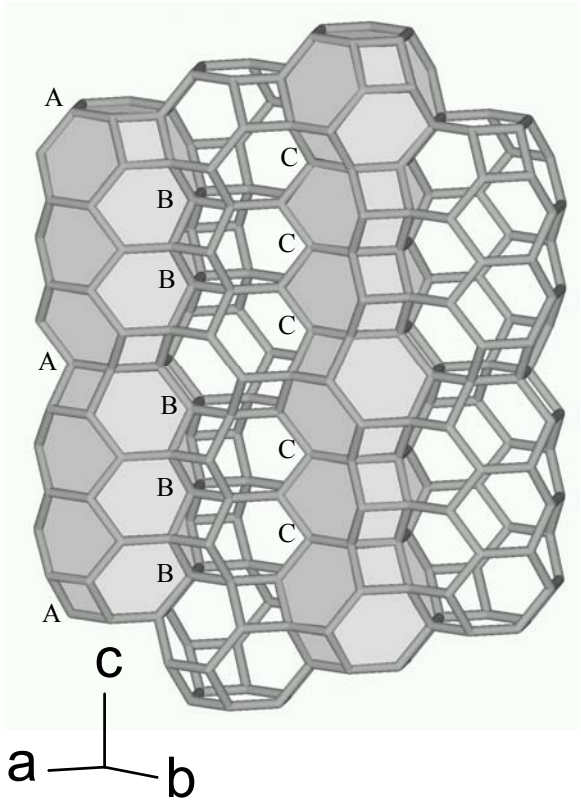
The framework structure consists of a hexagonal arrangement of *lio* ($4^6 6^6 6^6 6^3 6^2$) units forming pillars (Fig. MAR.1.2a) parallel **c** enclosing pillars of alternating *can* ($4^6 6^3 6^2$) and *toc* ($4^6 6^8$) units (Fig. MAR.1.2b) as shown in Fig. MAR.1.1 and MAR.1.2. Marinellite belongs to the ABC-6 family of frameworks (see CHA.1 and [99Gie1] for additional information) built by different stackings of 6-ring layers. The stacking sequence for marinellite is ABCBCBACBCBC... as shown in Fig. MAR.1.2d.



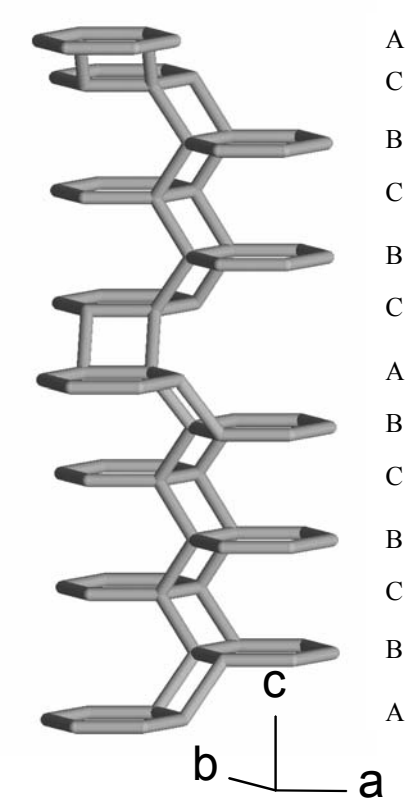
a Linkage of *lio* units forming pillars parallel [001].

b Linkage of *can* and *toc* units forming pillars parallel [001].

Fig. MAR.1.2. Building scheme and stacking sequence of the MAR-type framework. View parallel [110] rotated by 10° about about [$\bar{1}$ 10] and [001] (except figure d).



c Linkage of units and stacking sequence of 6-rings in the (110) plane in solid and transparent representation.



d The stacking sequence of layers shown by the stacking of 6-rings parallel [001]. View parallel [$\bar{1}$ $\bar{2}$ 0] rotated by 7° about [100] and 6° about [001]. The choice of 6-rings differs from figure c).

Fig. MAR.1.2 (continued). Building scheme and stacking sequence of the MAR-type framework. View parallel [110] rotated by 10° about about [$\bar{1}$ 10] and [001] (except figure d).

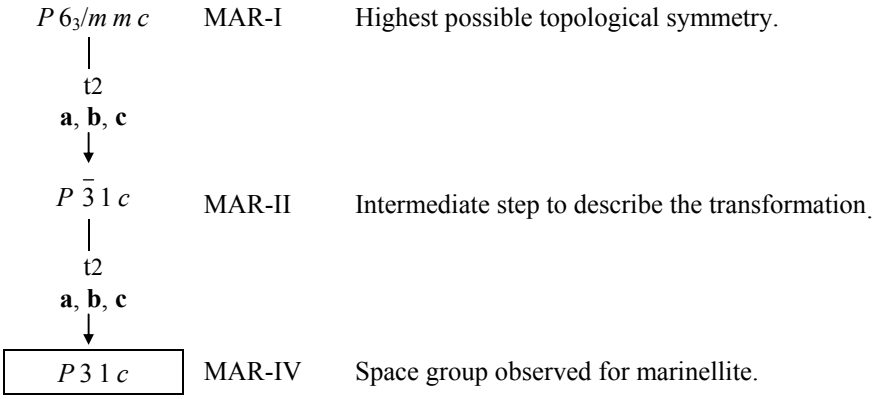


Fig. MAR.1.3 The Bärnighausen tree illustrating the symmetry relationship of the MAR types.

Table MAR.1.1 Atomic site relationships of the MAR types.

MAR-I $P\,6_3/m\,m\,c$	MAR-II $P\,\bar{3}\,1\,c$	MAR-IV $P\,3\,1\,c$
T1 [24(l), 1]	T11 [12(i), 1]	T11a [6(c), 1] T11b [6(c), 1]
	T12 [12(i), 1]	T12a [6(c), 1] T12b [6(c), 1]
T2 [24(l), 1]	T21 [12(i), 1]	T21a [6(c), 1] T21b [6(c), 1]
	T22 [12(i), 1]	T22a [6(c), 1] T22b [6(c), 1]
T3 [12(j), *m* . .]	T3 [12(i), 1]	T31 [6(c), 1] T32 [6(c), 1]
T4 [12(j), *m* . .]	T4 [12(i), 1]	T41 [6(c), 1] T42 [6(c), 1]
O1 [24(l), 1]	O11 [12(i), 1]	O11a [6(c), 1] O11b [6(c), 1]
	O12 [12(i), 1]	O12a [6(c), 1] O12b [6(c), 1]
O2 [24(l), 1]	O21 [12(i), 1]	O21a [6(c), 1] O21b [6(c), 1]
	O22 [12(i), 1]	O22a [6(c), 1] O22b [6(c), 1]
O3 [24(l), 1]	O31 [12(i), 1]	O31a [6(c), 1] O31b [6(c), 1]
	O32 [12(i), 1]	O32a [6(c), 1] O32b [6(c), 1]
O4 [12(k), . *m* .]	O4 [12(i), 1]	O41 [6(c), 1] O42 [6(c), 1]
O5 [12(k), . *m* .]	O5 [12(i), 1]	O51 [6(c), 1] O52 [6(c), 1]
O6 [12(k), . *m* .]	O6 [12(i), 1]	O61 [6(c), 1] O62 [6(c), 1]
O7 [12(k), .m.]	O7 [12(i), 1]	O71 [6(c), 1] O72 [6(c), 1]

Table MAR.1.1 (continued).

MAR-I $P6_3/m\,m\,c$		MAR-II $P\bar{3}1\,c$		MAR-IV $P31\,c$
O8 [12(k), . *m* .]	→	O8 [12(i), 1]	→	O81 [6(c), 1] O82 [6(c), 1]
O9 [6(h), *m m* 2]	→	O9 [6(h), . . 2]	→	O9 [6(c), 1]
O10[6(h), *m m* 2]	→	O10 [6(h), . . 2]	→	O10 [6(c), 1]

MAR.2 Compounds and crystal data

Table MAR.2.1 Chemical data.

FD = framework density CE = cation exchange TT = thermal treatment REF = reference
SM = source of material SR = sorbate T = temperature of thermal treatment [K]

code	chemical composition	FD	SM	CE	SR	TT	T	REF
MAR-IV *P*31*c*								
MAR2003a01	$Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O	15.8	M	-	SO_4, Cl, H_2O	-	-	2003Bon1

Table MAR.2.2 Structural parameters of MAR-type compounds.

code	*a* [Å]	*c* [Å]	*V* [Å^3]	*T* [K]	reference
MAR-IV *P*31*c*					
MAR2003a01	12.880(2)	31.761(6)	4563	n.s.	2003Bon1

MAR.3 Framework structure of MAR-IV compound (*P*31*c*, IT #159)

Table MAR.3.1 Atomic coordinates and site definitions for marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1).

atom	*x*	*y*	*z*	*B* [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Si11a	0.9171(8)	0.5809(7)	0.0975(3)	0.71(8)	1	6(c)	6
Al 11b	0.0815(9)	0.4170(9)	0.9297(4)	0.87(8)	1	6(c)	6
Al 12a	0.0814(9)	0.4110(9)	0.5972(4)	0.87(8)	1	6(c)	6
Si12b	0.9164(8)	0.5839(8)	0.4302(3)	0.71(8)	1	6(c)	6
Si21a	0.5863(8)	0.6698(8)	0.1800(3)	0.71(8)	1	6(c)	6
Al21b	0.4202(8)	0.343(1)	0.8455(3)	0.63(8)	1	6(c)	6
Al22a	0.4189(8)	0.343(1)	0.6804(3)	0.63(8)	1	6(c)	6

Table MAR.3.1 (continued) Atomic coordinates and site definitions for marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1).

atom	x	y	z	B [Å2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Si22b	0.5850(7)	0.6716(8)	0.3468(3)	0.71(8)	1	6(c)	6
Si31	0.9170(7)	0.5840(7)	0.2634(3)	0.6(2)	1	6(c)	6
Al32	0.0769(7)	0.4137(7)	0.7637(4)	0.6(2)	1	6(c)	6
Si41	0.2510(7)	-0.0016(9)	0.0144(3)	0.71(8)	1	6(c)	6
Al42	0.7480(8)	0.0022(9)	0.0132(4)	0.9(2)	1	6(c)	6
O11a	0.333(3)	0.013(3)	0.052(1)	4.1(6)	1	6(c)	6
O11b	0.688(2)	0.995(2)	0.9655(5)	0.7(2)	1	6(c)	6
O12a	0.639(2)	0.970(2)	0.5487(5)	0.7(2)	1	6(c)	6
O12b	0.327(3)	0.007(3)	0.471(1)	4.1(6)	1	6(c)	6
O21a	0.330(2)	0.356(2)	0.1321(7)	1.0(2)	1	6(c)	6
O21b	0.662(3)	0.659(3)	0.886(1)	2.8(4)	1	6(c)	6
O22a	0.664(3)	0.650(3)	0.635(1)	2.8(4)	1	6(c)	6
O22b	0.364(2)	0.343(2)	0.3836(6)	1.0(2)	1	6(c)	6
O31a	0.665(2)	0.661(2)	0.2171(8)	1.9(3)	1	6(c)	6
O31b	0.354(2)	0.338(2)	0.7994(6)	1.0(2)	1	6(c)	6
O32a	0.330(2)	0.360(2)	0.7166(6)	1.0(2)	1	6(c)	6
O32b	0.647(2)	0.681(2)	0.2999(8)	1.9(3)	1	6(c)	6
O41	0.103(3)	0.217(1)	0.5123(5)	2.1(2)	1	6(c)	6
O42	0.872(3)	0.752(1)	0.5250(5)	2.1(2)	1	6(c)	6
O51	0.212(3)	0.418(2)	0.6062(6)	2.6(2)	1	6(c)	6
O52	0.776(4)	0.547(2)	0.4300(6)	2.6(2)	1	6(c)	6
O61	0.441(3)	0.887(2)	0.5942(5)	2.6(2)	1	6(c)	6
O62	0.545(4)	0.082(2)	0.4407(5)	2.6(2)	1	6(c)	6
O71	0.795(2)	0.594(1)	0.6873(4)	1.3(2)	1	6(c)	6
O72	0.203(2)	0.405(1)	0.3548(4)	1.3(2)	1	6(c)	6
O81	0.432(2)	0.876(2)	0.1826(5)	1.5(2)	1	6(c)	6
O82	0.555(3)	0.128(2)	0.8468(5)	1.5(2)	1	6(c)	6
O9	0.800(2)	0.595(1)	0.2714(4)	1.6(2)	1	6(c)	6
O10	0.564(2)	0.119(1)	0.2652(6)	1.7(2)	1	6(c)	6
S1	0	0	0.1163(7)	5.9(5)	3 . .	2(a)	2
OA1	0	0	0.07030(0)	9.47	3 . .	2(a)	2
OB1	0.072(6)	0.121(4)	0.131(1)	3.2(8)	1	6(c)	6
S2	0	0	0.2559(4)	3.0(2)	3 . .	2(a)	2
OA2	0	0	0.3020(7)	9.47	3 . .	2(a)	2
OB2	0.038(6)	0.113(5)	0.232(2)	4.7(8)	1	6(c)	6
OA2b	0	0	0.2099(7)	9.47	3 . .	2(a)	2
OB2b	0.068(5)	0.115(3)	0.277(1)	2.8(7)	1	6(c)	6
S3	0	0	0.4092(4)	2.8(2)	3 . .	2(a)	2
OA3	0	0	0.450(2)	9.47	3 . .	2(a)	2
OB3	0.062(6)	0.121(3)	0.3886(9)	6.0(7)	1	6(c)	6
S4	1/3	2/3	0.467(1)	8.7(8)	3 . .	2(b)	2
OA4	1/3	2/3	0.421(2)	9.47	3 . .	2(b)	2
OB4	0.40(1)	0.62(1)	0.491(3)	8(2)	1	6(c)	6
OA4b	1/3	2/3	0.513(2)	9.47	3 . .	2(b)	2
OB4b	0.463(4)	0.727(8)	0.444(1)	3.2(8)	1	6(c)	6
Cl5	0.372(2)	0.667(3)	0.0589(9)	3.4(6)	1	6(c)	6
K1	0.2320(8)	0.1159(9)	0.1808(3)	3.9(2)	1	6(c)	5.58
K2	0.2302(6)	0.1164(9)	0.3391(2)	2.8(2)	1	6(c)	5.40

Table MAR.3.1 (continued) Atomic coordinates and site definitions for marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1).

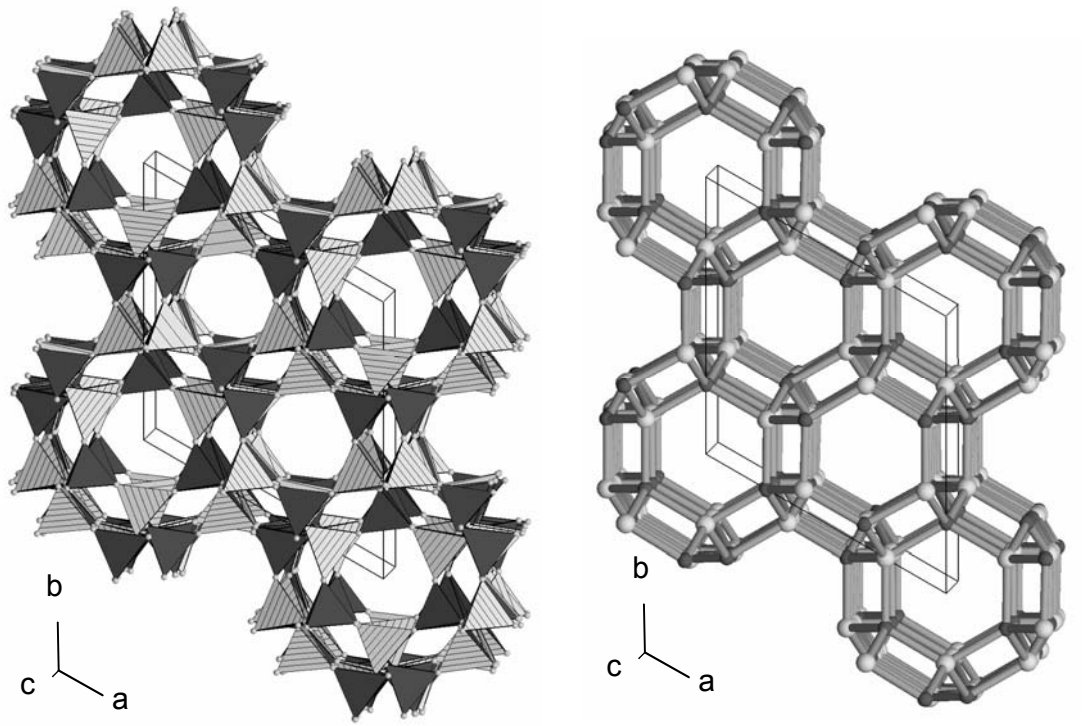
atom	x	y	z	B [Å2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Na1	0.201(4)	0.401(2)	0.0856(7)	3.1(2)	1	6(c)	3.00
Na1b	0.160(2)	0.316(1)	0.1001(4)	3.1(2)	1	6(c)	0.42
Na2	0.6882(7)	0.844(2)	0.2608(4)	2.4(2)	1	6(c)	0.60
Na3	0.153(2)	0.839(2)	0.4259(3)	1.6(2)	1	6(c)	6
Ca1	0	0	0.5256(6)	1.3(2)	3 . .	2(a)	1.08
Ca1b	0	0	0.507(1)	1.3(2)	3 . .	2(a)	2
Na4	1/3	2/3	0.159(1)	1.7(4)	3 . .	2(b)	2
Na4b	1/3	2/3	0.186(1)	1.7(4)	3 . .	2(b)	2
Na5	1/3	2/3	0.3783(9)	1.0(3)	3 . .	2(b)	2
Na5b	1/3	2/3	0.3553(9)	1.0(3)	3 . .	2(b)	2
Na6	2/3	1/3	0.102(2)	3.9(6)	3 . .	2(b)	2
Na6b	2/3	1/3	0.065(2)	3.9(6)	3 . .	2(b)	2
Na7	2/3	1/3	0.283(1)	2.4(3)	3 . .	2(b)	2
Na7b	2/3	1/3	0.247(1)	2.4(3)	3 . .	2(b)	2
Na8	2/3	1/3	0.469(1)	1.7(4)	3 . .	2(b)	2
Na8b	2/3	1/3	0.452(1)	1.7(4)	3 . .	2(b)	2
Na9	0.019(1)	0.511(2)	0.0161(5)	2.4(2)	1	6(c)	6
Na9b	0.919(2)	0.457(3)	0.0036(6)	2.4(2)	1	6(c)	6
W1	0.31(1)	0.609(5)	0.265(3)	7(2)	1	6(c)	6
W2	2/3	1/3	0.357(2)	4.7(8)	3 . .	2(b)	2
W3	0.712(5)	0.34(1)	0.185(2)	13(2)	1	6(c)	6

Table MAR.3. 2 Selected interatomic distances and angles for marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si11a - O51	1.62(5)	160(1)	Al 11b - O62	1.68(5)	156(1)
Si11a - O61	1.65(3)	155(2)	Al 11b - O12b	1.70(3)	152(1)
Si11a - O21a	1.70(4)	138(2)	Al 11b - O52	1.72(3)	152(2)
Si11a - O12a	1.71(2)	148(1)	Al 11b - O21b	1.74(4)	149(2)
Mean	1.67	150	mean	1.71	152
Al 12a - O22a	1.64(4)	152(2)	Si12b - O62	1.60(3)	156(1)
Al 12a - O51	1.66(3)	160(1)	Si12b - O52	1.62(6)	152(2)
Al 12a - O61	1.68(5)	155(2)	Si12b - O11b	1.65(2)	149(1)
Al 12a - O11a	1.72(3)	154(1)	Si12b - O22b	1.66(3)	152(1)
Mean	1.68	155	Mean	1.63	152
Si21a - O71	1.58(2)	163(1)	Al21b - O22b	1.67(3)	152(1)
Si21a - O31a	1.60(3)	146(2)	Al21b - O31b	1.68(2)	145(2)
Si21a - O81	1.64(4)	145(1)	Al21b - O82	1.74(2)	144(1)
Si21a - O22a	1.67(3)	152(2)	Al21b - O72	1.74(2)	159(1)
Mean	1.62	152	Mean	1.71	152

Table MAR.3.2 (continued) Selected interatomic distances and angles for marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1).

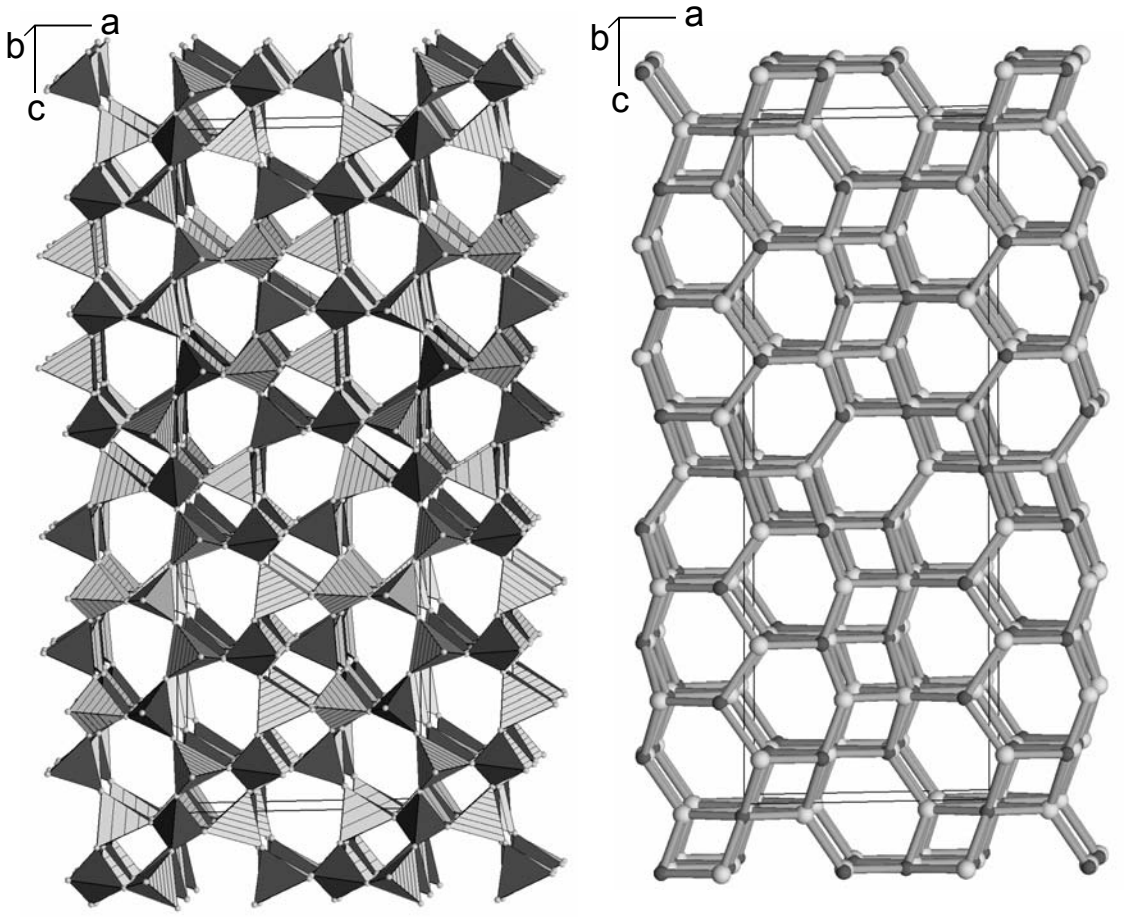
	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Al22a - O81	1.70(2)	145(1)	Si22b - O72	1.59(2)	159(1)
Al22a - O21a	1.70(3)	138(2)	Si22b - O82	1.60(4)	144(1)
Al22a - O32a	1.71(3)	142(1)	Si22b - O21b	1.61(3)	149(2)
Al22a - O71	1.77(2)	163(1)	Si22b - O32b	1.67(3)	139(1)
Mean	1.72	147	Mean	1.62	148
Si31 - O9	1.60(3)	161(1)	Al32 - O9	1.73(2)	161(1)
Si31 - O10	1.61(2)	150(1)	Al32 - O10	1.73(3)	150(1)
Si31 - O31b	1.63(3)	145(2)	Al32 - O31a	1.76(3)	146(2)
Si31 - O32a	1.64(2)	142(1)	Al32 - O32b	1.76(3)	139(1)
Mean	1.62	152	Mean	1.75	149
Si41 - O11a	1.54(3)	154(1)	Al42 - O12a	1.67(3)	148(1)
Si41 - O42	1.59(4)	155(1)	Al42 - O11b	1.68(2)	149(1)
Si41 - O41	1.61(3)	152(1)	Al42 - O41	1.73(3)	152(1)
Si41 - O12b	1.66(4)	152(1)	Al42 - O42	1.74(5)	155(1)
Mean	1.60	153	Mean	1.71	151



a Polyhedral representation. View parallel [001] rotated by 1° about [210] and [010].

b Ball and stick model corresponding to a).

Fig. MAR.3.1.1 Projections of the crystal structure of marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1). SiO_4 tetrahedra are dark grey, AlO_4 tetrahedra are light grey and hatched.



c Polyhedral representation. View parallel [010] rotated by 2° about [210] and [001].

d Ball and stick model corresponding to a).

Fig. MAR.3.1.1 (continued). Projections of the crystal structure of marinellite, $Na_{32}K_{11}Ca_6 \cdot Al_{36}Si_{36}O_{144} \cdot 8SO_4$ 1.6Cl 3.4H_2O (MAR2003a01, 2003Bon1). SiO_4 tetrahedra are dark grey, AlO_4 tetrahedra are light grey and hatched.

MAR.4 Chemical composition

	D																
H																	He
Li	Be											B	C	N	***O***	F	Ne
Na	Mg											**Al**	**Si**	P	**S**	**Cl**	Ar
K	**Ca**	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

Fig. MAR.4.1 Chemical elements (highlighted) occurring in marinellite. Framework cations are in grey fields.

MAR.5 Flexibility and apertures

There is insufficient information about the MAR-type framework to infer anything about its flexibility.

The overall spread of values of the individual T-O-T angles in the MAR-type framework ranges only from ca. 138° to 163°, with a mean value of 151°. This is much larger than the mean value observed in the sample of 2436 T-O-T values for silicoaluminates zeolite frameworks generally, which is 141° [95Bau1].

The MAR-type has only 6-ring openings.

MAR.6 Other information

Nothing has been reported about useful properties of the MAR-type.

MAR.7 References

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