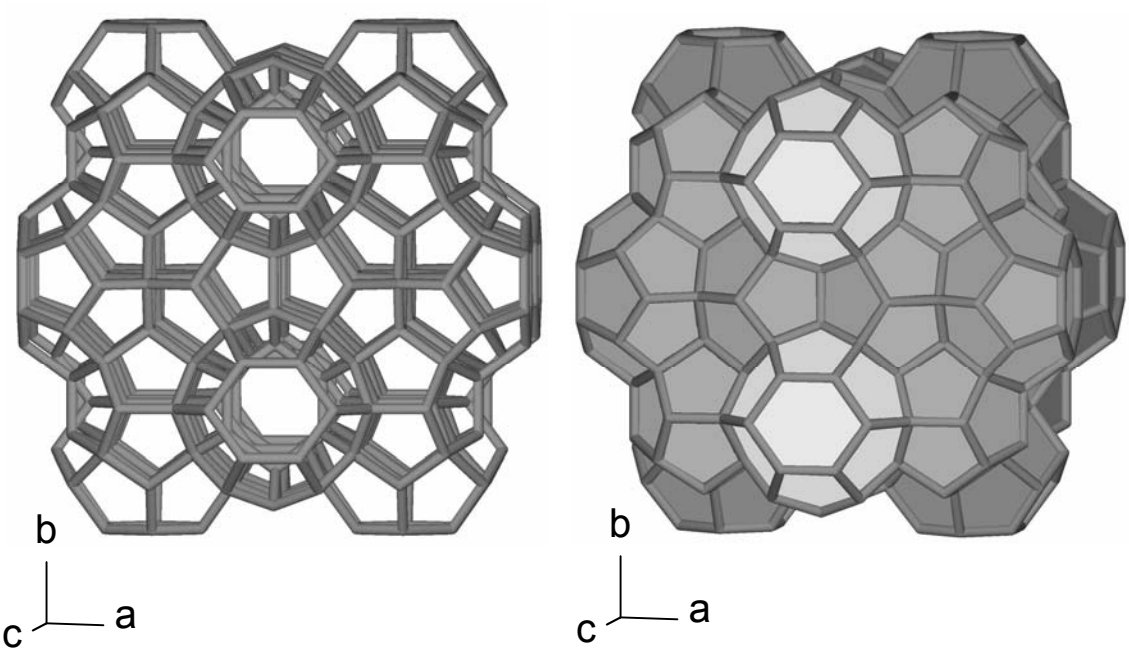
MEP

MEP.1 Zeolite framework type and topology

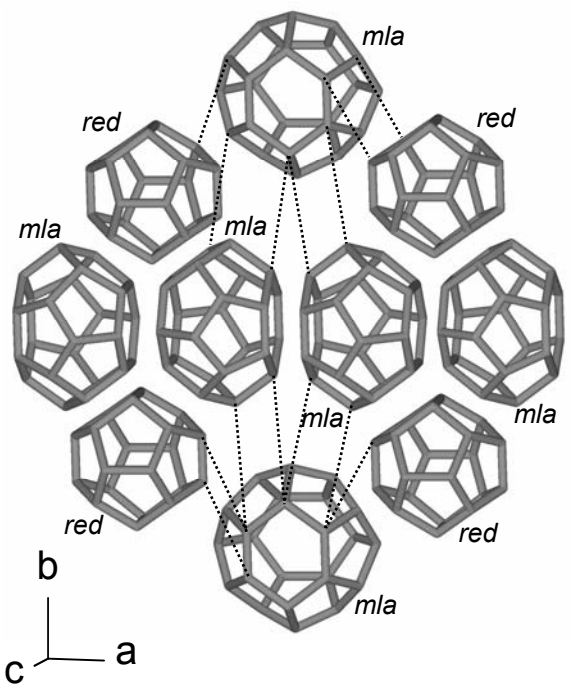
The framework type code is named after the mineral **ME**lano**P**hlogite, a clathrate-type silica polymorph with organic and inorganic guest molecules in the voids of the silica host. The mineral is tetragonal at room temperature (MEP-XII) [72Žák1, 2001Nak1] and undergoes a phase transition to cubic symmetry (MEP-I) at 338K [83Gie1]. The framework structure (Fig. MEP.1.1) is isostructural with the cubic gas hydrates of type I [54von1, cited after 83Gie1]. It can be described by a close packing of *mla* ($5^{12}6^2$) and *red* (5^{12}) units as shown in Figs. MEP.1.1b and MEP.1.2.



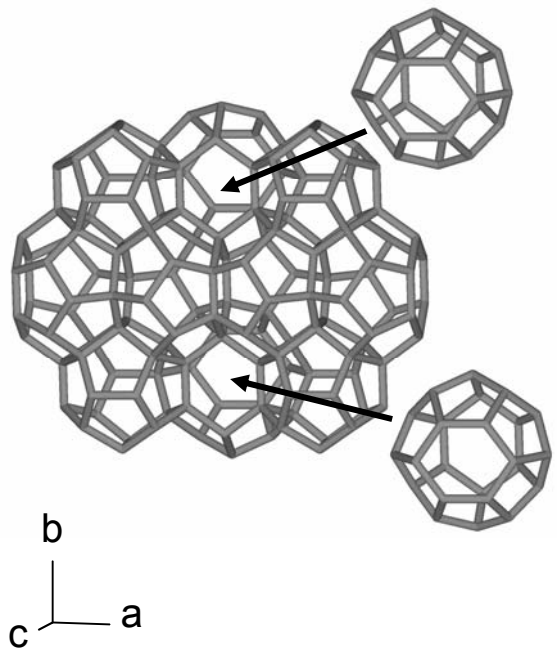
a Skeleton model. View parallel **c** rotated by 2° about **a** and **b**.

b The framework shown in a) with solid units. View parallel **c** rotated by 5° about **a** and 10° about **b**.

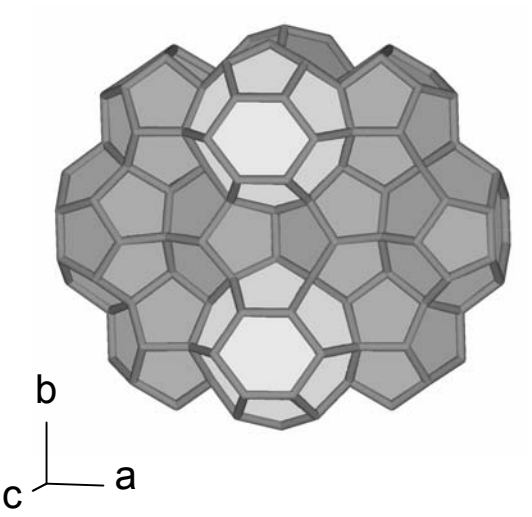
Fig. MEP.1.1 The framework structure of MEP-type zeolites in the highest possible topological symmetry $P\,m\,\bar{3}\,n$.



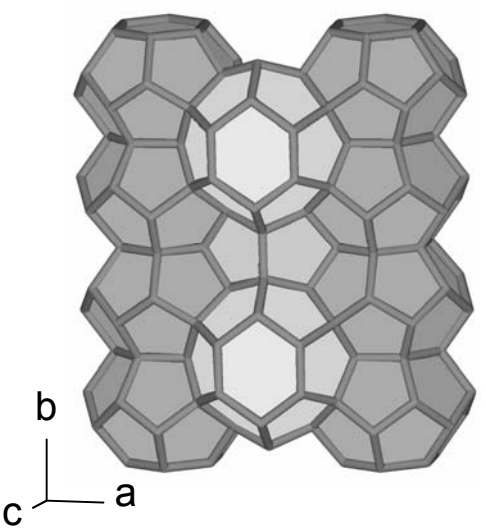
a Linkage of *mla* and *red* units. The *mla* units form pillars (**kgw** units) parallel to the basis vectors of the unit cell.



b The complete assemblage shown in a) with additional *mla* units placed on top of two *mla* units in the layer.



c The complete assemblage shown in b) with solid units.



d The top layer linked to the layer in c).

Fig. MEP.1.2 Building scheme of the MEP-type framework. View parallel **c** rotated by 10° about **a** and **b**.

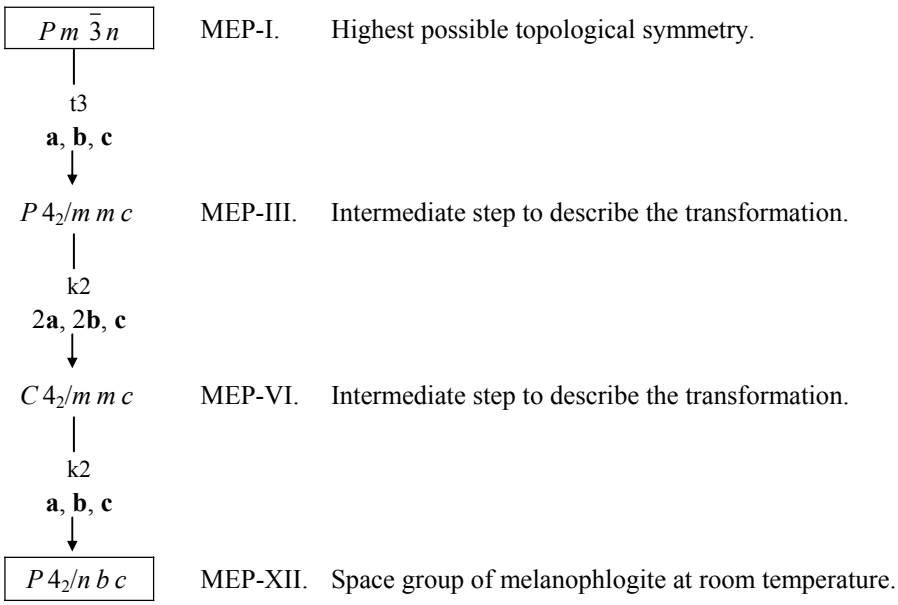


Fig. MEP.1.3 Symmetry relationships of the MEP types.

The diffraction data for melanophlogite at 357 K have been refined [2005Nak1] not only in space group $P\,m\,\bar{3}\,n$ but also in $P\,\bar{4}\,3\,n$, that is without the center of symmetry. The results showed the usual problems occurring when attempting refinements in unnecessarily low symmetry and consequently the authors preferred the centrosymmetric space group.

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

MEP-I $P\,m\,\bar{3}\,n$	MEP-III $P\,4_2/m\,m\,c$	MEP-VI $C\,4_2/m\,m\,c$	MEP-XII $P\,4_2/n\,b\,c$
T1 [24(k), *m* . .]	T11 [8(p), . *m* .]	T11 [32(p), 1]	T11a [16(k), 1]
			T11b [16(k), 1]
	T12 [8(o), . *m* .]	T12a [16(o), . *m* .]	T12a [16(k), 1]
		T12b [16(o), . *m* .]	T12b [16(k), 1]
	T13 [8(q), *m* . .]	T13a [16(n), *m* . .]	T13a [16(k), 1]
		T13b [16(n), *m* . .]	T13b [16(k), 1]
T2 [16(i), . 3 .]	T2 [16(r), 1]	T21 [32(p), 1]	T21a [16(k), 1]
			T21b [16(k), 1]
		T22 [32(p), 1]	T22a [16(k), 1]
			T22b [16(k), 1]
T3 [6(c), $\bar{4}$ *m*. 2]	T31 [4(l), *m* 2 *m*.]	T31a [8(j), *m* 2 *m*.]	T31a [8(h), . 2 .]
		T31b [8(j), *m* 2 *m*.]	T31b [8(h), . 2 .]
	T32 [2(f), $\bar{4}$ *m* 2]	T32 [8(e), 2 . 22]	T32 [8(j), . . 2]

Table MEP.1.1 (continued).

MEP-I $P\,m\,\bar{3}\,n$	MEP-III $P\,4_2/m\,m\,c$	MEP-VI $C\,4_2/m\,m\,c$	MEP-XII $P\,4_2/n\,b\,c$
O1 [48(l), 1]	O11 [16(r), 1]	O11a [32(p), 1]	O11a1 [16(k), 1]
			O11a2 [16(k), 1]
		O11b [32(p), 1]	O11b1 [16(k), 1]
			O11b2 [16(k), 1]
	O12 [16(r), 1]	O12a [32(p), 1]	O12a1 [16(k), 1]
			O12a2 [16(k), 1]
		O12b [32(p), 1]	O12b1 [16(k), 1]
			O12b2 [16(k), 1]
	O13 [16(r), 1]	O13a [32(p), 1]	O13a1 [16(k), 1]
			O13a2 [16(k), 1]
		O13b [32(p), 1]	O13b1 [16(k), 1]
			O13b2 [16(k), 1]
O2 [24(k), *m* . .]	O21 [8(p), . *m* .]	O21 [32(p), 1]	O21a [16(k), 1]
			O21b [16(k), 1]
	O22 [8(o), . *m* .]	O22a [16(o), . *m* .]	O22a [16(k), 1]
		O22b [16(o), . *m* .]	O22b [16(k), 1]
	O23 [8(q), *m* . .]	O23a [16(n), *m* . .]	O23a [16(k), 1]
		O23b [16(n), *m* . .]	O23b [16(k), 1]
O3 [12(f), *mm 2* ..]	O31 [4(j), *m* 2*m* .]	O31a [8(i), *m* 2*m* .]	O31a [8(i), . 2 .]
		O31b [8(i), *m* 2*m* .]	O31b [8(i), . 2 .]
	O32 [4(k), *m* 2*m* .]	O32 [16(n), *m* . .]	O32 [16(k), 1]
	O33 [4(i), 2*m m* .]	O33 [16(o), . *m* .]	O33 [16(k), 1]
O4 [8(e), . 3 2]	O4 [8(n), . . 2]	O41 [16(l), . . 2]	O41a [8(j), . . 2]
			O41b [8(j), . . 2]
		O42 [16(m),. . 2]	O42 [16(k), 1]

MEP.2 Compounds and crystal data

Table MEP.2.1 Chemical data.

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

code	chemical composition	FD	SM	CE	TE/SR	TT	T	REF
MEP-I ***P m $\bar{3}$ n***								
MEP1965a01	$Si_{46}O_{92} \cdot S_2C_3O_6H_{24}$[1])	19.1	M	-	C_xH_y[1]), H_2O, CO_2	-	-	65Kam1
MEP1983a01	$Si_{46}O_{92} \cdot 1.8CH_4$ $1.02CO_2$ $3.54N_2$	19.0	M	-	CH_4, CO_2, N_2	-	-	83Gie1
MEP2005a03	$Si_{46}O_{92} \cdot 1.8CH_4$ $1.02CO_2$ $3.54N_2$ [2])	19.1	M	-	CH_4, CO_2, N_2	-	-	2005Nak1
MEP2006a01	$Si_{46}O_{92} \cdot 1.8CH_4$ $1.02CO_2$ $3.54N_2$ [2])	19.1	M	-	CH_4, CO_2, N_2	-	-	2006Nak1
MEP-XII ***P 4$_2$/n b c***								
MEP2001a01	$Si_{184}O_{368} \cdot 7.2CH_4$ $4.08CO_2$ $14.16N_2$[2])	19.1	M	-	CH_4, CO_2, N_2	-	-	2001Nak1
MEP2005a01	$Si_{184}O_{368} \cdot 7.2CH_4$ $4.08CO_2$ $14.16N_2$ [2])	19.2	M	-	CH_4, CO_2, N_2	-	-	2005Nak1
MEP2005a02	$Si_{184}O_{368} \cdot 7.2CH_4$ $4.08CO_2$ $14.16N_2$ [2])	19.1	M	-	CH_4, CO_2, N_2	-	-	2005Nak1

[1]) The exact composition of the hydrocarbons could not be determined. Sulfur could be present as H_2S, SO_2, SO_3, or perhaps bonded to the organic constituents [65Kam1].
[2]) Chemical composition assumed to be the same as in MEP1983a01.

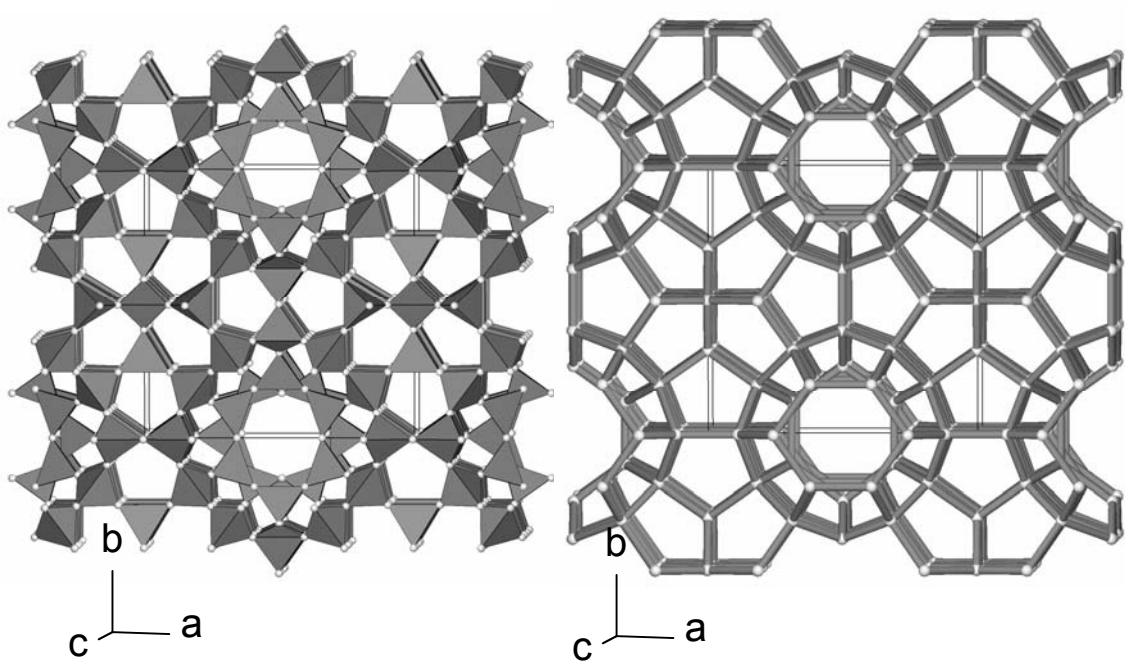
Table MEP.2.2 Structural parameters of the MEP-type compounds.

code	*a* [Å]	*V* [Å^3]	*T* [K]	reference
MEP-I ***P m $\bar{3}$ n***				
MEP1965a01	13.40	2406	n.s.	65Kam1
MEP1983a01	13.436(3)	2426	473	83Gie1
MEP2005a03	13.4104(9)	2412	357	2005Nak1
MEP2006a01	13.4104(9)	2412	357	2006Nak1

code	*a* [Å]	*c* [Å]	shift	matrix	coord. trans.	*V* [Å^3]	*T* [K]	reference
MEP-XII ***P 4$_2$/n b c***								
MEP2001a01	26.818(2)	13.365(1)	¼, 0, 0	**a**, **b**, **c**	*x*-¼, *y*, *z*	9612	297	2001Nak1
MEP2005a01	26.786(2)	13.3351(4)	¼, 0, 0	**a**, **b**, **c**	*x*-¼, *y*, *z*	9568	223	2005Nak1
MEP2005a02	26.808(3)	13.394(4)	¼, 0, 0	**a**, **b**, **c**	*x*-¼, *y*, *z*	9626	333	2005Nak1

MEP.3 Framework structures

MEP.3.1 MEP-I compound ($Pm\bar{3}n$, IT #223)



a Polyhedral representation. View parallel **c** rotated by 1° about **a** and **b**.

b Ball and stick model corresponding to a).

Fig. MEP.3.1.1 Projections of the MEP-I crystal structure of the high-temperature form of melanophlogite, $Si_{46}O_{92} \cdot 1.8CH_4\ 1.02CO_2\ 3.54N_2$ (MEP1983a01, 83Gie1).

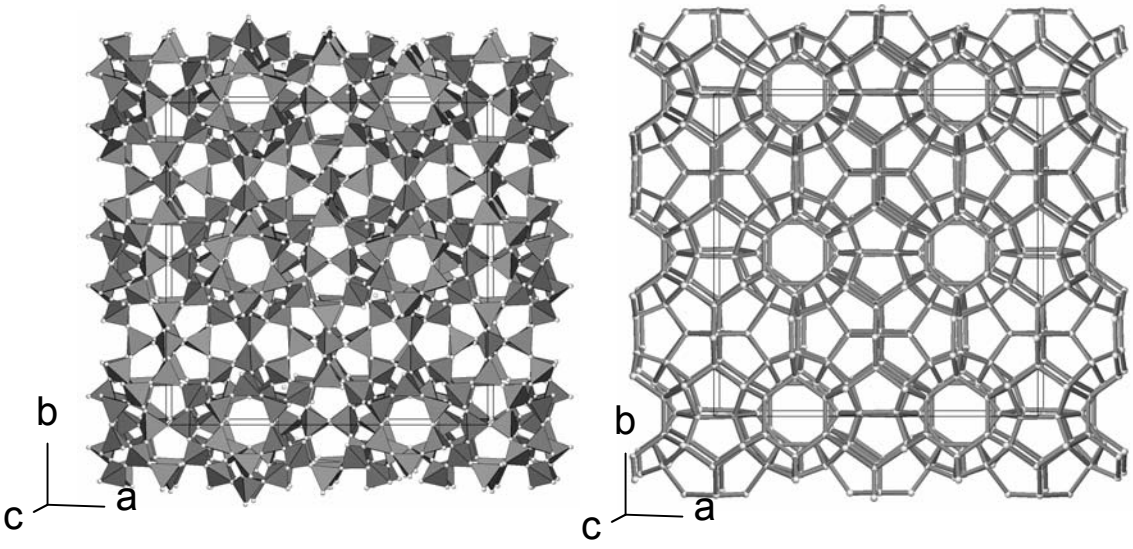
Table MEP.3.1.1 Atomic coordinates and site definitions for MEP-I, $Si_{46}O_{92} \cdot 1.8CH_4\ 1.02CO_2\ 3.54N_2$ (MEP1983a01, 83Gie1).

atom	*x*	*y*	*z*	B_{eq} [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Si1	0	0.3098(1)	0.1142(1)	1.71	*m* . .	24(k)	24
Si2	0.1826(1)	*x*	*x*	1.72	. 3 .	16(i)	16
Si3	¼	0	½	1.43	$\bar{4}$ *m*. 2	6(c)	6
O1	0.0963(2)	0.2465(2)	0.1360(2)	4.88	1	48(l)	48
O2	0	0.4056(2)	0.1813(2)	4.78	*m* . .	24(k)	24
O3	0.3423(3)	0	0	2.76	*m m* 2..	12(f)	12
O4	¼	¼	¼	5.81	. 3 2	8(e)	8
(C,N)1	¼	½	0	39.4	$\bar{4}$ *m* .2	6(d)	1.02 / 3.54
C2	0	0	0	13.7	*m* $\bar{3}$.	2(a)	1.8

Table MEP.3.2 Selected interatomic distances and angles for MEP-I, $Si_{46}O_{92} \cdot 1.8CH_4\ 1.02CO_2\ 3.54N_2$ (MEP1983a01, 83Gie1).

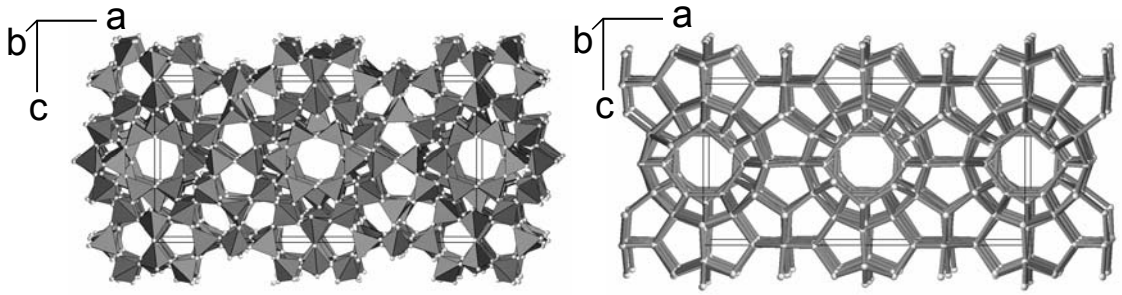
	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si1 - O2	1.571(3)	179.0(2)	Si2 - O4	1.569(1)	180.0
Si1 - O1	1.576(3)	166.9(2)	Si2 - O1	1.573(3)	166.9(2)
Si1 - O1	1.576(3)	166.9(2)	Si2 - O1	1.573(3)	166.9(2)
Si1 - O3	1.595(2)	148.2(3)	Si2 - O1	1.573(3)	166.9(2)
mean	1.580	165.3	mean	1.572	170.2
Si7 - O2	1.569(3)	179.0(2)			
Si7 - O2	1.569(3)	179.0(2)			
Si7 - O2	1.569(3)	179.0(2)			
Si7 - O2	1.569(3)	179.0(2)			
mean	1.569	179.0			

MEP.3.2 MEP-XII compound ($P\,4_2/n\,b\,c$, IT #133)



a Polyhedral representation. View parallel **c** rotated by 2° about **a** and **b**.

b Ball and stick model corresponding to a).



c Polyhedral representation. View parallel **b** rotated by 1° about **a** and **c**.

d Ball and stick model corresponding to c).

Fig. MEP.3.2.1 Projections of the MEP-XII crystal structure of melanophlogite, $Si_{184}O_{368} \cdot 7.2CH_4\ 4.08CO_2\ 14.16N_2$ (MEP2001a01, 2001Nak1).

Table MEP.3.2.1 Atomic coordinates and site definitions for MEP-XII, melanophlogite, $Si_{184}O_{368} \cdot 7.2CH_4$ $4.08CO_2$ $14.16N_2$ (MEP2001a01, 2001Nak1).

atom full name	atom short name	*x*	*y*	*z*	B_{eq} [Å^2]	site sym-metry	Wyckoff position	no. of atoms in unit cell
Si11a	Si11a	0.00299(5)	0.15934(4)	0.09941(7)	1.05	1	16(k)	16
Si11b	Si11b	0.49701(5)	0.65235(4)	0.12865(7)	1.07	1	16(k)	16
Si12a	Si12a	0.05728(5)	0.00588(4)	0.31027(8)	1.12	1	16(k)	16
Si12b	Si12b	0.55725(5)	-0.00847(5)	0.30894(8)	1.17	1	16(k)	16
Si13a	Si13a	0.15568(5)	0.05722(5)	-0.00631(8)	1.20	1	16(k)	16
Si13b	Si13b	0.65493(5)	0.05733(5)	0.00311(8)	1.20	1	16(k)	16
Si21a	Si21a	0.09199(5)	0.09456(4)	0.17469(8)	1.07	1	16(k)	16
Si21b	Si21b	0.59046(5)	0.58852(5)	0.18954(8)	1.13	1	16(k)	16
Si22a	Si22a	0.59326(5)	0.08642(4)	0.19196(8)	1.16	1	16(k)	16
Si22b	Si22b	0.08983(5)	0.59715(4)	0.17183(8)	1.14	1	16(k)	16
Si31a	Si31a	0.12501(7)	0	½	1.07	. 2 .	8(i)	8
Si31b	Si31b	0.62530(7)	0	½	0.95	. 2 .	8(i)	8
Si32	Si32	0.00162(4)	0.24838(4)	¼	0.95	. . 2	8(j)	8
O11a1	O11A	0.0495(1)	0.1234(1)	0.1151(2)	2.79	1	16(k)	16
O11a2	O11B	0.5457(1)	0.6220(2)	0.1528(2)	4.26	1	16(k)	16
O11b1	O11C	0.5503(1)	0.1171(1)	0.1384(2)	3.40	1	16(k)	16
O11b2	O11D	0.0469(1)	0.6329(1)	0.1322(2)	3.24	1	16(k)	16
O12a1	O12A	0.0675(1)	0.0499(1)	0.2331(3)	3.66	1	16(k)	16
O12a2	O12B	0.5697(1)	0.5464(1)	0.2607(3)	3.58	1	16(k)	16
O12b1	O12C	0.5699(1)	0.0381(1)	0.2406(3)	3.68	1	16(k)	16
O12b2	O12D	0.0667(1)	0.5590(1)	0.2485(2)	3.29	1	16(k)	16
O13a1	O13A	0.1316(1)	0.0735(1)	0.0976(2)	3.16	1	16(k)	16
O13a2	O13B	0.6167(1)	0.5638(1)	0.0950(2)	2.95	1	16(k)	16
O13b1	O13C	0.6337(1)	0.0702(1)	0.1111(2)	3.11	1	16(k)	16
O13b2	O13D	0.1138(1)	0.5676(1)	0.0800(2)	2.66	1	16(k)	16
O21a	O21a	0.0104(1)	0.2094(1)	0.1619(2)	2.13	1	16(k)	16
O21b	O21b	0.4912(1)	0.6970(1)	0.2055(2)	2.76	1	16(k)	16
O22a	O22a	0.0907(1)	0.0142(1)	0.4069(2)	2.61	1	16(k)	16
O22b	O22b	0.5910(2)	-0.0093(1)	0.4056(3)	3.29	1	16(k)	16
O23a	O23a	0.2038(1)	0.0906(1)	-0.0285(2)	2.29	1	16(k)	16
O23b	O23b	0.7031(1)	0.0903(1)	-0.0196(3)	2.82	1	16(k)	16
O31a	O31a	0.1725(2)	0	0	1.92	. 2 .	8(h)	8
O31b	O31b	0.6709(2)	0	0	2.13	. 2 .	8(h)	8
O32	O32	-0.0001(1)	0.1737(1)	-0.0170(2)	1.76	1	16(k)	16
O33	O33	0.0001(2)	0.0068(1)	0.3425(2)	2.21	1	16(k)	16
O41a	O41a	0.1187(1)	0.1313(1)	¼	3.53	..2	8(j)	8
O41b	O41b	0.6292(2)	0.6208(2)	¼	4.18	..2	8(j)	8
O42	O42	0.6195(1)	0.1185(1)	0.2759(2)	3.21	1	16(k)	16
(C,N)1	(C,N)1	¾	0	¼	37.64	$\bar{4}$ . .	4(d)	0.68/2.36
(C,N)2	(C,N)2	¾	½	¼	41.32	2.22	4(c)	0.68/2.36
C3	C3	0.0003(8)	0.1243(3)	0.5117(7)	30.79	1	16(k)	2.72
N3	N3	0.0003(8)	0.1243(3)	0.5117(7)	30.79	1	16(k)	9.44
C4	C4	0.0006(6)	0	0	6.106	. 2 .	8(h)	7.20

Nonstandard setting, origin at *n* 2/*b* . , at -¼, ½, -¼ from $\bar{4}$.

Table MEP.3.2.1 (continued)
Symmetry operators:

x, y, z	-y+¼, x-¼, z+½	-x+½, -y, z	y+¼, -x+¼, z+½
-x, y+½, z	y-¼, x+¼, z+½	x+½, -y+½, z	-y-¼, -x-¼, z+½
-x, -y+½, -z	y-¼, -x-¼, -z+½	x+½, y+½, -z	-y-¼, x+¼, -z+½
x, -y, -z	-y+¼, -x+¼, -z+½	-x+½, y, -z	y+¼, x-¼, -z+½

Table MEP.3.2 Selected interatomic distances and angles for the room temperature form, MEP-XII, melanophlogite, $Si_{184}O_{368} \cdot 7.2CH_4\ 4.08CO_2\ 14.16N_2$ (MEP2001a01, 2001Nak1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si11a - O11D	1.576(3)	168.2(2)	Si11b - O11B	1.572(4)	172.2(2)
Si11a - O11A	1.590(3)	157.3(2)	Si11b - O21b	1.585(3)	157.6(2)
Si11a - O21a	1.594(3)	157.3(2)	Si11b - O11C	1.588(3)	157.9(2)
Si11a - O32	1.605(3)	145.2(2)	Si11b - O32	1.600(3)	145.2(2)
Mean	1.591	157.0	Mean	1.586	158.2
Si12a - O12B	1.586(3)	163.5(2)	Si12b - O22b	1.578(5)	170.1(2)
Si12a - O22a	1.588(3)	158.0(2)	Si12b - O12C	1.584(3)	165.8(3)
Si12a - O12A	1.591(3)	163.4(2)	Si12b - O12D	1.598(3)	160.4(2)
Si12a - O33	1.593(5)	148.1(2)	Si12b - O33	1.603(5)	148.1(2)
Mean	1.590	158.3	Mean	1.591	161.1
Si13a - O13B	1.590(3)	158.3(2)	Si13b - O13D	1.589(3)	154.5(2)
Si13a - O13A	1.593(3)	159.5(2)	Si13b - O13C	1.589(3)	156.9(2)
Si13a - O23a	1.598(3)	155.4(2)	Si13b - O23b	1.595(3)	159.4(3)
Si13a - O31a	1.602(2)	147.3(4)	Si13b - O31b	1.597(2)	148.9(4)
Mean	1.596	155.1	Mean	1.593	154.9
Si21a - O12A	1.573(3)	163.4(2)	Si21b - O41b	1.575(5)	171.1(4)
Si21a - O41a	1.580(2)	166.2(2)	Si21b - O11B	1.577(4)	172.2(2)
Si21a - O13A	1.584(3)	159.5(2)	Si21b - O12B	1.578(3)	163.5(2)
Si21a - O11A	1.591(3)	157.3(2)	Si21b - O13B	1.591(3)	158.3(2)
Mean	1.582	161.6	Mean	1.580	166.3
Si22a - O4 2	1.579(3)	160.7(2)	Si22b - O12D	1.575(3)	160.4(2)
Si22a - O12C	1.579(3)	165.8(3)	Si22b - O11D	1.589(3)	168.2(2)
Si22a - O11C	1.586(3)	157.9(2)	Si22b - O42	1.593(3)	160.7(2)
Si22a - O13C	1.592(3)	156.9(2)	Si22b - O13D	1.596(3)	154.5(2)
Mean	1.584	160.3	Mean	1.588	161.0
Si31a - O23a	1.591(3)	155.4(2)	Si31b - O22b	1.581(5)	170.1(2)
Si31a - O23a	1.591(3)	155.4(2)	Si31b - O22b	1.581(5)	170.1(2)
Si31a - O22a	1.594(3)	158.0(2)	Si31b - O23b	1.582(3)	159.4(3)
Si31a - O22a	1.594(3)	158.0(2)	Si31b - O23b	1.582(3)	159.4(3)
Mean	1.592	156.7	Mean	1.581	164.8
Si32 - O21a	1.592(3)	157.3(2)			
Si32 - O21a	1.592(3)	157.3(2)			
Si32 - O21b	1.593(3)	157.6(2)			
Si32 - O21b	1.593(3)	157.6(2)			
Mean	1.593	157.5			

MEP.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. MEP.4.1 Chemical elements (highlighted) occurring in MEP-type compounds. Framework cations are in grey fields.

MEP.5 Flexibility and apertures

The value of the mean T-O-T angles for MEP1983a01 (MEP-I) and MEP2001a01 (MEP-XXII) is about 164°, with individual angles ranging from 145° to 180°. This mean angle is clearly larger than the maximum of the distribution of T-O-T angles in silicoaluminate zeolites (about 143° [95Bau1]). There is insufficient information about the MEP-type framework to deduce anything about its flexibility.

The largest apertures in the MEP framework are 6-rings.

MEP.6 Other information

Useful properties of melanophlogite have not been reported so far. The compound has been prepared synthetically [82Gie1]. Calcined melanophlogite can be freed of its pore filling at above 873 K. The guest-free melanophlogite has been studied by MAS-NMR [97Liu1]. Apparently it undergoes different phase transitions when compared with the guest-bearing phase: a cubic-cubic transition at 413 K, and a cubic-orthorhombic transition at 333K. The thermochemistry of guest-free melanophlogite has been investigated [2003Nav1]. The similarities of the MEP framework-type and the frameworks of DOH, DDR and MTN types have been explored recently [2004van1].

MEP.7 References

54von1 von Stackelberg, M., Müller, H.R.: Z. Elektrochem. **58** (1954) 25.

65Kam1 Kamb, B.: Science **148** (1965) 232.

72Žák1 Žák, L.: Amer. Mineral. **57** (1972) 779.

82Gie1 Gies, H., Gerke, H., Liebau, F.: N. Jb. Mineral. Mh. (1982) 119.

83Gie1 Gies, H.: Z. Kristallogr. **164** (1983) 247.

95Bau1 Baur, W. H.: Proc. Second Polish-German Zeolite Colloquium, Toruń (1995) 171.

97Liu1 Liu, S., Welch, M.D., Klinowski, J.: J. Phys. Chem. B **101** (1997) 2811.

2001Nak1 Nakagawa, T., Kihara, K., Harada, K.: Amer. Mineral. **86** (2001) 1506.

2003Nav1 Navrotsky, A., Xu, H., Moloy, E.C., Welch, M.D.: Am. Mineral. **88** (2003) 1612.

2004van1 van Koningsveld, H., Gies, H.: Stud. Surf. Sci. Catal. **154** (2004) 1295.

2005Nak1 Nakagawa, T., Kihara, K., Fujinami, S.: J. Mineral. Petrolog. Sciences **100** (2005) 247.

2006Nak1 Nakagawa, T., Kihara, K..: J. Mineral. Petrolog. Sciences **101** (2006) 14.

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