OFF

OFF.1 Zeolite framework type and topology

The framework type code is named after the mineral **OFF**retite, $CaKMg \cdot Al_5Si_{13}O_{36} \cdot 16H_2O$, first described by Gonnard [1890Gon1, cited after 72Gar1]. A first description of its aluminosilicate framework structure was given by Bennett and Gard [67Ben1] in space group $P\bar{6}m2$ representing the highest possible topological symmetry of OFF-type structures adopted by all known offretite minerals. Offretite is commonly intergrown with erionite (ERI) which both belong to the ABC-6 family of frameworks (see CHA.1 for additional information, see also [2006Gie1]) built by different stackings of 6-ring layers. The stacking sequence for offretite is AAB... as shown in Fig. OFF.1.2e. The framework structure (Fig. OFF.1.1) can be described as being built from *kno* ($4^3 8^3 12^2$) units forming the 12-ring channel (**off** unit, Fig. OFF.1.3) crosslinked by an alternating sequence of *can* ($4^6 6^3 6^2$) and *hpr* ($4^6 6^2$) units forming the **ofr** pillar and crosslinked by a **tix** chain of *gme* ($4^6 4^3 6^2 8^3$) units as shown in Fig. OFF.1.2.

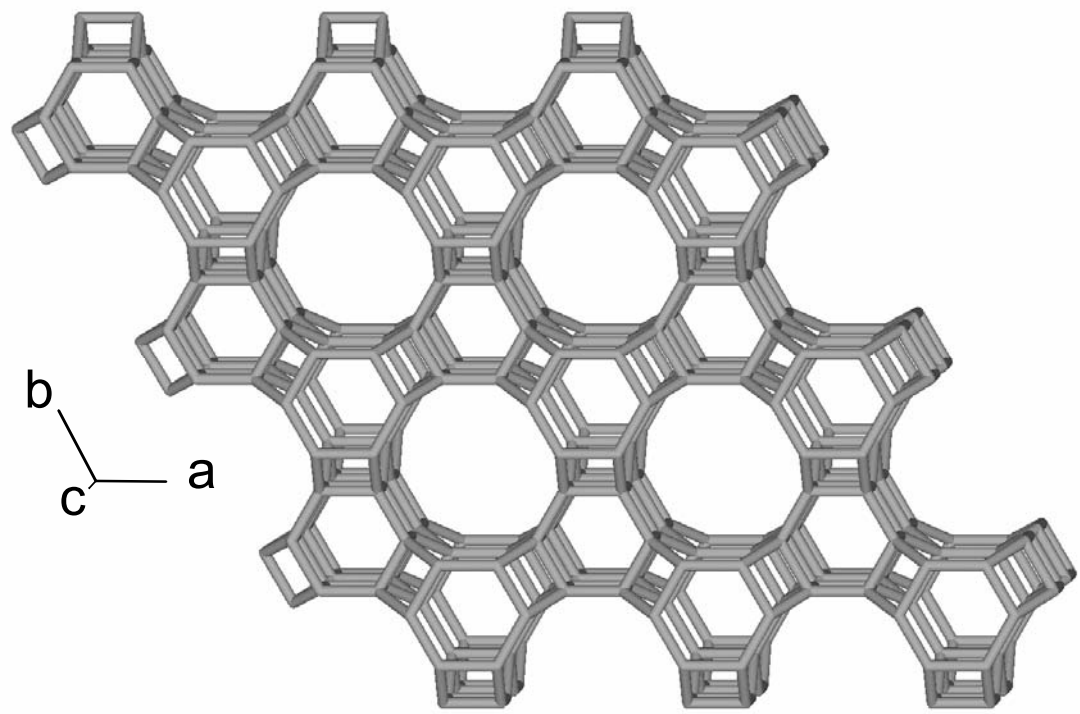
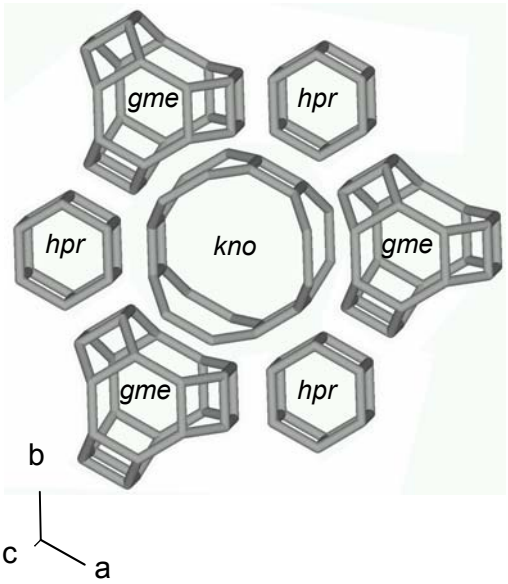
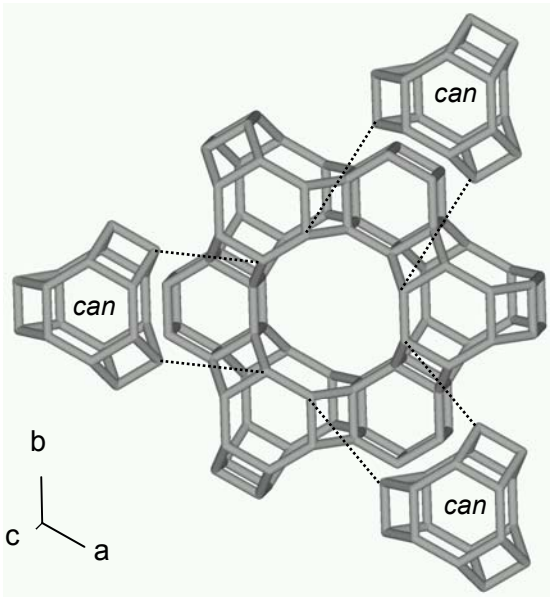


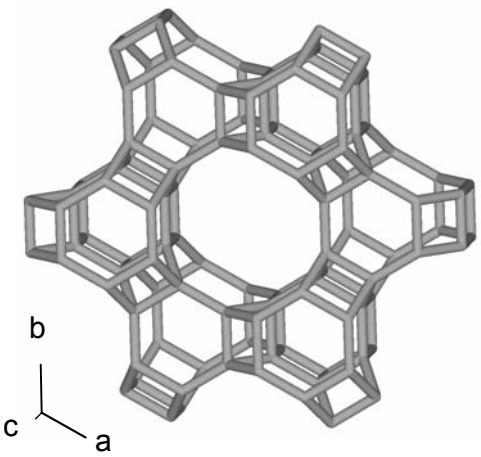
Fig. OFF.1.1. The framework structure of OFF-type compounds in the highest possible topological symmetry $P\bar{6}m2$. View parallel [001] rotated by 5° about [100] and [120].



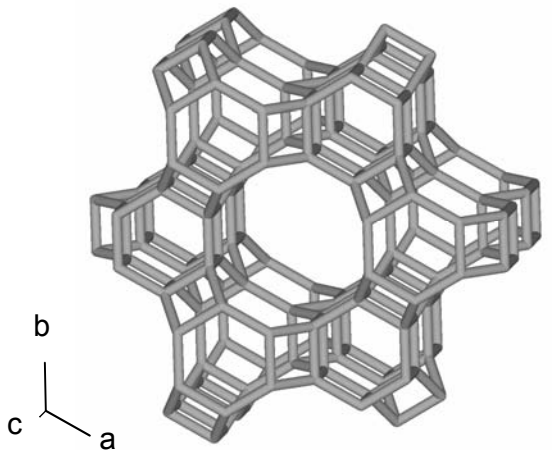
a Linkage of units around the *kno* unit.



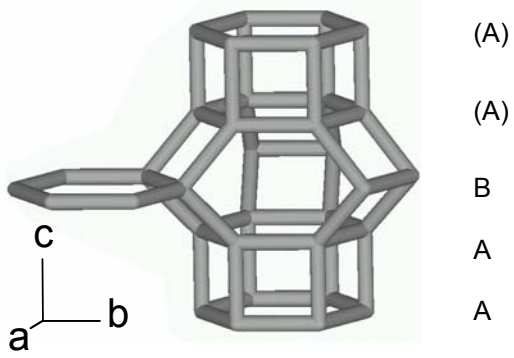
b The assemblage shown in a) extended by *can* units.



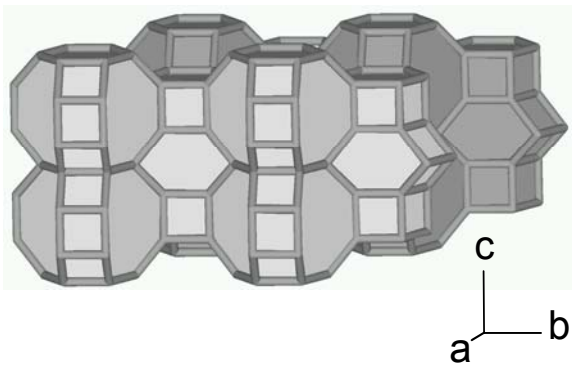
c The complete assemblage shown in b).



d The assemblage shown in c) extended by another layer.



e The stacking sequence of layers.



f Units shown nontransparently.

Fig. OFF.1.2 Building scheme of OFF-type zeolites. a) to d) View parallel [001] rotated by 5° about [210] and 10° about [010], e) and f) View parallel [210] rotated by 10° about [010] and 5° about [001].

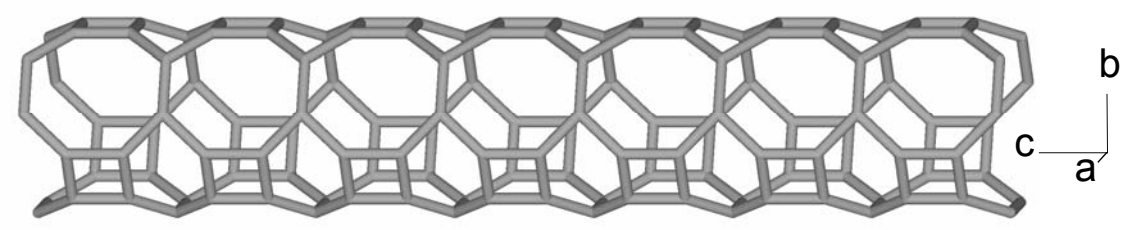


Fig. OFF.1.3 The 12-ring channel (**off** unit) parallel [001]. View parallel **a** rotated by 10° about **b** and **c**.

OFF.2 Compounds and crystal data

Table OFF.2.1 Chemical data.

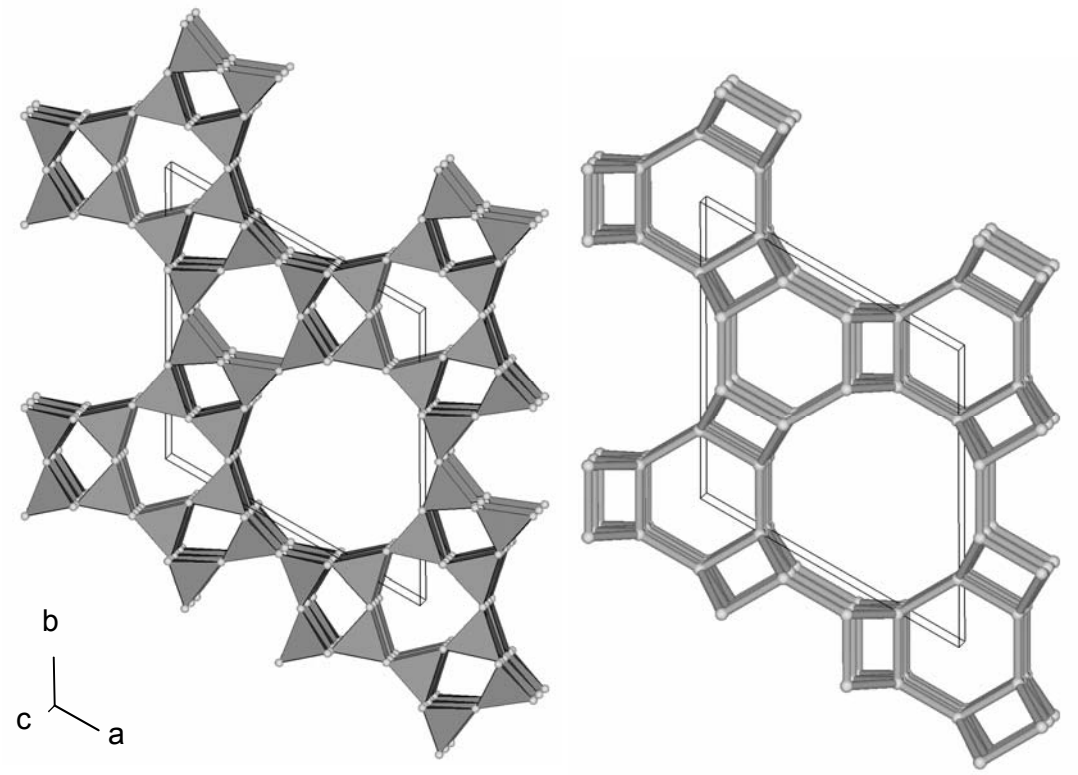
FD = framework density CE = cation exchange TT = thermal treatment REF = reference
SM = source of material SR = sorbate T = temperature of thermal treatment [K]

code	chemical composition	FD	SM	CE	SR	TT	T	REF
***P* $\bar{6}$*m* 2**								
OFF1972a01	$K_{1.1}Ca_{1.1}Mg_{0.7} \cdot Al_{5.2}Si_{12.8}O_{36} \cdot 15.2H_2O$	15.5	M	-	H_2O	-	-	72Gar1
OFF1975a01	$KCaMg \cdot Al_{5.2}Si_{12.8}O_{36}$	16.2	M	-	-	D	773	75Mor1
OFF1976a01	$KCaMg \cdot Al_{5.2}Si_{12.8}O_{36}$	16.2	M	-	-	D	773	76Mor1
OFF1976b01	$KCaMg \cdot Al_{5.2}Si_{12.8}O_{36} \cdot CO$	16.1	M	-	CO	D	773	76Mor2
OFF1988a01	$Si_{18}O_{36}$	16.0	T	-	-	-	-	88van1
OFF1989b01	$Si_{18}O_{36}$	16.0	T	-	-	-	-	89Uyt1
OFF1996a01	$K_{1.1}Ca_{1.1}Mg_{1.1} \cdot Al_{5.5}Si_{12.5}O_{36} \cdot 17.6H_2O$	15.4	M	-	H_2O	-	-	96Alb1
OFF1998a01	$K_{0.9}Ca_{1.1}Mg \cdot Al_{5.4}Si_{12.6}O_{36} \cdot 16.6H_2O$	15.3	M	-	H_2O	-	-	98Gua1
OFF1998a02	$K_{0.8}Ca_{1.5}Mg_{0.7} \cdot Al_{5.5}Si_{12.5}O_{36} \cdot 16.7H_2O$	15.4	M	-	H_2O	-	-	98Gua1
OFF1998a03	$K_{0.9}CaMg_{1.1} \cdot Al_{5.3}Si_{12.8}O_{36} \cdot 16.9H_2O$	15.5	M	-	H_2O	-	-	98Gua1

Table OFF.2.2 Structural parameters of OFF-type compound.

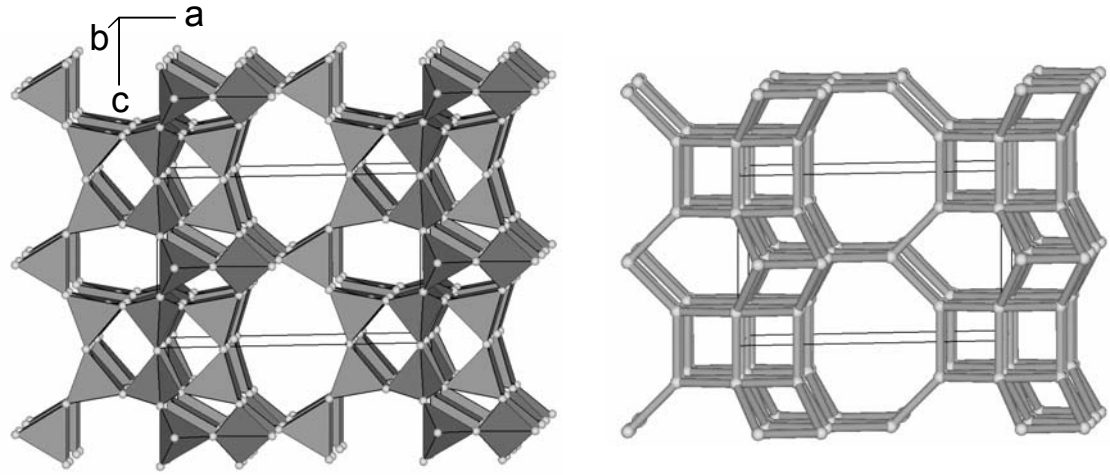
code	*a* [Å]	*c* [Å]	*V* [Å^3]	*T* [K]	reference
***P* $\bar{6}$*m* 2**					
OFF1972a01	13.291(2)	7.582(6)	1160	n.s.	72Gar1
OFF1975a01	13.229(5)	7.338(4)	1112	RT	75Mor1
OFF1976a01	13.229(5)	7.338(4)	1112	n.s.	76Mor1
OFF1976b01	13.261(6)	7.347(4)	1119	n.s.	76Mor2
OFF1988a01	13.10	7.56	1124	-	88van1
OFF1989b01	13.10	7.56	1124	-	89Uyt1
OFF1996a01	13.331(2)	7.593(1)	1169	n.s.	96Alb1
OFF1998a01	13.390(2)	7.598(1)	1180	n.s.	98Gua1
OFF1998a02	13.308(3)	7.597(2)	1165	n.s.	98Gua1
OFF1998a03	13.293(2)	7.608(1)	1164	n.s.	98Gua1

OFF.3 Framework structure of OFF-1 compound ($P\bar{6}\,m2$, IT #187)



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

b Ball and stick model corresponding to a).



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

b Ball and stick model corresponding to c).

Fig. OFF.3.1 Projections of the crystal structure of offretite, $KCaMg \cdot Al_5Si_{13}O_{36} \cdot 18H_2O$ (OFF1996a01, 96Alb1).

Table OFF.3.1. Atomic coordinates and site definitions for offretite, $KCaMg \cdot Al_5Si_{13}O_{36} \cdot 18H_2O$ (OFF1996a01, 96Alb1).

atom	*x*	*y*	*z*	B_{eq} [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
(Si,Al)1	0.0007(2)	0.2334(2)	0.2089(1)	0.92	1	12(o)	8.52 / 3.48
(Si,Al)2	0.0923(2)	0.4236(2)	½	0.72	*m* . .	6(m)	3.78 / 2.22
O1	0.0243(3)	0.3486(3)	0.3213(4)	2.22	1	12(o)	12
O2	0.0961(3)	-*x*	0.2558(9)	1.69	. *m* .	6(n)	6
O3	0.8738(3)	-*x*	0.2602(8)	2.54	. *m* .	6(n)	6
O4	0.0103(8)	0.2718(6)	0	2.47	*m* . .	6(l)	6
O5	0.2286(5)	-*x*	½	2.40	*m m* 2	3(k)	3
O6	0.4570(4)	-*x*	½	2.02	*m m* 2	3(k)	3
K1	0	0	½	2.40	$\bar{6}$ *m* 2	1(b)	1
Mg1	⅓	⅔	0	1.63	$\bar{6}$ *m* 2	1(c)	1
Ca1	⅔	⅓	0.395(2)	2.29	3 *m* .	2(i)	0.64(2)
Ca2	⅔	⅓	0.281(1)	6.66	3 *m* .	2(i)	0.68(2)
OW7	⅓	⅔	0.268(1)	2.11	3 *m* .	2(h)	2
OW8	0.245(1)	-*x*	0	3.86	*m m* 2	3(j)	1.14(6)
OW9	0.167(1)	0.527(1)	0	5.97	*m* . .	6(l)	2.88(6)
OW10	0.7635(7)	-*x*	½	6.40	*m m* 2	3(k)	3
OW11	0.5631(5)	-*x*	0.188(1)	10.17	. *m* .	6(n)	6
OW12[1])	0.769(3)	-*x*	0	2.60	*m m* 2	3(j)	0.51(6)

[1]) coordinates corrected from 0.231, -*x*, 0 [96Alb1] to 0.769, -*x*, 0.

Table OFF.3.2 Selected interatomic distances and angles for offretite, $KCaMg \cdot Al_5Si_{13}O_{36} \cdot 18H_2O$ (OFF1996a01, 96Alb1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
(Si,Al)1 - O3	1.624(4)	147.8(4)	(Si,Al)2 - O6	1.635(1)	174.9(3)
(Si,Al)1 - O1	1.644(3)	141.1(2)	(Si,Al)2 - O5	1.640(7)	152.6(3)
(Si,Al)1 - O4	1.652(1)	147.6(3)	(Si,Al)2 - O1	1.660(3)	141.1(2)
(Si,Al)1 - O2	1.657(5)	138.4(3)	(Si,Al)2 - O1	1.660(3)	141.1(2)
mean	1.644	143.8	mean	1.649	152.4

OFF.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
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

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

OFF.5 Flexibility and apertures

There is insufficient information available about the OFF-type to judge its flexibility.

The 12-ring openings in the OFF-type framework are buckled and therefore smaller than in the FAU-type: less than 7 Å as compared with about 7.5 Å in FAU.

OFF.6 Other information

There is a number of reports about catalytic properties of OFF-type compounds, and a few patents have been issued. For example copper(II) ion-exchanged offretite is said to help in reducing nitric oxide with ammonia [2005Aro1]. Methanol can be converted to gasoline by both aluminosiloicate and gallosilicate offretites [97Alb1].

OFF.7 References

1890Gon1 Gonnard, M.F.: C. R. Acad. Sci. Paris **111** (1890) 1002.

67Ben1 Bennett, J.M., Gard, J.A.: Nature **214** (1967) 1005.

72Gar1 Gard, J.A., Tait, J.M.: Acta Crystallogr. B**28** (1972) 825.

75Mor1 Mortier, W.J., Pluth, J.J., Smith, J.V.: Nature **256** (1975) 718.

76Mor1 Mortier, W.J., Pluth, J.J., Smith, J.V.: Z. Kristallogr. **143** (1976) 319.
76Mor2 Mortier, W.J., Pluth, J.J., Smith, J.V.: Z. Kristallogr. **144** (1976) 32.

88van1 van Genechten, K.A., Mortier, W.J.: Zeolites **8** (1988) 273.

89Uyt1 Uytterhoeven, L., Mortier, W.J., Geerlings, P.: J. Phys. Chem. Solids **50** (1989) 479.

96Alb1 Alberti, A., Cruciani, G., Galli, E., Vezzalini, G.: Zeolites **17** (1996) 457.

97Alb1 Alba, M.D., Romero, A.A., Occelli, M.L., Klinowski, J.: J. Phys. Chem. B **101** (1997) 5166.

98Gua1 Gualtieri, A., Artioli, G., Passaglia, E., Bigi, S., Viani, A., Hanson, J.C.: Amer. Mineral. **83** (1998) 590.

2005Aro1 Arous, W., Tounsi, H., Djemel, S., Ghorbel, A., Delahay, G.: Catal. Commun. **6** (2005) 281.

2006Gie1 Gies, H., van Koningsveld, H. *in* Baerlocher, C., McCusker, L.B.: Database of Zeolite Structures, http://www.iza-structure.org/databases/

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