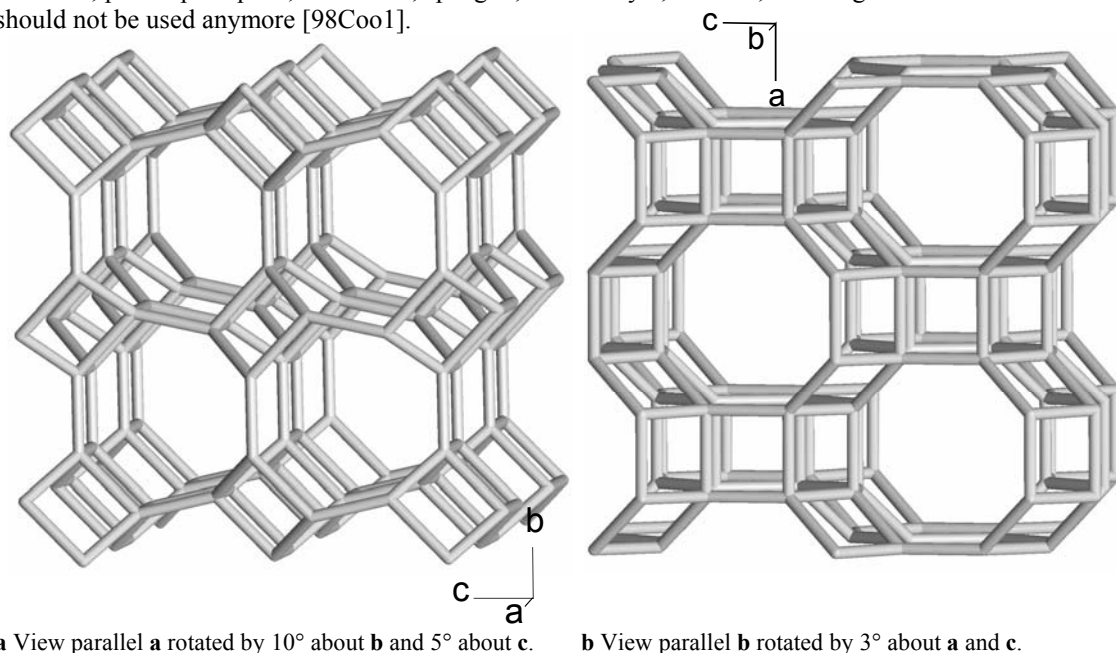


## PHI

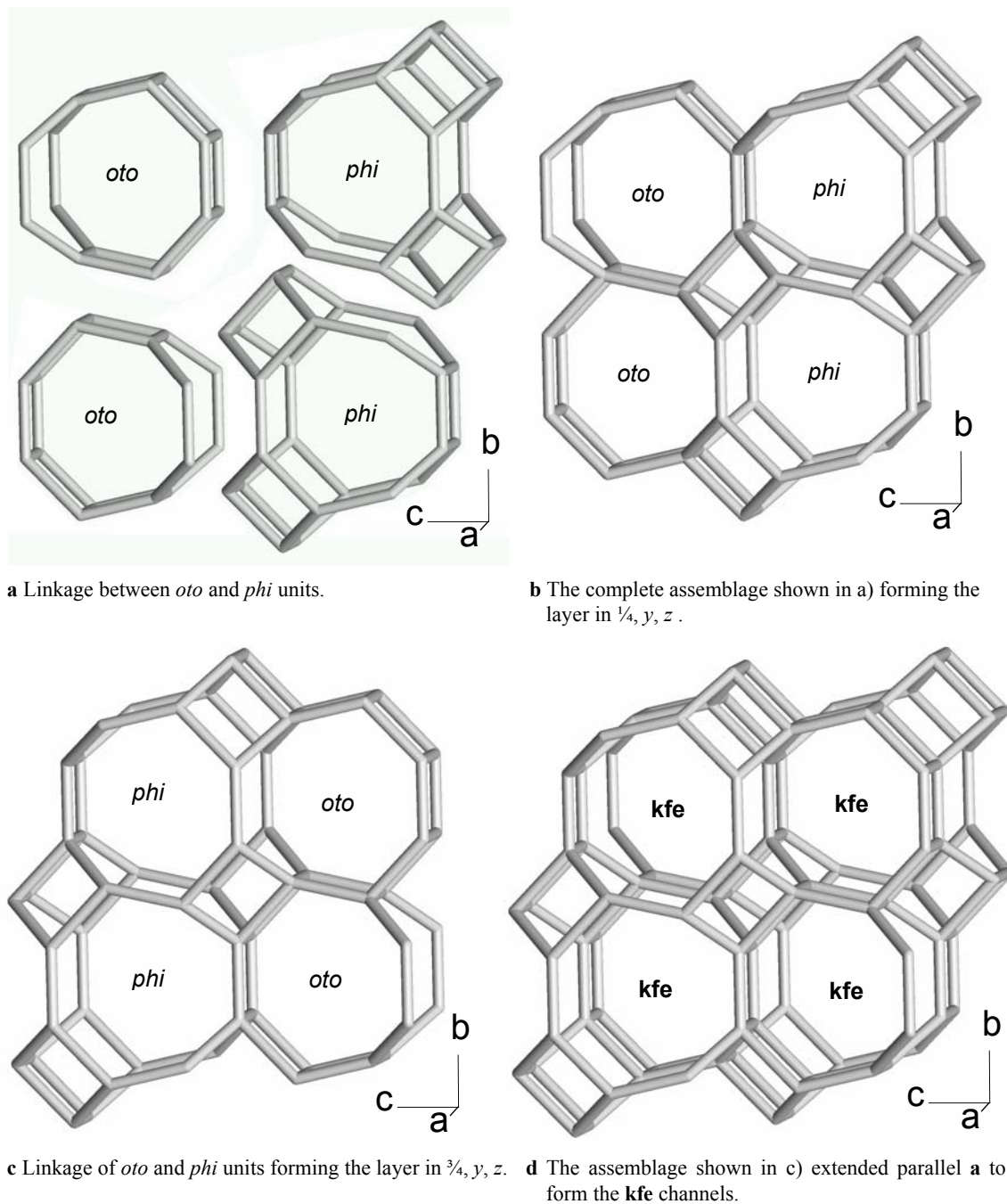
### PHI.1 Zeolite framework type and topology

The framework type code is named after the mineral **PH**illipsite, representing a series of minerals with general composition  $(K, Na, Ca_{0.5}, Ba_{0.5})_x Al_x Si_{16-x} O_{32} \cdot 12H_2O$  with  $x \approx 4 - 7$  [98Coo1]. In order to distinguish between the different species with varying alkali and alkaline earth contents Coombs et al. [98Coo1] recommended to add the predominant element as a suffix to the name phillipsite (see examples in Table 2.2.1 of the introduction). A Ba-rich form of the mineral is named harmotome, forming a continuous series with phillipsite-Ca [98Coo1]. The name harmotome was introduced by Häuy [1801Häu1, cited after 98Coo1] renaming andreasbergolite described by Delamétherie [1795Del1, cited after 98Coo1]. The name phillipsite was given by Levy [1825Lev1, cited after 98Coo1] for a mineral found in Acireale on the slopes of Etna, Sicily, Italy, with an aluminosilicate framework isotypic with harmotome. Synthetic variants with the PHI-type framework are amongst others Ca-L [61Bar1], Ba-M [64Bar1], ZK-19 [69Küh1], and ACP-PHI1 [97Fen1]. The names andreasbergolite, andreolite, barytkreuzstein, christianite, ercinite, harmotomite, hercynite, kalkkreuzstein, marburgite, morvenite, normalin, pseudophillipsite, sasbachite, spangite, staurobaryte, wellsite, and zeagonite are discredited and should not be used anymore [98Coo1].

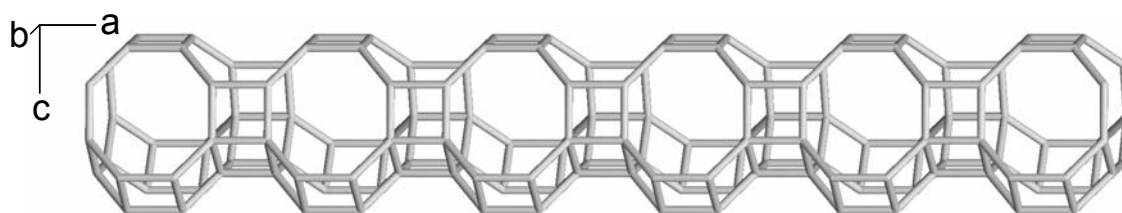


**Fig. PHI.1.1.** The framework structure of PHI-type compounds in the highest possible topological symmetry  $Bmm\bar{b}$ .

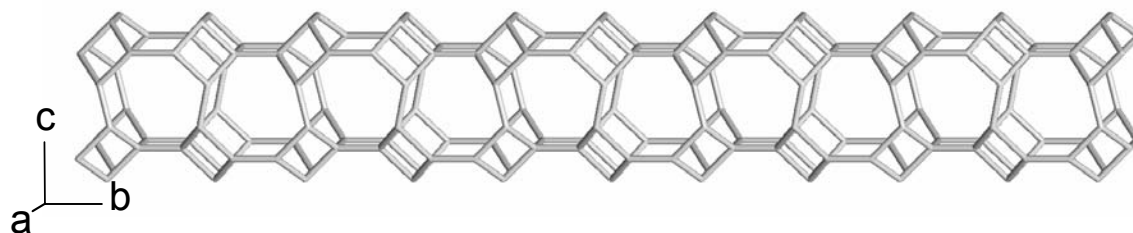
The crystal structure of harmotome was solved by Sadanaga [61Sad1] in space group  $P2_1/m$  but refined and described in  $P2_1$  which has been shown in [74Rin1] to be better described in the higher monoclinic symmetry. The crystal structure of phillipsite was determined by Steinfink [62Ste1] in space group  $B2m$  erroneously assigned due to unrecognized twinning [73Rin1]. Consequently, the two structures are not listed in Tables PHI.2.1 and PHI.2.2 although the framework topologies had been correctly determined.



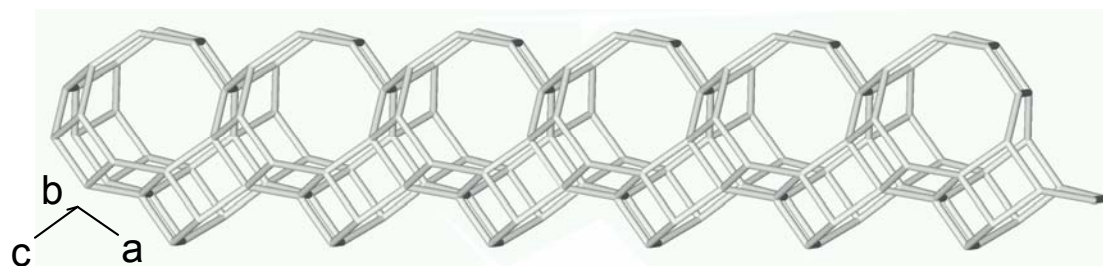
**Fig. PHI.1.2.** Building scheme of the PHI-type framework corresponding to the model shown in Fig. PHI.1.1a. View parallel *a* rotated by  $10^\circ$  about *b* and  $5^\circ$  about *c*.



**a** The 8-ring channel (**kfe** unit) parallel **a**. View parallel **b** rotated by  $10^\circ$  about **a** and **c**.

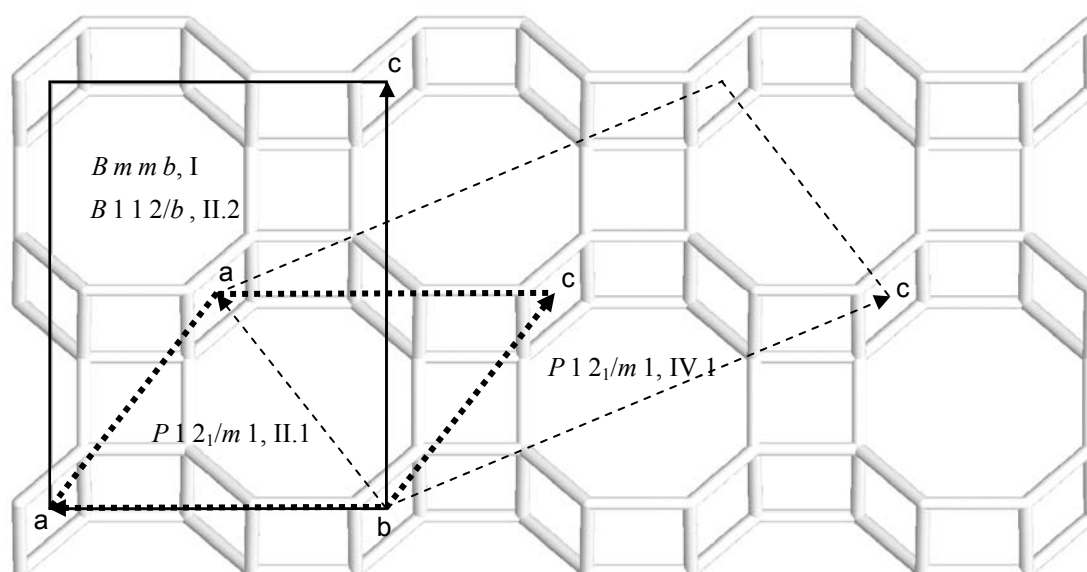


**b** The 8-ring channel (**kgu** unit) parallel **b**. View parallel **a** rotated by  $10^\circ$  about **b** and **c**.



**c** The 8-ring channel parallel  $-\mathbf{a}+\mathbf{c}$  (corresponding to **c** in the monoclinic setting of the PHI-II.1 structure). View parallel **b** rotated by  $1^\circ$  about  $-\mathbf{a}+\mathbf{c}$  and  $10^\circ$  about  $(-\mathbf{a}+\mathbf{c})\times\mathbf{b}$ .

**Fig. PHI.1.3** Channels in PHI-type frameworks.



**Fig. PHI.1.4** Relationships between orthorhombic and monoclinic settings of the standardized unit cells.

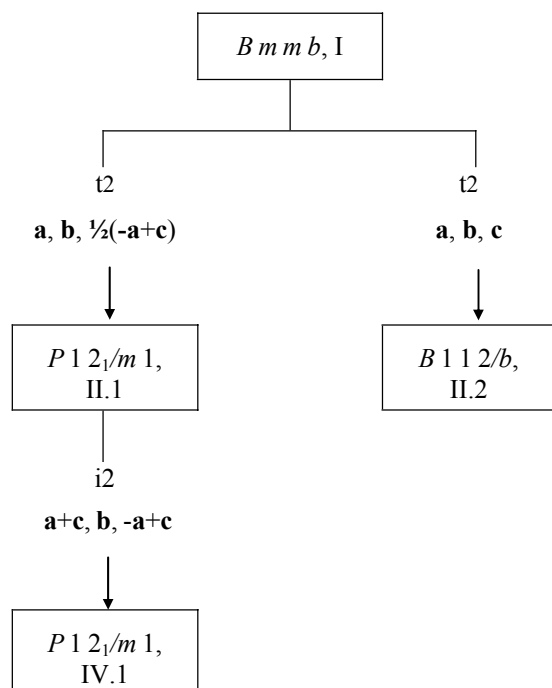
The PHI-IV.1 type crystal structure is described in [99Gua1]. However, Framework atom positions are not published and coordinates provided by private communication are not complete and result in a very distorted framework with individual O-T-O angles ranging from 75° to 155°. Assuming that the unit cell parameters and the space group are correctly determined, the supercell is listed in Fig. PHI.1.4 and PHI.1.5 and in Tables PHI.2.1 and PHI.2.2 but it is not described in chapter 3.

The framework structure can be described as being built from *oto* ( $4^2 4^2 4^1 8^2 8^1$ ) and *phi* ( $4^4 4^2 4^1 8^2 8^2 8^1$ ) units as shown in Fig. PHI.1.2 forming 8-ring channels parallel **a** (**kfe** units, Fig. PHI.1.3a) formed by an alternating sequence of *oto* and *phi* units, parallel **b** (**kgu** units, Fig. PHI.1.3b) formed by *phi* units only, and parallel **-a+c** formed by *phi* units with *oto* units in the joints.

The highest possible topological symmetry of the aristotype assumes space group  $Bmm\bar{b}$ . The Na-exchanged phillipsite (PHI1995a03, [95Hal1]) assigned to the high symmetry space group is probably better described in the monoclinic space group  $P2_1/m$ . Therefore, the orthorhombic structures are listed in Tables PHI.2.1 and PHI.2.2 only. They are not described in chapter PHI.3. Crystal structure descriptions in space groups  $P2_1$  ([61Sad1], [86Stu1], [95Hal1]),  $B2mb$  [62Ste1], and  $Pmma$  [95Hal1] are questionable and consequently are not listed in the Bärnighausen tree in Fig. PHI.1.5 and in the tables PHI.2.1 and PHI.2.2. An Mg-exchanged phillipsite studied by Gualtieri (sample 1 in [2001Gua1]) and refined in space group  $B2mb$  does not have the PHI-type topology and therefore is not listed here.

The relationships between orthorhombic and monoclinic settings of the standardized unit cells are shown in Fig. PHI.1.4. The PHI-IV.1 structure in space group  $P2_1/m$  is derived by the transformation **a+c**, **b**, **-a+c** to achieve a right-handed unit cell with a monoclinic angle  $> 90^\circ$ .

Thus the literature reflects a considerable confusion about the symmetry of PHI-type compounds. Instead of the six different space groups in which the compounds have so far been described, most likely only two space groups are sufficiently well documented:  $P12_1/m1$  (type PHI-II.1) and  $B112/b$  (type PHI-II.2).

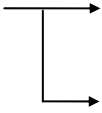
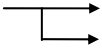
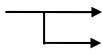
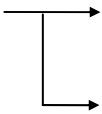
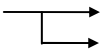
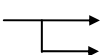
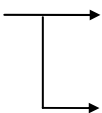
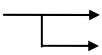
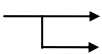
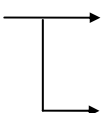
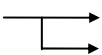
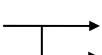
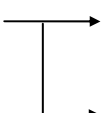
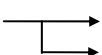
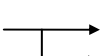
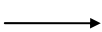
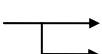
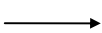
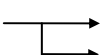
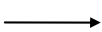
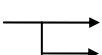


**Fig. PHI.1.5** The Bärnighausen tree illustrating the symmetry relationships of the PHI types.

**Table PHI.1.1** Atomic site relationships of the PHI types.

PHI-I $Bmm\bar{b}$		PHI-II.2 $B112/b$
T1 [16(h), 1]	→	T11 [8(f), 1] T12 [8(f), 1]
T2 [16(h), 1]	→	T21 [8(f), 1] T22 [8(f), 1]
O1 [16(h), 1]	→	O11 [8(f), 1] O12 [8(f), 1]
O2 [16(h), 1]	→	O21 [8(f), 1] O22 [8(f), 1]
O3 [8(g), . m .]	→	O3 [8(f), 1]
O4 [8(f), m . .]	→	O4 [8(f), 1]
O5 [8(f), m . .]	→	O5 [8(f), 1]
O6 [8(e), 2 . .]	→	O6 [8(f), 1]

**Table PHI.1.1** (continued) Atomic site relationships of the PHI types

PHI-I <i>B m m b</i>		PHI-II.1 <i>P 1 2<sub>1</sub>/m 1</i>		PHI-IV.1 <i>P 1 2<sub>1</sub>/m 1</i>
T1 [16(h), 1]		T11 [4(f), 1]		T11a [4(f), 1] T11b [4(f), 1]
		T12 [4(f), 1]		T12a [4(f), 1] T12b [4(f), 1]
T2 [16(h), 1]		T21 [4(f), 1]		T21a [4(f), 1] T21b [4(f), 1]
		T22 [4(f), 1]		T22a [4(f), 1] T22b [4(f), 1]
O1 [16(h), 1]		O11 [4(f), 1]		O11a [4(f), 1] O11b [4(f), 1]
		O12 [4(f), 1]		O12a [4(f), 1] O12b [4(f), 1]
O2 [16(h), 1]		O21 [4(f), 1]		O21a [4(f), 1] O21b [4(f), 1]
		O22 [4(f), 1]		O22a [4(f), 1] O22b [4(f), 1]
O3 [8(g), . <i>m</i> .]		O31 [2(e), <i>m</i> ]		O31a [2(e), <i>m</i> ] O31b [2(e), <i>m</i> ]
		O32 [2(e), <i>m</i> ]		O32a [2(e), <i>m</i> ] O32b [2(e), <i>m</i> ]
O4 [8(f), <i>m</i> . .]		O4 [4(f), 1]		O41 [4(f), 1] O42 [4(f), 1]
O5 [8(f), <i>m</i> . .]		O5 [4(f), 1]		O51 [4(f), 1] O52 [4(f), 1]
O6 [8(e), 2 . .]		O6 [4(f), 1]		O61 [4(f), 1] O62 [4(f), 1]

## PHI.2 Compounds and crystal data

**Table PHI.2.1** Chemical data.

M = mineral/comp. name SM = source of material SR = sorbate T = temperature of thermal treatment [K]  
FD = framework density CE = cation exchange TT = thermal treatment REF = reference

code	chemical composition	M	FD	S M	CE	SR	TT	T	REF
<b>PHI-I B m m b</b>									
PHI1988a01	Si <sub>32</sub> O <sub>64</sub>		16.3	T	-	-	-	-	88van1
PHI1995a03	Ca <sub>0.2</sub> K <sub>2.0</sub> Na <sub>6.6</sub> · Al <sub>9.6</sub> Si <sub>22.4</sub> O <sub>64</sub> · 25.3H <sub>2</sub> O	[phillipsite]	15.9	M	Na	H <sub>2</sub> O	-	-	95Hal1
<b>PHI-II.1 P 1 2<sub>1</sub>/m 1</b>									
PHI1973a01	Ca <sub>1.7</sub> K <sub>2.0</sub> Na <sub>0.4</sub> · Al <sub>5.3</sub> Si <sub>10.6</sub> O <sub>32</sub> · 13.4H <sub>2</sub> O	phillipsite-K	15.8	M	-	H <sub>2</sub> O	-	-	73Rin1
PHI1974a01	Ca <sub>1.7</sub> K <sub>2.0</sub> Na <sub>0.4</sub> · Al <sub>5.3</sub> Si <sub>10.6</sub> O <sub>32</sub> · 12H <sub>2</sub> O	phillipsite-K	15.8	M	-	H <sub>2</sub> O	-	-	74Rin1
PHI1974a02	Ca <sub>0.5</sub> Ba <sub>1.9</sub> K <sub>0.1</sub> · Al <sub>4.7</sub> Si <sub>11.3</sub> O <sub>32</sub> · 11.8H <sub>2</sub> O	harmotome	16.0	M	-	H <sub>2</sub> O	-	-	74Rin1
PHI1986a01	Ba <sub>2</sub> · Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> · 12H <sub>2</sub> O	harmotome	16.0	M	-	H <sub>2</sub> O	-	-	86Stu1
PHI1986a02	Ba <sub>2</sub> · Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> · 12H <sub>2</sub> O	harmotome	16.2	M	-	H <sub>2</sub> O	-	-	86Stu1
PHI1990a01	Ba <sub>2</sub> · Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> · 12H <sub>2</sub> O	harmotome	16.0	M	-	H <sub>2</sub> O	-	-	90Stu1
PHI1990a02	Ba <sub>2</sub> · Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> · 12H <sub>2</sub> O	harmotome	16.2	M	-	H <sub>2</sub> O	-	-	90Stu1
PHI1990a03	Ba <sub>2</sub> · Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> · 12H <sub>2</sub> O	harmotome	16.1	M	-	H <sub>2</sub> O	-	-	90Stu1
PHI1995a01	Ca <sub>1.2</sub> K <sub>1.6</sub> Na <sub>0.6</sub> · Al <sub>4.8</sub> Si <sub>11.3</sub> O <sub>32</sub> · 12H <sub>2</sub> O	phillipsite-K	15.8	M	-	H <sub>2</sub> O	-	-	95Hal1
PHI1995a02	Ca <sub>0.1</sub> K <sub>1.0</sub> Na <sub>3.3</sub> · Al <sub>4.9</sub> Si <sub>11.3</sub> O <sub>32</sub> · 13H <sub>2</sub> O	[phillipsite]	15.9	M	Na	H <sub>2</sub> O	-	-	95Hal1
PHI1999a02	Ba <sub>0.14</sub> Ca <sub>0.04</sub> K <sub>0.04</sub> Na <sub>0.06</sub> Sr <sub>1.90</sub> · Al <sub>4.50</sub> Si <sub>11.50</sub> O <sub>32</sub> · 10.80H <sub>2</sub> O	[phillipsite]	16.3	M	Sr	H <sub>2</sub> O	-	-	99Gua1
PHI1999a03	Ba <sub>0.07</sub> Ca <sub>0.04</sub> K <sub>0.04</sub> Na <sub>0.05</sub> Sr <sub>1.70</sub> · Al <sub>3.80</sub> Si <sub>12.20</sub> O <sub>32</sub> · 11.30H <sub>2</sub> O	[phillipsite]	16.4	M	Sr	H <sub>2</sub> O	-	-	99Gua1
PHI1999b01	Ca <sub>0.54</sub> K <sub>2.08</sub> Na <sub>1.38</sub> · Al <sub>4.72</sub> Si <sub>11.30</sub> O <sub>32</sub> · 11.33H <sub>2</sub> O	phillipsite-K	15.9	M	-	H <sub>2</sub> O	-	-	99Gua2
PHI1999b02	Cs <sub>4.20</sub> Na <sub>0.47</sub> · Al <sub>4.72</sub> Si <sub>11.30</sub> O <sub>32</sub> · 11.33H <sub>2</sub> O	[phillipsite]	15.8	M	Cs	H <sub>2</sub> O	-	-	99Gua2
PHI1999b03	K <sub>2.42</sub> Na <sub>2.21</sub> · Al <sub>4.59</sub> Si <sub>11.40</sub> O <sub>32</sub> · 11.21H <sub>2</sub> O	(phillipsite)	15.8	S	-	H <sub>2</sub> O	-	-	99Gua2
PHI1999b04	Cs <sub>3.24</sub> Na <sub>1.36</sub> · Al <sub>4.59</sub> Si <sub>11.40</sub> O <sub>32</sub> · 11.2H <sub>2</sub> O	(phillipsite)	15.7	S	Cs	H <sub>2</sub> O	-	-	99Gua2
PHI2000a01	(NH <sub>4</sub> ) <sub>5.04</sub> Na <sub>0.60</sub> · Al <sub>5.90</sub> Si <sub>10.00</sub> O <sub>32</sub> · 9.1H <sub>2</sub> O	[phillipsite]	15.7	M	NH <sub>4</sub>	H <sub>2</sub> O	-	-	2000Gua1
PHI2000a02	(NH <sub>4</sub> ) <sub>4.40</sub> Na <sub>0.20</sub> · Al <sub>4.41</sub> Si <sub>11.60</sub> O <sub>32</sub> · 8.1H <sub>2</sub> O	[phillipsite]	15.8	M	NH <sub>4</sub>	H <sub>2</sub> O	-	-	2000Gua1
PHI2000a03	(NH <sub>4</sub> ) <sub>3.40</sub> Na <sub>0.40</sub> · Al <sub>3.80</sub> Si <sub>12.16</sub> O <sub>32</sub> · 7.8H <sub>2</sub> O	[phillipsite]	15.9	M	NH <sub>4</sub>	H <sub>2</sub> O	-	-	2000Gua1
PHI2000c01	Ba <sub>0.04</sub> Ca <sub>1.50</sub> K <sub>2.40</sub> Na <sub>0.50</sub> · Al <sub>5.90</sub> Si <sub>10.10</sub> O <sub>32</sub> · 10.6H <sub>2</sub> O	phillipsite	15.7	M	-	H <sub>2</sub> O	-	-	2000Gua2

**Table PHI.2.1** (PHI-II.1  $P12_1/m1$ , continued)

code	chemical composition	M	FD	SM	CE	SR	TT	T	REF
PHI2001a01	$\text{Ba}_{0.02}\text{Ca}_{0.28}\text{K}_{0.15}\text{Li}_{4.87}$ $\text{Na}_{0.31} \cdot \text{Al}_{5.78}\text{Si}_{10.17}\text{O}_{32} \cdot$ $13.92\text{H}_2\text{O}$	[phillipsite]	15.9	M	Li	$\text{H}_2\text{O}$	-	-	2001Gua1
PHI2001b01	$\text{Ba}_{0.2}\text{Ca}_{0.1}\text{K}_{0.4}\text{Mg}_{1.8}\text{Na}_{0.4} \cdot$ $\text{Al}_{5.3}\text{Si}_{10.7}\text{O}_{32} \cdot 14.6\text{H}_2\text{O}$	[phillipsite]	16.0	M	Mg	$\text{H}_2\text{O}$	-	-	2001Gua2
PHI2001b02	$\text{Ba}_{0.1}\text{Ca}_{0.1}\text{K}_{0.4}\text{Mg}_{1.2}\text{Na}_{0.9} \cdot$ $\text{Al}_{4.5}\text{Si}_{11.6}\text{O}_{32} \cdot 11.5\text{H}_2\text{O}$	[phillipsite]	16.0	M	Mg	$\text{H}_2\text{O}$	-	-	2001Gua2
PHI2002a01	$\text{Ba}_{2.83}\text{Ca}_{0.02}\text{K}_{0.02}\text{Na}_{0.12} \cdot$ $\text{Al}_{5.90}\text{Si}_{10.10}\text{O}_{32} \cdot 10.7\text{H}_2\text{O}$	[phillipsite]	16.1	M	Ba	$\text{H}_2\text{O}$	D	332	2002San1
PHI2002a02	$\text{Ba}_{2.83}\text{Ca}_{0.02}\text{K}_{0.02}\text{Na}_{0.12} \cdot$ $\text{Al}_{5.90}\text{Si}_{10.10}\text{O}_{32} \cdot 2.52\text{H}_2\text{O}$	[phillipsite]	17.5	M	Ba	$\text{H}_2\text{O}$	D	482	2002San1
PHI2002a03	$\text{Ba}_{2.83}\text{Ca}_{0.02}\text{K}_{0.02}\text{Na}_{0.12} \cdot$ $\text{Al}_{5.90}\text{Si}_{10.10}\text{O}_{32}$	[phillipsite]	18.2	M	Ba	-	D	551	2002San1
<b>PHI-IV.1 <math>P12/m1</math></b>									
PHI1999a01	$\text{Ba}_{0.08}\text{Ca}_{0.32}\text{K}_{0.10}\text{Na}_{0.10}\text{Sr}_{5.26}$ $\cdot \text{Al}_{11.80}\text{Si}_{20.20}\text{O}_{64} \cdot$ $22.40\text{H}_2\text{O}$	[phillipsite]	16.1	M	Sr	-	-	-	99Gua1
<b>PHI-II.2 <math>B112/b</math></b>									
PHI1997a01	$(\text{NH}_4)_4(\text{C}_5\text{N}_2\text{H}_{16})_4 \cdot$ $\text{Al}_4\text{Co}_{12}\text{P}_{16}\text{O}_{64}$	ACP-PHI1	15.0	S	-	$\text{H}_2\text{P}$ MDA	-	-	97Fen1

**Table PHI.2.2** Structural parameters of PHI-type compounds.

code	$a$ [Å]	$b$ [Å]	$c$ [Å]	$\beta, \gamma$ [°]	$V$ [Å <sup>3</sup> ]	$T$ [K]	reference
<b>PHI-I <math>Bmm</math></b>							
PHI1988a01	9.89	14.06	14.10	90	1961	-	88van1
PHI1995a03	10.0163(3)	14.1585(5)	14.2328(4)	90	2018	n.s.	95Hal1
<b>PHI-II.1 <math>P12_1/m1</math></b>							
PHI1973a01	9.865(2)	14.300(4)	8.668(2)	124.20(3)	1011	n.s.	73Rin1
PHI1974a01	9.865(2)	14.300(4)	8.668(2)	124.20(3)	1011	RT	74Rin1
PHI1974a02	9.879(2)	14.139(2)	8.693(2)	124.81(1)	997	RT	74Rin1
PHI1986a01	9.869(2)	14.1295(7)	8.7092(9)	124.74(1)	998	293	86Stu1
PHI1986a02	9.84(2)	14.09(2)	8.68(1)	124.78(1)	988	100	86Stu1
PHI1990a01	9.869(2)	14.1295(7)	8.7092(9)	124.74(1)	998	293	90Stu1
PHI1990a02	9.84(2)	14.09(2)	8.68(1)	124.78(1)	988	100	90Stu1
PHI1990a03	9.884(6)	14.100(5)	8.655(4)	124.59(5)	993	15	90Stu1
PHI1995a01	9.9436(2)	14.2128(3)	8.7062(3)	124.833(3)	1010	n.s.	95Hal1
PHI1995a02	10.0159(2)	14.1579(3)	8.6928(3)	125.043(3)	1009	n.s.	95Hal1
PHI1999a02	9.8624(7)	14.0028(7)	8.6283(6)	124.56(7)	981	n.s.	99Gua1
PHI1999a03	9.8627(5)	13.9718(9)	8.5949(6)	124.52(7)	976	n.s.	99Gua1
PHI1999b01	9.9664(8)	14.195(1)	8.696(1)	124.89(1)	1009	n.s.	99Gua2
PHI1999b02	10.051(5)	14.195(7)	8.693(5)	125.16(3)	1014	n.s.	99Gua2
PHI1999b03	10.0386(8)	14.183(1)	8.6704(8)	125.08(7)	1010	n.s.	99Gua2
PHI1999b04	10.067(2)	14.235(3)	8.709(2)	125.06(2)	1022	n.s.	99Gua2
PHI2000a01	10.0507(5)	14.2016(8)	8.7281(8)	125.123(5)	1019	100	2000Gua1
PHI2000a02	10.0122(8)	14.194(1)	8.728(2)	125.02(1)	1016	100	2000Gua1
PHI2000a03	9.9596(3)	14.2015(4)	8.7051(5)	124.990(3)	1009	100	2000Gua1
PHI2000c01	9.8881(5)	14.4040(8)	8.6848(5)	124.271(3)	1018	n.s.	2000Gua2

**Table PHI.2.2** (PHI-II.1  $P12_1/m1$ , continued)

code	$a$ [Å]	$b$ [Å]	$c$ [Å]	$\beta, \gamma$ [°]	$V$ [Å <sup>3</sup> ]	$T$ [K]	reference
PHI2001a01	9.8719(4)	14.1791(5)	8.7184(7)	124.4(2)	1007	n.s.	2001Gua1
PHI2001b01	9.8257(7)	14.1341(8)	8.6911(8)	124.04(1)	1000	n.s.	2001Gua2
PHI2001b02	9.9743(6)	14.147(1)	8.6355(8)	124.886(7)	1000	n.s.	2001Gua2
PHI2002a01	9.8327(2)	14.1373(3)	8.7114(2)	124.608(2)	997	332	2002San1
PHI2002a02	9.8791(3)	13.7051(4)	8.3189(3)	125.556(3)	916	482	2002San1
PHI2002a03	9.9331(4)	13.3044(7)	8.1821(4)	125.663(4)	879	551	2002San1
<b>PHI-IV.1 <math>P12_1/m1</math></b>							
PHI1999a01	16.503(9)	14.043(8)	8.687(7)	99.4(1)	1986	n.s.	99Gua1
<b>PHI-II.2 <math>B112/b</math></b>							
PHI1997a01	10.2233(4)	14.3041(6)	14.6052(5)	90.162(1)	2136	293	97Fen1

**Table PHI.2.3** Transformation matrices. Entries not listed are not transformed.

code	shift	matrix	coord. transform.	reference
<b>PHI-I <math>Bmb</math></b>				
PHI1988a01	$-\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$	<b>a, -c, b</b>	$x+\frac{1}{4}, -z+\frac{1}{2}, y-\frac{1}{4}$	88van1
PHI1995a03	$\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$	<b>a, -c, b</b>	$x-\frac{1}{4}, -z+\frac{1}{2}, y-\frac{1}{4}$	95Hal1
<b>PHI-II.1 <math>P12_1/m1</math></b>				
PHI1999a01	$\frac{1}{4}, \frac{1}{2}, -\frac{1}{4}$	<b>c, -b, a</b>	$z+\frac{1}{4}, -y+\frac{1}{2}, x-\frac{1}{4}$	99Gua1
<b>PHI-II.2 <math>B112/b</math></b>				
PHI1997a01	$\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$	<b>a, c, -b</b>	$x-\frac{1}{4}, z-\frac{1}{2}, -y+\frac{1}{4}$	97Fen1

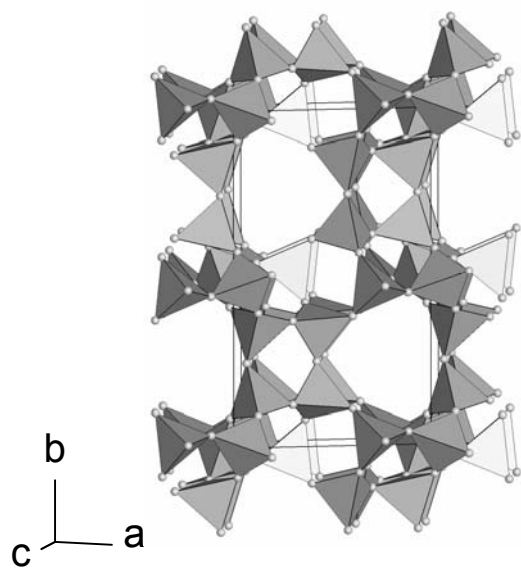
## PHI.3 Framework structures

### PHI.3.1 PHI-II.1 ( $P12_1/m1$ , IT #11)

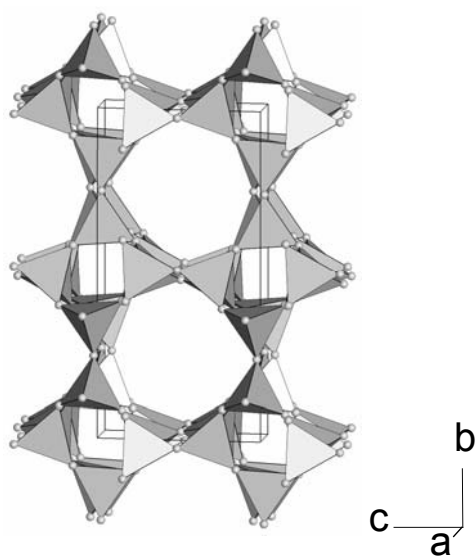
**Table PHI.3.1.2** Selected interatomic distances and angles for PHI-II.1, phillipsite,  $\text{Ca}_{1.7}\text{K}_{2.0}\text{Na}_{0.4} \cdot \text{Al}_{5.3}\text{Si}_{10.6}\text{O}_{32} \cdot 12\text{H}_2\text{O}$  (PHI1974a01, 74Rin1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
(Si,Al)11 - O4	1.647(5)	151.5(3)	(Si,Al)12 - O4	1.643(5)	151.5(3)
(Si,Al)11 - O12	1.667(4)	142.9(3)	(Si,Al)12 - O21	1.645(4)	143.8(3)
(Si,Al)11 - O6	1.670(4)	142.9(3)	(Si,Al)12 - O11	1.658(4)	139.8(2)
(Si,Al)11 - O22	1.670(4)	138.5(3)	(Si,Al)12 - O6	1.658(3)	142.9(3)
mean	1.664	144.0	mean	1.651	144.5
(Si,Al)21 - O31	1.642(2)	148.1(4)	(Si,Al)22 - O5	1.648(4)	148.1(3)
(Si,Al)21 - O5	1.649(5)	148.1(3)	(Si,Al)22 - O32	1.651(2)	141.8(2)
(Si,Al)21 - O12	1.661(4)	142.9(3)	(Si,Al)22 - O21	1.653(4)	143.8(3)
(Si,Al)21 - O22	1.663(3)	138.5(3)	(Si,Al)22 - O11	1.666(4)	139.8(2)
mean	1.654	144.4	mean	1.654	143.4

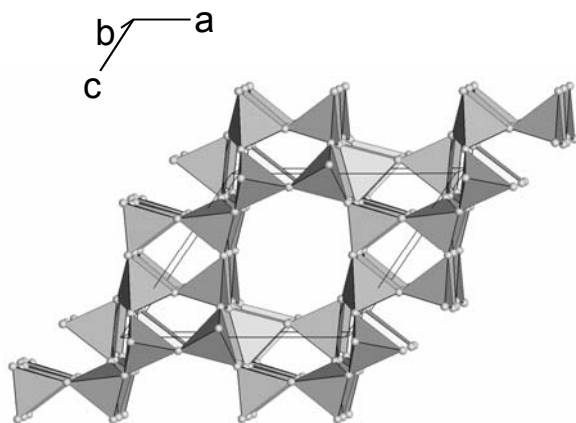




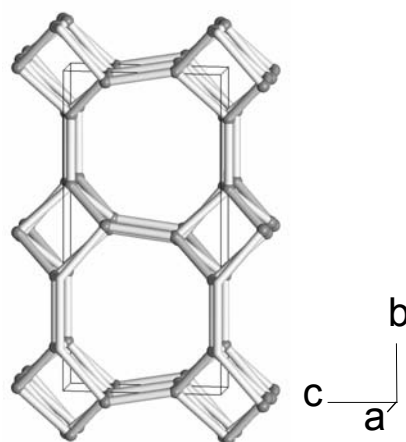
**a** View parallel **c** rotated by  $2^\circ$  about **b** and **a**.



**b** View parallel **a** rotated by  $2^\circ$  about **b** and **c**.



**c** View parallel **b** rotated by  $1^\circ$  about **a** and  $2^\circ$  about **c**.



**d** Ball and stick model corresponding to **b**.

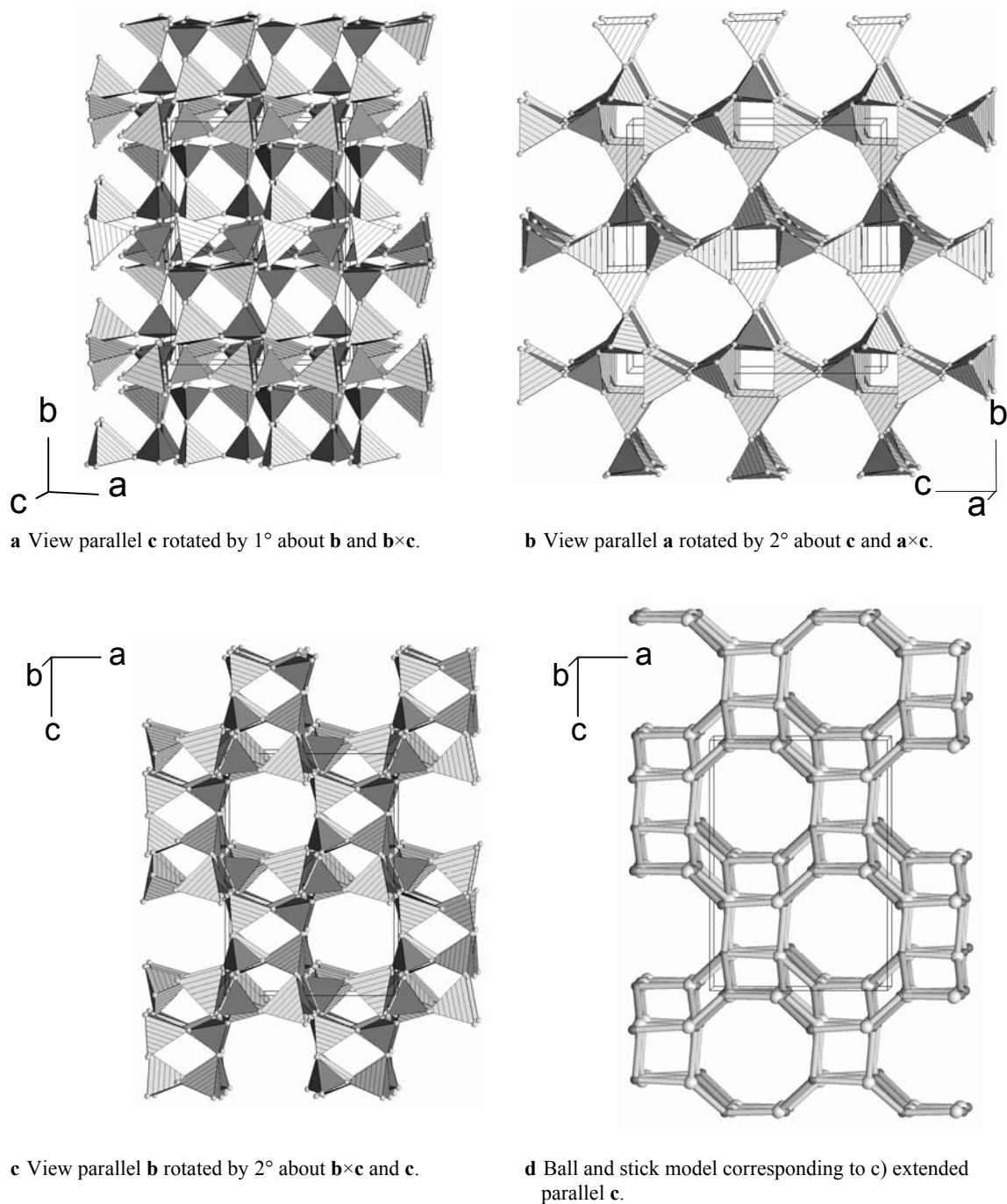
**Fig. PHI.3.1.1** Projections of the PHI-II.1 crystal structure of phillipsite,  $\text{Ca}_{1.7}\text{K}_{2.0}\text{Na}_{0.4} \cdot \text{Al}_{5.3}\text{Si}_{10.6}\text{O}_{32} \cdot 12\text{H}_2\text{O}$  (PHI1974a01, 74Rin1).

**Table PHI.3.1.1** Atomic coordinates and site definitions for PHI-II.1, phillipsite,  $\text{Ca}_{1.7}\text{K}_{2.0}\text{Na}_{0.4} \cdot \text{Al}_{5.3}\text{Si}_{10.6}\text{O}_{32} \cdot 12\text{H}_2\text{O}$  (PHI1974a01, 74Rin1).

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> [Å <sup>2</sup> ]	site symmetry	Wyckoff position	no. of atoms in unit cell
(Si,Al)11	0.0604(2)	0.4922(1)	0.2844(3)	1.11	1	4(f)	2.68 / 1.32
(Si,Al)12	0.7362(2)	0.4752(1)	0.2805(3)	1.08	1	4(f)	2.68 / 1.32
(Si,Al)21	0.8796(2)	0.6396(1)	0.9579(3)	1.14	1	4(f)	2.68 / 1.32
(Si,Al)22	0.5794(2)	0.6409(1)	0.9981(3)	1.06	1	4(f)	2.68 / 1.32
O11	0.6445(6)	0.5766(3)	0.1878(6)	1.94	1	4(f)	4
O12	0.0254(5)	0.5846(3)	0.1494(6)	1.85	1	4(f)	4
O21	0.6100(5)	0.3870(3)	0.1728(6)	1.89	1	4(f)	4
O22	0.1335(6)	0.4024(3)	0.2289(7)	2.04	1	4(f)	4
O31	0.0665(8)	$\frac{1}{4}$	0.0196(9)	2.12	<i>m</i>	2(e)	2
O32	0.4186(8)	$\frac{1}{4}$	0.9384(9)	1.94	<i>m</i>	2(e)	2
O4	0.8957(6)	0.4560(3)	0.2713(7)	2.06	1	4(f)	4
O5	0.6978(6)	0.6262(3)	0.9217(7)	2.32	1	4(f)	4
O6	0.7872(5)	0.4795(3)	0.4982(6)	1.90	1	4(f)	4
K1	0.8480(3)	$\frac{1}{4}$	0.2076(4)	4.11	<i>m</i>	2(e)	2
Ca1	0.6080(4)	0.6262(3)	0.4401(5)	2.67	1	4(f)	1.65(2)
OW1	0.755(1)	$\frac{3}{4}$	0.473(1)	6.90	<i>m</i>	2(e)	2
OW2	0.155(1)	$\frac{3}{4}$	0.438(1)	7.53	<i>m</i>	2(e)	2
OW3	0.3208(8)	0.8525(6)	0.174(1)	8.63	1	4(f)	4
OW4	0.508(1)	$\frac{1}{4}$	0.438(2)	21.25	<i>m</i>	2(e)	2
OW5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	14.61	$\bar{1}$	2(d)	2

**PHI.3.2 PHI-II.2 (*B* 1 1 2/*b*, IT #15)****Table PHI.3.2.2** Selected interatomic distances and angles for PHI-II.2, ACP-PHI1,  $(\text{NH}_4)_4(\text{C}_5\text{N}_2\text{H}_{16})_4 \cdot \text{Al}_4\text{Co}_{12}\text{P}_{16}\text{O}_{64}$  (PHI1997a01, 97Fen1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
(Co,Al)11 - O6	1.852(6)	142.4(5)	P12 - O21	1.502(9)	150.3(6)
(Co,Al)11 - O12	1.861(6)	139.1(4)	P12 - O4	1.504(6)	142.2(4)
(Co,Al)11 - O4	1.863(6)	142.2(4)	P12 - O11	1.515(6)	140.3(4)
(Co,Al)11 - O22	1.866(7)	143.1(5)	P12 - O6	1.524(6)	142.4(5)
mean	1.861	141.7	mean	1.511	143.8
P21 - O3	1.503(6)	155.6(6)	(Co,Al)11 - O21	1.816(9)	150.3(6)
P21 - O22	1.503(7)	143.1(5)	(Co,Al)11 - O5	1.860(5)	131.0(4)
P21 - O12	1.526(6)	139.1(4)	(Co,Al)11 - O3	1.860(6)	155.6(6)
P21 - O5	1.527(6)	131.0(4)	(Co,Al)11 - O11	1.878(6)	140.3(4)
mean	1.515	142.2	mean	1.854	144.3



**Fig. PHI.3.2.1** Projections of the PHI-II.2 crystal structure of ACP-PHI1,  $(\text{NH}_4)_4(\text{C}_5\text{N}_2\text{H}_{16})_4 \cdot \text{Al}_4\text{Co}_{12}\text{P}_{16}\text{O}_{64}$  (PHI1997a01, 97Fen1).



## PHI.5 Flexibility and apertures

The value of the mean T-O-T angles for six precisely determined crystal structures of the PHI-type (PHI1973a01, PHI1974a01, PHI1974a02, PHI1990a0, PHI1990a02 and PHI1990a03) is about 144°, with individual angles ranging from 135° to 161°. This range of values T-O-T for the PHI-type is smaller than observed for the LTA-type compounds where it varies from 125° to 179° (see the LTA chapter and [92Bau1]). The full range of values displayed by numerous zeolite frameworks of different types is 115° to 180° as observed in a sample of 2436 T-O-T values [95Bau1]. The mean angle in PHI-type compounds is similar to the maximum of the distribution of T-O-T angles in silicoaluminates zeolites (about 143° [95Bau1]).

The crystal structure of only one dehydrated sample of a PHI-type compound has been experimentally determined (PHI2002a03). Its unit cell volume is 13% smaller than the volume of the corresponding hydrated sample (PHI2002a01). This might indicate that the PHI-type framework is collapsible (see the NAT chapter and [92Bau2]).

The 8-rings in the framework of PHI-type are compressed, deformed and buckled with diameters ranging from around 3 Å to ca. 4.3 Å and therefore clearly narrower than in the LTA-type, where they measure over 4 Å.

## PHI.6 Other information

Inasmuch as phillipsite is a constituent of voluminous sedimentary rocks it is potentially available in large amounts. It is being considered for various uses, such as wastewater treatment [94Pas1] or water purification [2001Kal1]. Soil amendment and cement manufacture are other possible uses [99Col1].

## PHI.7 References

- 1795Del1 Delam  therie, J.C.: Th  orie de la Terre, Vol. 1. Maradan, Paris.
- 1801Ha  1 Ha  y, R.J. : Trait   de min  ralogie, Vol. 3. Louis, Paris.
- 1825Lev1 L  vy, A.: Annals of Philosophy, new ser. **10** (1825) 361.
- 61Bar1 Barrer, R.M.: J. Chem. Soc. (1961) 983.
- 61Sad1 Sadanaga, R., Marumo, F., Tak  uchi, Y. : Acta Crystallogr. **14** (1961) 1153.
- 62Ste1 Steinfink, H. : Acta Crystallogr. **15** (1962) 644.
- 64Bar1 Barrer, R.M.: J. Chem. Soc. (1964) 2296.
- 69K  h1 K  hl, G.H.: Amer. Mineral. **54** (1969) 1607.
- 73Rin1 Rinaldi, R., Pluth, J.J., Smith, J.V. in: Proceedings of the Third International Conference on Molecular Sieves, Uytterhoeven, J.B. (ed.), Leuven University Press (1973) 100.
- 74Rin1 Rinaldi, R., Pluth, J.J., Smith, J.V.: Acta Crystallogr. **B30** (1974) 2426.

- 
- 86Stu1 Stuckenschmidt, E.: Dissertation Johann Wolfgang Goethe-Universität Frankfurt (1986).
- 88van1 van Genechten, K.A., Mortier, W.J.: Zeolites **8** (1988) 273.
- 90Stu1 Stuckenschmidt, E., Fuess, H., Kvik, Å.: Eur. J. Mineral. **2** (1990) 861.
- 92Bau1 Baur, W.H.: J. Solid State Chem. **97** (1992) 243.
- 92Bau2 Baur, W.H.: Proc. Polish-German Zeolite Colloquium, Toruń (1992) 11.
- 94Pas1 Passaglia, E. Azzolini, S.: Mater. Engin. **5** (1994) 343.
- 95Bau1 Baur, W. H.: Proc. Second Polish-German Zeolite Colloquium, Toruń (1995) 171.
- 95Hal1 Haller, M.: Thesis Johann Wolfgang Goethe-Universität Frankfurt (1995).
- 97Fen1 Feng, P., Bu, X., Stucky, G.D.: Nature **388** (1997) 735.
- 98Coo1 Coombs, D.S., Alberti, A., Armbruster, T., Artioli, G., Colella, C., Galli, E., Grice, J.D., Liebau, F., Mandarino, J.A., Minato, H., Nickel, E.H., Passaglia, E., Peacor, D.R., Quartieri, S., Rinaldi, R., Ross, M., Sheppard, R.A., Tillmanns, E., Vezzalini, G.: Eur. J. Mineral. **10** (1998) 1037.
- 99Col1 Collela, C.: Stud. Surf. Sci. Catal. **125** (1999) 641.
- 99Gua1 Gualtieri, A.F., Passaglia, E., Galli, E., Viani, A.: Microporous Mesoporous Mater. **31** (1999) 33.
- 99Gua2 Gualtieri, A.F., Caputo, D., Colella, C.: Microporous Mesoporous Mater. **32** (1999) 319.
- 2000Gua1 Gualtieri, A.F.: Acta Crystallogr. **B56** (2000) 584.
- 2000Gua2 Gualtieri, A.F.: J. Appl. Crystallogr. **33** (2000) 267.
- 2001Kal1 Kalló, D.: Rev. Mineral. Geochem. **45** (2001) 519.
- 2001Gua1 Gualtieri, A.F.: Zeolites and Mesoporous Materials at the Dawn of the 21<sup>st</sup> Century. Stud. Surf. Sci. Catal. **135**. Galarneau, A., Di Renzo, F., Fajula, F., Viedrine, J. (eds.), Amsterdam: Elsevier (2001) 147 (01-O-04).
- 2001Gua2 Gualtieri, A.F.: Mater. Science Forum **378-381** (2001) 677.
- 2002San1 Sani, A., Cruciani, G., Gualtieri, A.F.: Phys. Chem. Miner. **29** (2002) 351.

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