

Crystal-chemistry of phillipsites from the Neapolitan Yellow Tuff

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Abstract: The crystal-chemistry of a series of natural phillipsites [ideal unit formula: $K_2(Na,Ca_{0.5})_3[Al_5Si_{11}O_{32}] \cdot 12H_2O$, $Z = 1$, with $a \sim 9.96$, $b \sim 14.20$, $c \sim 8.71$ Å, and $\beta \sim 124.97^\circ$, space group $P2_1/m$] from the Neapolitan Yellow Tuff was investigated by electron-microprobe analysis in the energy dispersive mode and powder X-ray diffraction using an in-house conventional diffractometer. A significantly different population of the extra-framework cations (*i.e.*, K, Na and Ca) and water molecules was observed for crystals from different localities. All phillipsites from NYT can be described as “K-rich phillipsites”, due to the significantly high amount of potassium among the extra-framework cations. Rietveld structure refinements have been performed. The refined unit-cell parameters of the phillipsite samples show a little, but significant, control of the crystal-chemistry. The unit-cell volumes range between ~ 1008.7 and ~ 1011.6 Å³. Samples with the highest amount of Na and the lowest amount of K show the largest unit-cell volume, whereas the smallest unit-cell volumes are observed for the samples with the lowest amount of Na and the highest amount of Ca. As to the unit-cell lengths, the longest *c*-axis with the highest distortion of the monoclinic unit-cell (*i.e.*, with the highest β angle value) is observed for the samples with the lowest amount of Ca and the highest amount of K. The structure refinements performed in this study show a good general agreement with the complex configuration of the extra-framework population recently found on the basis of single-crystal data, with (1) one or two mutually exclusive K-rich sites, $\sim 0\text{--}0.3$ Å apart (*i.e.*, K1 and K2); (2) one site partially occupied by Ca + Na; (3) seven independent sites occupied by water molecules (W1, W2, W3, W4, W4', W5 and W6).

Key-words: phillipsite, zeolites, crystal-chemistry, X-ray diffraction, Neapolitan Yellow Tuff.

1. Introduction

Phillipsite is a common natural zeolite with ideal composition $K_2(Na,Ca_{0.5})_3[Al_5Si_{11}O_{32}] \cdot 12H_2O$ (Coombs *et al.*, 1997; Passaglia & Sheppard, 2001). This zeolite typically occurs in amygdaloidal vugs of massive volcanic rocks (*e.g.*, basalt), in palagonitic basalts and tuffs as an alteration product of volcanic glass, or in diagenetically altered sediments in “closed hydrologic systems” (*e.g.*, saline lake and hot spring deposits) and “open hydrologic systems” (*e.g.*, soils and land surface deposits, burial diagenetic environments, deep-sea sediments) (Galli & Loschi-Ghittoni, 1972; Gottardi & Galli, 1985; Langella *et al.*, 2001; Passaglia & Sheppard, 2001; Sheppard & Hay, 2001; Gatta *et al.*, 2009). Phillipsite crystals usually occur in spherical radial aggregates and ubiquitously twinned (Černý, 1964; Rinaldi *et al.*, 1974) and intergrown with several other zeolites (*e.g.*, faujasite, offretite, gismondine, garronite and gobbinsite) (Rinaldi *et al.*, 1975; Passaglia & Sheppard, 2001, and references therein).

The crystal structure of phillipsite was solved by Rinaldi *et al.* (1974) on the basis of single-crystal X-ray diffraction data, and recently re-investigated by Gatta *et al.* (2009). The symmetry of natural phillipsite is monoclinic, with space group $P2_1/m$, $a \sim 9.865$, $b \sim 14.300$, $c \sim 8.693$ Å and $\beta \sim 124.81^\circ$ (Fig. 1). The crystal-chemistry of natural and NH_4^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , and Si^{2+} -exchanged phillipsites, the high-temperature and high-pressure behaviour have been object of several investigations (Steinfink, 1962; Černý *et al.*, 1977; Stuckenschmidt *et al.*, 1990; García *et al.*, 1992; Gualtieri *et al.*, 1999a and b, 2000; Gualtieri, 2000; Passaglia *et al.*, 2000; Sani *et al.*, 2002; Gatta & Lee, 2007).

As highlighted in several studies devoted to the crystal-chemistry of natural zeolites, phillipsites show a very wide range of Si/(Si + Al), K/(K + Ba) and Na/(Na + Ca) ratios (Alberti, 1978; Passaglia & Sheppard, 2001; Gatta *et al.*, 2009). A wide variation in the extra-framework population results from chemical composition of the precursor reacting glass, or chemical composition of the fluids interacting

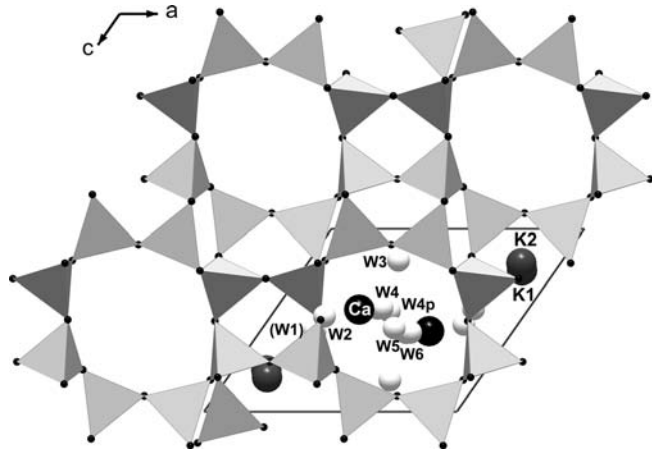


Fig. 1. The crystal structure of phillipsite viewed down [010]. Structural model by Gatta *et al.* (2009).

with this precursor, or post-formational exchange processes (de' Gennaro *et al.*, 1982, 1999).

Neapolitan Yellow Tuff (NYT) is one of the most studied Italian pyroclastic deposit. Its formation is linked to one of the most powerful and largest phreatomagmatic eruptions of Campi Flegrei (Southern Italy), dated about 15.000 ybp (Insinga *et al.*, 2006). More than 50 % of its volume was involved in syn- and post-depositional epigenetic processes, leading to the crystallization of zeolites, mainly phillipsite and subordinately chabazite and analcime (de' Gennaro *et al.*, 2000; Langella *et al.*, 2001). Chemical composition of phillipsites from NYT was reported in previous studies by various authors (Passaglia & Vezzalini, 1985; de' Gennaro *et al.*, 1990, 2000).

The present study reports new crystal-chemical data of different phillipsites from the major outcrops of the NYT, in order to give: (1) new insight into their extra-framework cationic population and (2) any crystal-chemical variation according to their spatial distribution. This is the first step of a wider project aimed to study this natural zeolite as potential nuclear waste disposal material due to its high ion-exchange selectivity for Cs^+ and Sr^{2+} (Gualtieri *et al.*, 1999a and b; Bosch *et al.*, 2004).

A description of the cation exchange mechanism of this zeolite, as well as a comprehension of the discrepancies often found between the extra-framework population deduced on the basis of the CEC experiments and that calculated from chemical analyses, require detailed structural refinements. The small size of the phillipsite crystals from the NYT hindered any single-crystal X-ray diffraction investigation. In this light, the multi-methodological characterization of NYT phillipsites was performed by electron-microprobe analysis in the energy-dispersive mode (EMPA-EDS) and powder X-ray diffraction, using an in-house conventional diffractometer. Previous powder diffraction investigations of phillipsite were, in fact, mainly performed by synchrotron source (Gualtieri *et al.*, 1999a and b, 2000; Sani *et al.*, 2002; Gatta & Lee, 2007), and only one was performed with in-house conventional X-ray diffractometer (Gualtieri, 2000). As highlighted by

Gualtieri (2000), Rietveld refinement based on conventional powder X-ray diffraction data can be obtained even for structurally complex materials, as natural phillipsite.

2. Sample description and mineralogy

The Neapolitan Yellow Tuff occurs as thick and widespread pyroclastic deposits on the periphery of Campi Flegrei, within the city of Napoli and in the Campanian Plain. The erupted products range from trachyte to phonolite in composition and probably represent the partial evacuation of a zoned magma reservoir. The physico-chemical conditions favourable to zeolitization process soon after the emplacement of the tuff are based on: (1) presence of sufficient water of phreatomagmatic origin for the enhancement of hydration-dissolution processes in the volcanic glass; (2) emplacement temperatures at least close to water vapour condensation; (3) highly fragmented volcanoclastic products and highly reactive alkali-trachytic glass that quickly buffered the acid pH of the system; (4) substantial thickness of the deposit, favouring natural thermal insulation and lengthy persistence of elevated temperatures. More details pertaining to the zeolitization mechanisms of the NYT are given in de' Gennaro *et al.* (2000).

Samples used for the present investigation were collected in five different outcrops of NYT scattered within the caldera of Campi Flegrei. The sites are: Torregaveta (P3, P3bis), Licola (P4 and P4ter), Policlinico (P5), Chiaiano (P6) and Grotta del Sole (P7) (Fig. 2). With the only exception of Torregaveta site, an outcrop located right close to the sea, all specimens were collected on abandoned quarry fronts which favoured the sampling at different stratigraphic heights. This allowed us to obtain a

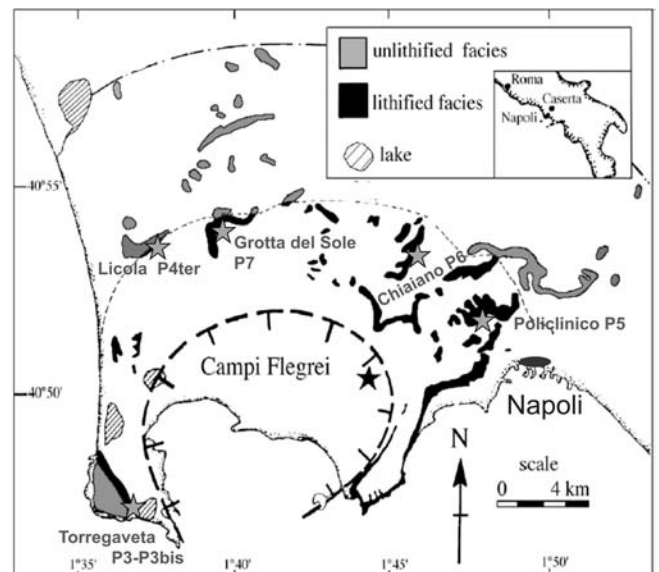


Fig. 2. Spatial distribution of the phillipsite samples (grey stars) belonging to the Neapolitan Yellow Tuff.

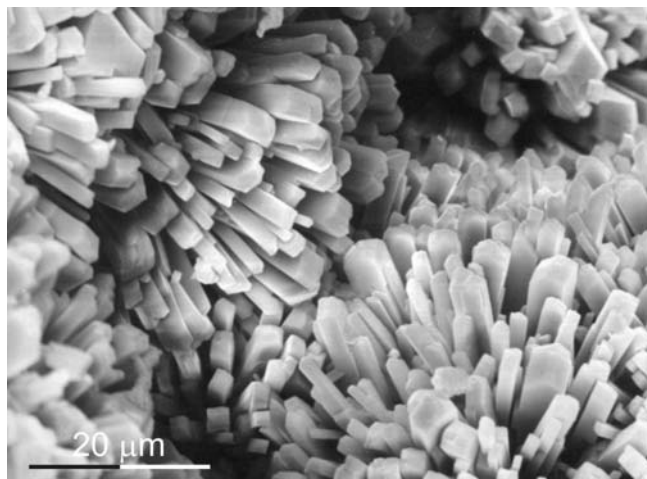


Fig. 3. SEM micrograph of phillipsite clusters from the sample P6.

homogeneous and representative sample of the outcrop. Phillipsite mostly occurs as clusters of needle-shaped crystals ranging in size from few to some tens of micrometres. No significant difference in shape and size was observed among samples of different outcrops. A typical example of phillipsite cluster (P6, Chiaiano) is shown in Fig. 3.

Common current uses of the NYT are in zootechny as anticlustering and in agriculture as soil amendants (Langella *et al.*, 1995). Other researches carefully describe its potential uses such as in the treatment of polluted waters (cationic exchange; Amicarelli *et al.*, 1989; de' Gennaro *et al.*, 2005), in gas treatments and thermal energy storage (adsorption; Ciambelli *et al.*, 1984), and in ceramics and lightweight aggregates preparation (Andreola *et al.*, 1994; de' Gennaro *et al.*, 2008).

3. Experimental methods

Once removed all traces of surface alterations, the rock samples of NYT were ground and sieved. The 60–125 mesh grain-size fraction was selected for further enrichment operations as it turned to be the richest in zeolites. A combination of ultrasonic bath, centrifugation and a final magnetic separation (Frantz isodynamic separator) led to a ~95 wt% zeolite-rich fraction, mainly represented by phillipsite and a few units percent of chabazite.

Zeolite-enriched powder samples were then embedded into a two-component epoxy resin and successively polished for obtaining suitable surfaces for microanalyses; those were performed on a coupled EMPA-EDS apparatus (Oxford Inca X-Act microanalyser and Jeol JSM-5310, respectively – CISAG, Federico II University) using a defocused beam (15 kV) in order to minimize Na and K migration under the electron beam. Natural international standards (albite for Na, Al and Si, diopside for Mg and Fe, orthoclase for K, wollastonite for Ca, rutile for Ti and rhodonite for Mn) were used. Chemical analyses with $E\% > \pm 10$ were discarded (Passaglia *et al.*, 1990). Results are reported in Table 1 and

plotted in Fig. 4; the latter also shows typical compositions of NYT phillipsites from literature (de' Gennaro & Langella, 1996; de' Gennaro *et al.*, 2000).

X-ray powder diffraction data of the samples P3, P3bis, P4, P4ter, P5, P6 and P7 were collected with an automated Panalytical X'Pert Pro modular diffractometer equipped with a RTMS fast detector X'Celerator. Operating conditions were: monochromatised $\text{CuK}\alpha$ radiation, 40 kV, 40 mA, 2θ -range from 4 to 100° , step size of $2\theta = 0.017^\circ$, counting time of 240 s per step, fixed 1° divergence slit and 2° antiscatter slit. Powders with grain size $< 10 \mu\text{m}$ were obtained by means of a McCrone micronising mill (agate cylinders and wet grinding time 15 min). To minimize preferred orientations, the sample was carefully side-loaded onto an aluminium sample holder with an oriented quartz mono-crystal underneath. The diffraction patterns were successfully indexed with the monoclinic unit-cell previously reported by Rinaldi *et al.* (1974) and Gatta *et al.* (2009) (*i.e.*, $a \sim 9.92$, $b \sim 14.31$, $c \sim 8.74 \text{ \AA}$, $\beta \sim 124.9^\circ$), and the reflection conditions agreed with the space group $P2_1/m$. The Rietveld structure refinements (Rietveld, 1969) were then performed with the GSAS computer package (Larson & Von Dreele, 1994), starting from the structural model of Gatta *et al.* (2009). The pseudo-Voigt profile function proposed by Thompson *et al.* (1987) was used to fit the experimental pattern. The asymmetry correction of Finger *et al.* (1994) was applied. No evidence of preferred orientation effects was found, for all the refinements. Neutral atomic scattering factors, from the GSAS library, were used. The scattering curve of Si was used at the tetrahedral sites (partially occupied by Si + Al), that of K at the two independent K-sites, whereas for the Ca-site a mixed scattering curve (30 % Ca + 70 % Na) was adopted. Scale factor, background (18 term polynomial-shifted Chebyshev function), zero shift, unit-cell parameters, and peak profile were first refined. Then, the atomic parameters were refined. All the atoms were refined isotropically; thermal parameters of the four independent tetrahedral sites (*i.e.*, T1, T2, T3, and T4), of the nine oxygen sites (*i.e.*, O1, O2, O3, O4, O5, O6, O7, O8, and O9) and of the two extra-framework K-sites (*i.e.*, K1 and K2) were refined by grouping them in three groups, and constraining the program to apply the same shifts within each group. The sites were labelled to maintain the labelling scheme used by Rinaldi *et al.* (1974) and Gatta *et al.* (2009). Stereochemical restraints were introduced for the tetrahedral bond-distances [$1.65(2) \text{ \AA}$ for T–O bonds, as obtained by single-crystal refinement; Gatta *et al.*, 2009] to avoid divergence in the first stages of refinement. The statistical weight of these restraints was gradually decreased to zero as the refinement proceeded. When the convergence was achieved, the residuals in the difference-Fourier map of the electron density, for all the refinements, were lower than $\pm 1.1 e^-/\text{\AA}$. The refined unit-cell parameters of the aforementioned phillipsite samples are listed in Table 2. Details pertaining to the data collection and structure refinement of the sample P7 are reported in Table 3, and the Rietveld full profile fit is shown in Fig. 5. This sample (P7) was selected because its structural data

Table 1. Chemical analysis of the phillipsite samples from NYT by EPMA-EDS. The chemical formula, obtained by averaging 10 point analyses per sample, was calculated on the basis of 32 oxygens.

Sample	P3	P3 bis	P4 ter	P5	P6	P7
SiO ₂	52.84	53.79	53.19	53.74	54.95	52.54
TiO ₂	0.15	0.16	0.12	0.15	0.09	0.13
Al ₂ O ₃	18.48	18.26	18.16	17.7	16.6	18.29
Fe ₂ O ₃	0.10	0.15	0.13	0.17	0.24	0.09
MnO	0.11	0.01	0.04	0.13	0.09	0.08
MgO	0.01	0.02	0.03	0.05	0.10	0.02
CaO	2.55	2.78	3.31	3.76	2.29	2.77
Na ₂ O	3.11	2.23	1.62	0.96	1.55	2.91
K ₂ O	8.78	9.44	9.66	9.09	9.71	8.24
H ₂ O ^a	14.00	13.68	13.78	14.25	14.63	15.05
TOT	100.05	100.52	100.04	99.86	100.08	100.13
Si/Al	2.43	2.5	2.49	2.58	2.81	2.44
R	0.71	0.71	0.71	0.72	0.74	0.71
Na/K	0.53	0.36	0.25	0.16	0.24	0.54
E%	-4.01	-3.67	-5.57	-3.55	-5.03	-2.95
CEC teor.	3.78	3.72	3.77	3.6	3.42	3.69
Si	11.27	11.37	11.33	11.47	11.73	11.29
Ti	0.02	0.03	0.02	0.02	0.01	0.02
Al	4.65	4.55	4.56	4.45	4.18	4.63
Fe	0.01	0.02	0.02	0.02	0.03	0.01
Mn	0.01	0	0.01	0.01	0.01	0.01
Mg	0	0.01	0.01	0.01	0.03	0.01
Ca	0.58	0.63	0.76	0.86	0.52	0.64
Na	1.29	0.91	0.67	0.40	0.64	1.21
K	2.39	2.54	2.63	2.48	2.65	2.26
H ₂ O	9.97	9.65	9.78	10.16	10.43	10.79

Note: R = Si/Si + Al; ^aWater was calculated by difference.

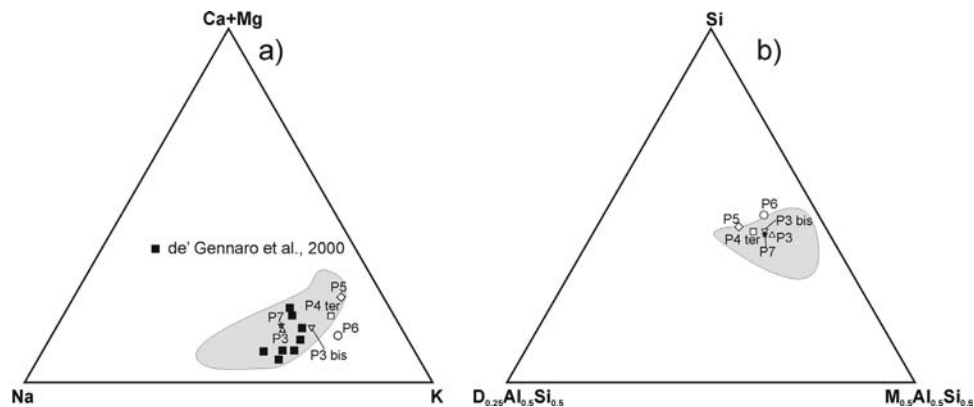


Fig. 4. Molar proportions of exchangeable cations (a) and chemical variability (b) in phillipsites from literature (shaded area from de' Gennaro & Langella, 1996) and from the present study.

Table 2. Refined unit-cell parameters of phillipsites from NYT.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	<i>R_p</i>	χ^2
P3	9.9682(6)	14.2104(9)	8.6999(9)	124.830(6)	1011.59(12)	0.0997	5.842
P3bis	9.9599(5)	14.2106(8)	8.7075(8)	124.891(6)	1010.88(11)	0.0893	4.861
P4	9.9637(7)	14.2070(11)	8.7110(10)	124.974(7)	1010.39(14)	0.0992	6.187
P4ter	9.9597(6)	14.2091(9)	8.7105(10)	124.919(7)	1010.76(12)	0.0905	5.646
P5	9.9512(5)	14.1930(8)	8.7292(7)	125.100(5)	1008.69(9)	0.0734	7.170
P6	9.9627(6)	14.1770(8)	8.7469(8)	125.149(6)	1010.15(9)	0.0801	9.034
P7	9.9792(5)	14.2075(8)	8.7071(8)	124.978(6)	1011.50(11)	0.0864	3.635

Table 3. Data pertaining to the structural refinement, refined positional, thermal displacement parameters (\AA^2) and bond-distances (\AA) of phillipsite P7.

Site (Wyck.)	<i>x</i>	<i>y</i>	<i>z</i>	Site occupancy	<i>U</i> _{iso}		
T1 (4 <i>f</i>)	0.7299(24)	0.0078(11)	0.2820(29)	1	0.009(1)	T1-O2 1.676(4)	K1-O1 (x 2) 3.002(3)
T2 (4 <i>f</i>)	0.4197(18)	0.1428(11)	0.0323(20)	1	0.009(1)	T1-O3 1.683(5)	K1-O5 (x 2) 2.998(3)
T3 (4 <i>f</i>)	0.0448(30)	0.0125(11)	0.2716(28)	1	0.009(1)	T1-O5 1.669(4)	K1-O8 3.208(13)
T4 (4 <i>f</i>)	0.0888(18)	0.1375(10)	0.0094(17)	1	0.009(1)	T1-O7 1.673(5)	K1-W1 3.001(4)
O1 (4 <i>f</i>)	0.0546(32)	0.1079(13)	0.1682(33)	1	0.015(2)		K1-W2 3.001(4)
O2 (4 <i>f</i>)	0.6551(35)	0.5966(17)	0.1774(26)	1	0.015(2)	T2-O2 1.661(4)	K1-W3 (x 2) 2.999(3)
O3 (4 <i>f</i>)	0.5971(26)	0.0980(17)	0.2066(23)	1	0.015(2)	T2-O3 1.662(6)	
O4 (4 <i>f</i>)	0.0604(20)	0.9088(17)	0.1945(28)	1	0.015(2)	T2-O6 1.663(5)	Ca-O3 2.733(10)
O5 (4 <i>f</i>)	0.8882(24)	0.0412(4)	0.2780(34)	1	0.015(2)	T2-O8 1.665(4)	Ca-O4 2.261(9)
O6 (4 <i>f</i>)	0.2833(19)	0.3663(18)	0.0835(23)	1	0.015(2)		Ca-O7 2.501(34)
O7 (4 <i>f</i>)	0.7988(26)	0.5125(25)	0.5052(30)	1	0.015(2)	T3-O1 1.660(6)	Ca-W2 2.227(9)
O8 (2 <i>e</i>)	0.5307(32)	3/4	-0.003(6)	1	0.015(2)	T3-O4 1.662(4)	Ca-W3 2.398(9)
O9 (2 <i>e</i>)	0.036(6)	1/4	-0.027(7)	1	0.015(2)	T3-O5 1.647(5)	Ca-W4 (I) 2.218(9)
K1(K2) (2 <i>e</i>)	0.8590(25)	1/4	0.2167(22)	0.8(1)	0.109(5)	T3-O7 1.654(4)	Ca-W4 (II) 3.002(18)
Ca (4 <i>f</i>)	0.6827(9)	0.3716(4)	0.5621(23)	0.3(1)	0.057(5)		Ca-W4' (I) 2.610(6)
W1 (2 <i>e</i>)	1.2252(23)	1/4	0.481(7)	1	0.12(5)	T4-O1 1.658(4)	Ca-W4' (II) 2.208(7)
W2 (2 <i>e</i>)	0.205(4)	3/4	0.486(5)	1	0.12(5)	T4-O4 1.665(6)	Ca-W5 (I) 2.425(6)
W3 (4 <i>f</i>)	0.251(4)	0.6359(22)	0.1264(28)	0.9(1)	0.12(5)	T4-O6 1.658(4)	Ca-W5 (I) 2.427(7)
W4 (4 <i>f</i>)	0.5432(23)	0.7917(12)	0.533(7)	0.4(1)	0.12(5)	T4-O9 1.655(5)	Ca-W6 2.206(9)
W4' (4 <i>f</i>)	0.518(4)	0.730(4)	0.534(4)	0.2(1)	0.092(5)		
W5 (4 <i>f</i>)	0.476(5)	1.012(4)	0.492(5)	0.6(1)	0.092(5)		
W6 (4 <i>f</i>)	0.4338(32)	0.9214(14)	0.3009(32)	0.5(1)	0.092(5)		
<i>a</i> = 9.9792(5) <i>b</i> = 14.2075(8) <i>c</i> = 8.7071(8) β = 124.978(6)						Sp. Gr.	<i>P</i> ₂₁ / <i>m</i>
N.obs	2437						
N. variables	81						
<i>R</i> _p	0.0864						
<i>wR</i> _p	0.1137						
χ^2	3.635						
<i>R</i> (<i>F</i> ²)	0.1173						

Note: For the T1, T2, T3 and T4 sites the scattering curve of silicon was used. For the K1 site the scattering curve of potassium was used, whereas for the Ca-site a mixed scattering curve (30 % Ca + 70 % Na) was adopted.

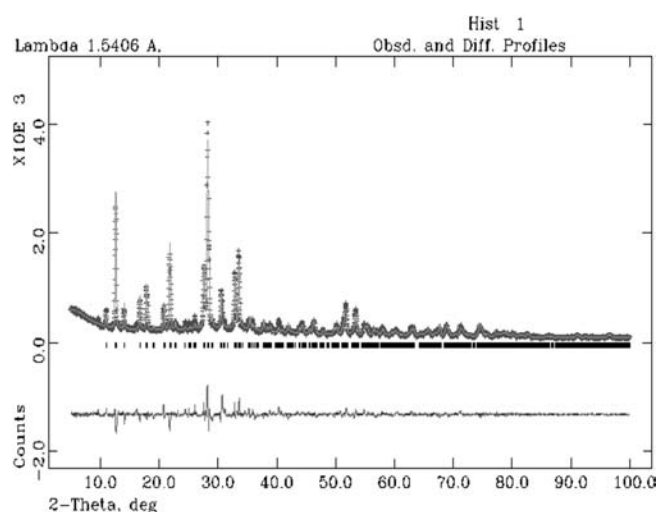


Fig. 5. Experimental (crosses) and calculated (solid line) diffraction patterns of phillipsite P7. Calculated peak positions and difference plots are shown at the bottom of the pattern.

show the most significant differences with respect to those recently reported on the basis of single-crystal data (Gatta

et al., 2009). The refined site occupancy of the extra-framework sites in P3, P3bis, P4, P4ter, P5, and P6 phillipsites are listed in Table S1 (deposited as Supplementary material, freely available online on the GSW site of the journal, <http://eurjmin.geoscienceworld.org/>).

4. Discussion and conclusions

The chemical compositions of the NYT phillipsites here investigated are in good agreement with those reported in previous studies (Passaglia *et al.*, 1990; de' Gennaro & Langella, 1996; de' Gennaro *et al.*, 2000). All phillipsites from NYT can be described as "K-rich phillipsites", due to the significantly high amount of K among the extra-framework cations (Table 1, Fig. 4a). Calcium reaches its highest value in the sample P5 from Policlinico (*i.e.*, 0.86 a.p.f.u., Table 1), thus suggesting a possible post-crystallization exchange process, due to the interaction with pore water. The two samples from Torregaveta outcrop (P3 and P3bis) display the highest Na content (*i.e.*, 1.29 and 0.91 a.p.f.u., respectively, Table 1), likely due to their location very close to the sea-side; however, the sample from Grotta

del Sole (P7) also shows a significantly high Na content, despite its “inner” location (Fig. 2). The Si/Al ratios range between 2.43 and 2.81 (*i.e.*, P3 and P6, respectively, Table 1) (Fig. 4b), and the *R* values (ranging between 0.71 and 0.74, Table 1) are in agreement with those reported by Passaglia & Sheppard (2001) for sedimentary phillipsites from hydromagmatic deposits, formerly improperly defined as “geoautoclave” system.

The refined unit-cell parameters of the aforementioned phillipsite samples show a little, but significant, control of the crystal-chemistry. The unit-cell volumes range between ~ 1008.7 and $\sim 1011.6 \text{ \AA}^3$. Samples with the highest amount of Na and the lowest amount of K show the largest unit-cell volume (*i.e.*, P3 and P7) (Tables 1 and 2). In contrast, the smallest unit-cell volume is observed for the samples with the lowest amount of Na and the highest amount of Ca (*i.e.*, P5 and P6, Tables 1 and 2). In addition, even the unit-cell lengths appear to change in response to the crystal-chemistry: the longest *c*-axis with the highest distortion of the monoclinic unit-cell (*i.e.*, with the highest β angle value) is observed for the sample with the lowest amount of Ca and the highest amount of K (*i.e.*, P6) (Tables 1 and 2).

The powder X-ray structure refinements showed a good agreement with the structural model reported by Gatta *et al.* (2009). The tetrahedral framework of phillipsite is built up by 4- and 8-membered rings, which represent the “secondary building units” (SBU code: 4 and 8; Framework Type: PHI; Armbruster & Gunter, 2001; Baerlocher *et al.*, 2001) (Fig. 1). The 4-membered rings are connected to one-another throughout the framework in arrays of four double crankshaft chains, parallel to [100]. Two main channel systems occur in the PHI framework-type: an 8-membered ring channel along [100] and an 8-membered ring channel along [010], which intersect each other (Fig. 1). The refined intra-tetrahedral bond-distances in this study show a highly disordered Si/Al-distribution in the tetrahedral framework (Table 3), according to the previous experimental findings (Rinaldi *et al.*, 1974; Gualtieri, 2000; Gatta *et al.*, 2009). The refined extra-framework population consists of: (1) two mutually exclusive K-rich sites, $\sim 0\text{--}0.3 \text{ \AA}$ apart (*i.e.*, K1 and K2, Fig. 1); (2) one site partially occupied by Ca + Na (labelled as “Ca”, Fig. 1); (3) seven independent sites occupied by water molecules, here labelled as W1, W2, W3, W4, W4', W5 and W6, with W1 and W2 lying at the Wyckoff special positions $2e$, and the W4 site splits into two sub-sites $\sim 0.4 \text{ \AA}$ apart with partial occupancies (W4 and W4') (Fig. 1, Table 3). The coordination-shells of the K1 and K2 sites consist of large and distorted polyhedra with coordination number CN = 9 (five framework oxygens + four H₂O molecules) (Table 3). In the sample P7, the distance between the K1 and K2 sites tends to 0 Å, toward one K-site (Table 3), whereas for all the other samples it approaches 0.3 Å. As already observed by Gatta *et al.* (2009), the coordination-shell of the Ca site consists of at least nine possible mutually exclusive configurations, with CN = 6–7 (three framework oxygens + four H₂O molecules, or three framework oxygens + three H₂O molecules, Table 3).

The structure refinements performed in this study show a good general agreement with the complex configuration of the extra-framework population previously found by Gatta *et al.* (2009) on the basis of single-crystal data, with some differences. In particular, the location of the water molecules shows little, but significant, difference and, in addition, the quality of powder data leads to a systematic over-estimation of the site occupancy factor of water molecules. The variance-covariance matrix shows, in fact, a strong correlation between the site occupancy factor of the water molecules, their thermal displacement parameters (which were restrained to one value for all the seven water sites) and their fractional coordinates.

Further refinements have been performed with the P3 and P7 phillipsite diffraction data adopting the structural model of the extra-framework population reported by Rinaldi *et al.* (1974), with two cations sites, mainly occupied by K and Ca/Na, and five water molecules sites. However, the final results were worse than those obtained using the structural model by Gatta *et al.* (2009). Previous powder structure refinements of NH₄⁺-, Na⁺-, K⁺-, Cs⁺-, Mg²⁺-, Ca²⁺-, Ba²⁺-, and Sr²⁺-exchanged phillipsites highlighted how the extra-framework configuration in this zeolite shows significant changes in response to the nature of the extra-framework cations. In other words, the number, the location and the occupancy of water molecule sites might be significantly different among natural/synthetic phillipsites.

According to Gualtieri (2000), our experiments show that powder diffraction data of microporous materials with complex crystal-structure and collected with conventional X-ray diffractometers may lead to good structural refinements if a reliable structure model, for example based on single-crystal structure data, is already available.

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