

## New insights into the crystal structure and crystal chemistry of the zeolite phillipsite

G. DIEGO GATTA,<sup>1,2,\*</sup> PIERGILIO CAPPELLETTI,<sup>3</sup> NICOLA ROTIROTI,<sup>1,2</sup> CARLA SLEBODNICK,<sup>4</sup>  
AND ROMANO RINALDI<sup>5</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy

<sup>2</sup>CNR-Istituto per la Dinamica dei Processi Ambientali, Milano, Italy

<sup>3</sup>Dipartimento di Scienze della Terra, Università Federico II, Via Mezzocannone 8, I-80134 Napoli, Italy

<sup>4</sup>Crystallography Laboratory, Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia 24061, U.S.A.

<sup>5</sup>Dipartimento di Scienze della Terra, Università degli Studi di Perugia, Piazza Università 1, I-06100 Perugia, Italy

### ABSTRACT

The crystal-structure, crystal-chemistry, and low-temperature behavior of a natural phillipsite-Na from the “Newer Volcanic Suite,” Richmond, Melbourne district, Victoria, Australia [ $\text{K}_{0.75}(\text{Na}_{0.88}\text{Ca}_{0.57})_{\Sigma 1.45}(\text{Al}_{2.96}\text{Ti}_{0.01}\text{Si}_{5.07})_{\Sigma 8.04}\text{O}_{16} \cdot 6.2\text{H}_2\text{O}$  ( $Z = 2$ ),  $a = 9.9238(6)$ ,  $b = 14.3145(5)$ ,  $c = 8.7416(5)$  Å,  $\beta = 124.920(9)^\circ$ , and  $V = 1018.20(9)$  Å<sup>3</sup>, space group  $P2_1/m$ ], have been investigated by means of in situ single-crystal X-ray diffraction, thermogravimetric analysis, and electron microprobe analysis in the wavelength dispersive mode. Two accurate structural refinements have been obtained on the basis of single-crystal X-ray diffraction data collected at 298 and 100 K, with:  $R_1(F)_{298\text{K}} = 0.035$ , 3678 unique reflections with  $F_o > 4\sigma(F_o)$  and 195 parameters, and  $R_1(F)_{100\text{K}} = 0.035$ , 3855 unique reflections,  $F_o > 4\sigma(F_o)$  and 195 parameters. In both refinements, the residuals in the final difference Fourier maps are  $< 1 e^-/\text{Å}^3$ . A configuration of the extra-framework population different from that reported in previous studies is found at room temperature, with two possible sites for potassium (K1 and K2), one sodium/calcium site (Ca), and seven independent sites partially occupied by water molecules (W1, W2, W3, W4, W4', W5, and W6). The low-temperature refinement shows that the framework component of the phillipsite structure is maintained within the  $T$ -range investigated. However, a change in the configuration of the extra-framework content occurs at low temperature: the occupancy of site K2 drastically decreases, while that of site K1 increases, the Ca site is split into two sub-sites (Ca1 and Ca2) and the number of water molecule sites decreases to six (W1, W2, W3, W4, W5, and W6). The rearrangement of the extra-framework population at low temperature is likely due to the change in shape (and size) of the micropores by tetrahedral tilting. The evolution of the “free diameters” with temperature shows that an “inversion” of the ellipticity of the eight-membered ring channel along [010] occurs. The evolution of the unit-cell parameters with  $T$  (measured at 298, 250, 200, 150, and 100 K) shows a continuous and linear trend, without evident thermo-elastic anomalies. The axial and volume thermal expansion coefficients ( $\alpha_i = l_j^{-1} \cdot \partial l_j / \partial T$ ,  $\alpha_v = V^{-1} \cdot \partial V / \partial T$ ) between 100 and 298 K, calculated by weighted linear regression, yield the following values:  $\alpha_a = 1.8(1) \times 10^{-5}$ ,  $\alpha_b = 1.2(1) \times 10^{-5}$ ,  $\alpha_c = 1.1(1) \times 10^{-5}$ , and  $\alpha_v = 3.7(1) \times 10^{-5} \text{K}^{-1}$ . The thermal expansion of phillipsite is significantly anisotropic ( $\alpha_a:\alpha_b:\alpha_c = 1.64:1.09:1$ ).

**Keywords:** Zeolite, phillipsite, crystal chemistry, low temperature, single-crystal X-ray diffraction