

Article

First Occurrence of Willhendersonite in the Lessini Mounts, Northern Italy

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Abstract: Willhendersonite is a rare zeolite, with very few occurrences reported globally (Terni Province, Italy; the Eifel Region, Germany; Styria, Austria). Moreover, the data available from these sites are very limited and do not allow a detailed picture of this zeolite's mineralogical and chemical characteristics. In this work, a new willhendersonite occurrence is reported from the Tertiary volcanic rocks of the Lessini Mounts, northern Italy. Morphology, mineralogy and chemical composition of selected crystals were studied by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), X-ray Diffraction (XRD), and electron probe microanalyser (EPMA). Willhendersonite occurs within basaltic rocks as isolated, colorless, transparent crystals with prismatic to flattened morphologies. Individual crystals often grow together to form small elongated clusters and trellis-like aggregates. The diffraction pattern exhibits 33 well-resolved diffraction peaks, all of which can be indexed to a triclinic cell with unit cell parameters $a = 9.239(2) \text{ \AA}$; $b = 9.221(2) \text{ \AA}$; and $c = 9.496(2) \text{ \AA}$, $\alpha = 92.324(2)^\circ$, $\beta = 92.677(2)^\circ$, $\gamma = 89.992^\circ$ (Space Group $P\bar{1}$). The chemical data point to significant variability from Ca-rich willhendersonite ($(K_{0.23}Na_{0.03})_{\Sigma=0.26}Ca_{1.24}(Si_{3.06}Al_{3.00}Fe^{3+}_{0.01})_{\Sigma=6.07}O_{12} \cdot 5H_2O$) to Ca-K terms ($(K_{0.94}Na_{0.01})_{\Sigma=0.95}Ca_{0.99}(Si_{3.07}Al_{2.93}Fe^{3+}_{0.00})_{\Sigma=6.00}O_{12} \cdot 5H_2O$). Willhendersonite from the Lessini Mounts highlights the existence of an isomorphous series between the Ca-pure crystals and Ca-K compositions, possibly extended up to a potassic end-member.



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Keywords: willhendersonite; chabazite; zeolites; Lessini Mounts

1. Introduction

Willhendersonite was first described by Peacor et al. [1], who studied specimens from mafic potassic lava at San Venanzo (Terni, Italy) and from a limestone xenolith within basalt at Mayen (Eifel area, Germany). Both these samples correspond to the schematic chemical formula $CaKAl_3Si_3O_{12} \cdot 5H_2O$, with space group $P\bar{1}$ and unit cell parameters $a = 9.206$; $b = 9.216$; and $c = 9.500 \text{ \AA}$, $\alpha = 92.34^\circ$, $\beta = 92.70^\circ$, $\gamma = 90.12^\circ$ [1,2]. Structural investigations [2,3] on single crystals from the German locality revealed the close structural relationship to chabazite, $CaAl_2Si_4O_{12} \cdot 6H_2O$, which has the same framework topology with framework type code CHA (chabazite, willhendersonite [4–6]). However, the Si/Al ordering leads to a reduction of the framework symmetry from topological $R\bar{3}m$ to topochemical $R\bar{3}$. Moreover, the presence of different degrees of ordering (Si,Al) and the position of extra-framework cations and water molecules further reduce the real symmetry to $P\bar{1}$ [2,7,8]. A further occurrence was reported by Walter et al. [9] from Wilhelmsdorf (Styria, Austria), and a chemical and crystallographic description of a Ca-rich willhendersonite from a melilitite plug at Colle Fabbri, a second locality within the volcanic rocks of the Terni province, was given by Vezzadini et al. [10]. Recently, single crystals of willhendersonite from Bellerberg (eastern Eifel District, Germany) were studied by X-ray diffraction methods between 100 and 500 °K, showing a phase transition from triclinic to rhombohedral symmetry [11]. These changes in the framework are accompanied by migration of cations, partly assuming unfavorably low coordinations in the high-temperature structure due to the loss of H_2O molecules. Re-

hydration at room temperature yields the triclinic structure of willhendersonite, although the single crystals become polysynthetically twinned [11].

Willhendersonite from Terni was chemically analyzed by Peacor et al. [1]. The data yield the empirical formula, based on 12 oxygens of $K_{0.90}Ca_{1.01}Al_{2.93}Si_{3.08}O_{12} \cdot 5.43H_2O$, which compares favorably with the ideal formula $KCaAl_3Si_3O_{12} \cdot 5H_2O$ ($Z = 2$). A large number of crystals from Colle Fabbri were chemically analyzed by Vezzalini et al. [10]. The obtained data showed chemical variability ranging from the holotype sample composition ($CaKAl_3Si_3O_{12} \cdot 5H_2O$), through intermediate compositions, to a Ca-pure term. The most common Ca/Ca + K ratio among the different varieties ranges from 1.0 to 0.9 and represents Ca-pure terms. The ratio 0.6 to 0.5, which is similar to that reported in the literature for willhendersonite from San Venanzo, is also quite common. The rarest compositions are the intermediate ones. The value of R is always close to 0.50, with calcium as the dominant extra-framework cation (0.98–1.54 apfu) [10]. The potassium content is relevant in samples from San Venanzo and Mayen (0.9 apfu and 0.74 apfu, respectively) but is very low (0.03 to 0.30 apfu) in the sample from Colle Fabbri [1,10]. In any case, all the data available in the literature for this zeolite come from only three areas (Terni, Styria, and Eifel). For this reason, it is of great importance to increase the amount of data, finding crystals of willhendersonite also in other locations.

The Tertiary basalts of the Lessini Mounts (Veneto Volcanic Province, Northern Italy) are known as suitable host rocks for the growth of secondary mineral associations [12]. Zeolites such as gmelinite, analcime, chabazite, and phillipsite have already been observed in the basaltic rock of Monte Calvarina [13]. Chabazite, phillipsite, harmotome, and analcime were discovered in the vugs of volcanite outcropping near Fittà [14]. Fibrous erionite and offretite with potential toxicological implications have been recently discovered in several localities of the Lessini Mounts [12,15–18]. Among these common zeolites, rare species such as willhendersonite and yugawaralite were recently found in northern Italy [12]. This study aims to present a mineralogical and chemical characterization of willhendersonite, found for the first time within vesicles of the basanitic rocks in the Lessini Mounts.

2. Geological Background

The Veneto Volcanic Province (Northern Italy) covers an area of about 2000 km² (Figure 1) and is the result of extensive volcanic activity that occurred from the Tertiary [19–21]. Several magmatic pulses occurred between the Late Paleocene and the Miocene, with the most significant part of the eruptions taking place in submarine environments [19–22]. The Veneto Volcanic Province can be subdivided into four main volcanic districts based on different tectono-magmatic features (Figure 1). They are the Lessini Mounts, the Marostica Hills, the Berici Hills, and the Euganean Hills. The main products are volcanoclastic rocks, hyaloclastites, pillow lavas, and lava flows of a mafic to ultramafic composition. Rocks of more acidic compositions are rare and only occur in the Euganean Hills.

The Lessini Mounts are located within an NNW-trending extensional structure, namely the Alpone-Agno graben [23,24], bounded to the west by the NNW-SSE Castelvetro normal fault (Figure 1). The volcanic sequence of the Lessini Mounts has a thickness of up to 400 m and is mainly represented by tuffs and lava flows, with several column-jointing eruptive necks and subordinate hyaloclastites and pillow lavas. The most abundant rock-types are basanites and alkali olivine basalts, while transitional basalts, tholeiites, nephelinite, hawaiites, trachy-basalts, and basaltic andesites are less abundant [20,21,25]. Petrological and geochemical data [20,21,25,26] indicate a within-continental-plate character for the magmatism in agreement with regional geodynamics, which places this magmatism in a context dominated by a tensional system.

Most of the Lessini volcanic rocks are often deeply weathered and show cavities and vugs of variable sizes that are almost always lined by a thin, microcrystalline crust, which is the substratum of well-shaped, secondary minerals [12]. The secondary phases are mainly zeolites and clay minerals, which represent ~90 vol.% of the total secondary

minerals; other silicates (apophyllite, gyrolite, prehnite, pectolite) are very rare, as are oxides (quartz) and carbonates (calcite, aragonite). Clay minerals are generally the first minerals that precipitated along the walls, whereas the core of the vesicles commonly contains well-shaped zeolites. The coating thickness is usually less than 0.5 mm, while the zeolite crystals range in size from <1 mm to 1 cm. Typical vesicle infillings consist of chabazite, phillipsite-harmotome, analcime, natrolite, gmelinite, and offretite, and these are the most represented types. Heulandite, stilbite, and erionite are less common, whereas willhendersonite and yugawaralite are very rare zeolite species.

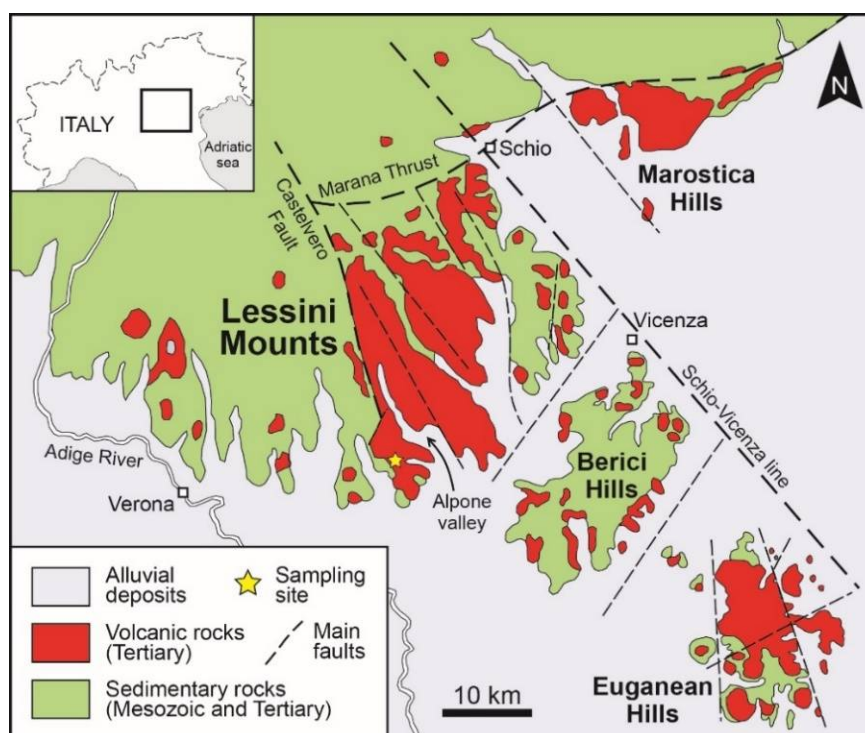


Figure 1. Simplified geological map of the Veneto Volcanic Province (modified from de Vecchi et al. [20]) showing the Lessini Mountains and the locations of the sampling site.

3. Materials and Methods

The investigated crystals were obtained from a suite of more than 300 samples of volcanic rocks from Lessini Mountains, Italy. The zeolite willhendersonite can be found in small cavities of basanitic rocks predominantly filled by chabazite and clay minerals.

Willhendersonite crystals were initially recognized from their physical properties using a binocular microscope, (Nikon TK-1270E, Tokyo, Japan) while powder X-ray diffraction (XRD) was used to confirm their mineralogical composition. Pure crystals were selected from each sample and extracted from the matrix under a binocular microscope. The separated crystals were carefully cleaned and repeatedly treated in an ultrasonic bath to remove any impurities and the microspheres of clay minerals already observed during the microscopic investigations. After cleaning, an aliquot of the separated crystals was carefully pulverized in an agate mortar. All of the powder samples were prepared by side-loading an aluminum holders to obtain a quasi-random orientation. The XRD patterns were recorded using a Philips X'Change PW 1830 X-ray diffractometer (Philips X'PERT, Malvern Panalytical, Almelo, The Netherlands); Cu K α radiation), with a monochromator on secondary optics. The samples were run between 2° and 65° 2 θ . The analytical conditions were a 35 kV accelerating potential, a 30 mA filament current, a 0.02° step, and a counting time of 1 s/step.

Morphological observations and semi-quantitative chemical compositions were performed by Scanning Electron Microscopy (SEM) and Energy Dispersion Spectroscopy

(EDS) using a Philips 515 equipped with EDAX 9900 (Eindhoven, The Netherlands) and a Jeol 6400 (Jeol, Japan) with an Oxford Link Isis. The operating conditions were a 15 kV accelerating potential and a 2 to 15 nA beam current. A defocused electron beam and a shortened accumulation time (from 100 s down to 50 s) were used to minimize the alkaline metals' migration. The standards used were natural minerals and synthetic phases.

Quantitative chemical compositions were determined by an Electron Probe Microanalyser (EPMA), a CAMECA Camebax 799 (Cameca sas, cedex, France), on the other aliquot of the previously separated and cleaned crystals, fixed with epoxy resin on polished thin sections. Operating conditions were 15 kV and 15 nA using the wavelength-dispersive method; errors were ± 2 –5% for major and ± 5 –10% for minor components. Standards comprised a series of pure elements, simple oxides, or simple silicate compositions. The analyses were selected on the basis of their low E% value (E% is the balance error of the electrical charges: $[Al - (K + 2Ca)] / (K + 2Ca)$ [27]). Zeolites with an E% > 10 were rejected.

4. Results

In the Lessini basanitic rocks, willhendersonite generally occurs as euhedral to subhedral small crystals (about 0.1–0.2 mm) with a prismatic, tabular, and flattened morphology on {001}, often with rectangular sections. Individual crystals often grow together to form small elongated clusters of characteristic twinned combinations (Figure 2). In these twinned aggregates, the crystals grow in three diverse orientations, each with faces nearly perpendicular to those of the others, which typically leads to the so-called “trellis-like” aggregates [1]. The crystals are colorless and perfectly transparent, with vitreous luster on crystal faces. The cleavage is perfect, parallel to {100}, {010}, and {001}. These three cleavage planes are equivalent to the rhombohedral cleavage of isostructural chabazite. Willhendersonite from the Lessini Mounts grows on a substrate mainly consisting of clay minerals. These latter typically form layers along the walls of pore spaces with botryoidal habits and appear in a wide range of colors varying from white, pink, yellow, brown, and green to black. Clay minerals are also present as micrometric spherules of a characteristic green-blue to red color, corresponding to saponite composition with a tri-octahedral structure [12].

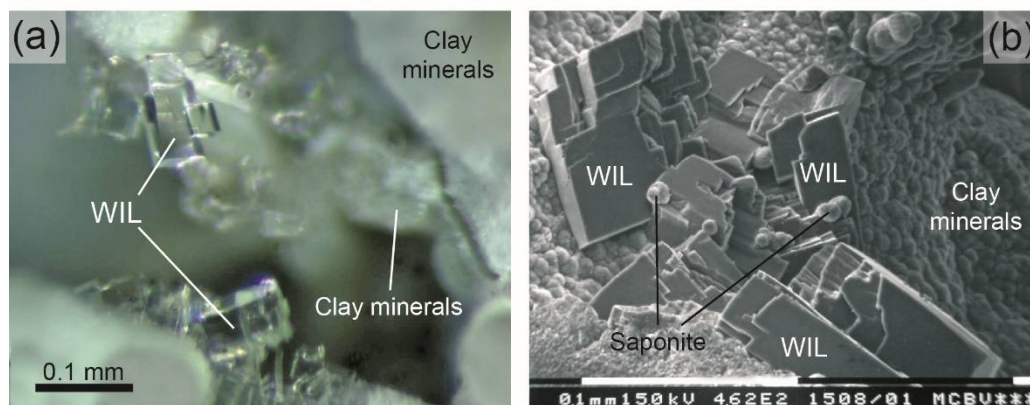


Figure 2. Willhendersonite from the Lessini Mounts: (a) stereomicroscopic image of colorless, transparent individual crystals of willhendersonite (WIL) associated to form small elongated clusters and grown on clay minerals; (b) SEM photomicrograph of willhendersonite twinned crystal aggregates (WIL) on a substrate of clay minerals with botryoidal shape and micrometric spherules of tri-octahedral saponite.

Powder X-ray diffraction data of separated willhendersonite crystals are listed in Table 1, while their diffraction pattern is shown in Figure 3. The unit-cell parameters of willhendersonite were determined by least-squares refinement of powder-diffractometer data, which was carried out in the space group $P\bar{1}$ starting from the positional parameters of the framework atoms by Tillmanns et al. [2]. High-purity quartz ($a = 4.9137$, $c = 5.4053$ Å) has been used for the refinement as an internal standard. The diffraction pattern exhibits

33 well-resolved diffraction peaks, all of which can be indexed to a triclinic cell with unit cell parameters $a = 9.239(2)$ Å; $b = 9.221(2)$ Å; and $c = 9.496(2)$ Å, $\alpha = 92.324(2)^\circ$, $\beta = 92.677(2)^\circ$, $\gamma = 89.992^\circ$ (Space Group $P\bar{1}$). The diffractogram perfectly fits that of the holotype willhendersonite and does not show other peaks relating to impurities, testifying to the purity of the analyzed crystals.

Table 1. X-ray powder diffraction data for willhendersonite from the Lessini Mounts.

2 Theta	I/I ₀	d (Å)	h	k	l	2 Theta	I/I ₀	d (Å)	h	k	l
9.32	34.77	9.4789	0	0	1	27.36	6.15	3.2601	−2	2	0
9.61	97.78	9.1915	0	1	0	28.89	6.17	3.0871	0	0	3
9.64	100	9.1591	1	0	0	29.47	20.59	3.0275	1	2	2
13.63	13.46	6.4914	1	1	0	30.04	22.37	2.9664	1	0	3
17.11	23.01	5.1774	1	1	1	30.75	56.75	2.9054	−1	−1	3
18.83	9.99	4.7407	0	0	2	31.42	8.74	2.8458	0	3	1
19.41	10.24	4.5979	2	0	0	31.77	15.93	2.8171	3	0	1
20.72	15.93	4.2871	0	−1	2	31.91	35.21	2.8028	−3	1	1
21.72	27.29	4.0873	−1	2	0	34.86	9.71	2.5741	−2	−2	2
21.68	25.71	4.1202	−2	1	0	35.47	15.13	2.5201	1	−3	2
22.63	16.21	3.9247	−1	−1	2	36.86	7.21	2.4384	1	2	3
23.16	23.16	3.8546	−2	−1	1	39.46	7.05	2.2814	−1	−1	4
23.46	25.29	3.8262	1	−1	2	41.55	8.75	2.1717	−3	3	0
23.86	17.57	3.7104	−1	2	1	44.22	6.95	2.0464	−4	1	2
23.96	15.76	3.7461	2	−1	1	49.47	6.97	1.8408	0	1	5
26.36	7.09	3.3813	−2	0	2	54.53	7.26	1.6863	0	−4	4

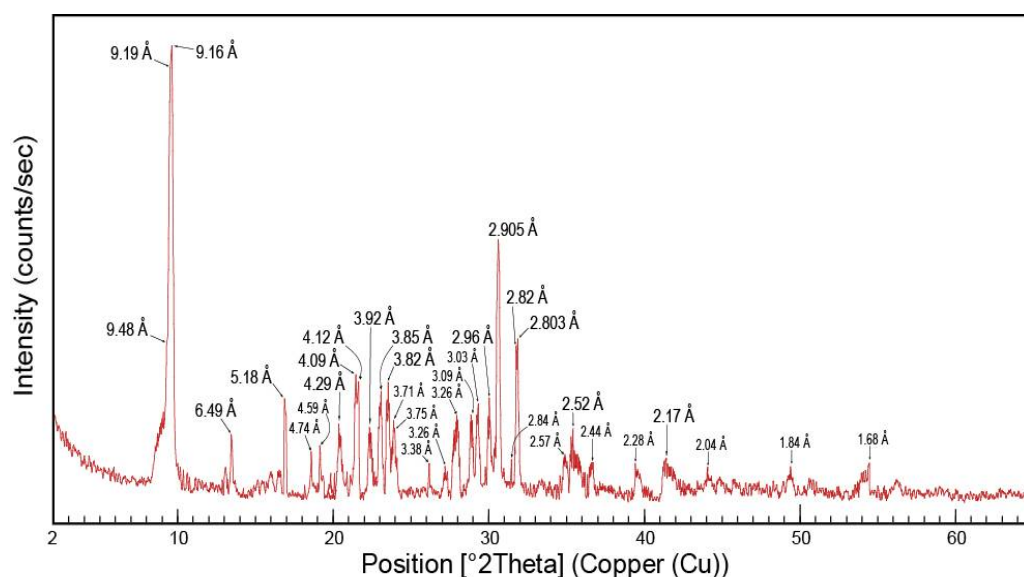


Figure 3. X-ray powder diffraction pattern for willhendersonite from the Lessini Mounts. All the diffraction peaks refer to willhendersonite.

A representative number of crystals from different specimens were extracted, carefully cleaned, and analyzed for chemical composition. The resultant analyses are presented in Tables 2 and 3. The collected chemical data show significant variability, mainly in the extra-framework cation content. Based on the $\text{Ca}/(\text{Ca} + \text{K})$ ratio, two different groups of crystals can be distinguished.

The first group of crystals correspond to a Ca-rich willhendersonite (Table 2), with an average chemical composition of $(\text{K}_{0.29}\text{Na}_{0.03})_{\Sigma=0.32}\text{Ca}_{1.24}(\text{Si}_{3.06}\text{Al}_{3.00}\text{Fe}^{3+}_{0.01})_{\Sigma=6.07}\text{O}_{12} \cdot 5\text{H}_2\text{O}$. The $\text{Ca}/(\text{Ca} + \text{K})$ ratio varies from 0.78 to 0.84 (average 0.81) and calcium is the dominant extra-framework cation (1.21–1.29 apfu), while potassium is very low (0.24–0.34 apfu) and the sodium is always <0.1 apfu.

Crystals of the second group are Ca-K willhendersonite (Table 3) and are characterized by an average chemical composition of $(K_{0.94}Na_{0.01})_{\Sigma=0.95}Ca_{0.99}(Si_{3.07}Al_{2.93}Fe^{3+}_{0.00})_{\Sigma=6.00}O_{12} \cdot 5H_2O$. They have a Ca/(Ca + K) ratio in the range of 0.49–0.54 (average 0.51), with significant calcium (1.04–0.96 apfu) and potassium (0.9–0.98 apfu) contents, while the sodium is always <0.1 apfu. For all samples, the tetrahedral content R ($R = Si/(Si + Al)$) is near to 0.50 (average 0.51).

Table 2. Representative chemical compositions of Ca-rich willhendersonite from Lessini Mounts. * The H_2O content is calculated by difference to 100; Mg, Sr, and Ba were checked but were always below the detection limit; E% is the balance error of the electrical charges: $[Al - (K + 2Ca)]/(K + 2Ca)$; R is the tetrahedral content ($Si/(Si + Al)$) and St-d is standard deviation.

	WIL1	WIL2	WIL5	WIL8	WIL9	WIL10	WIL14	WIL15	WIL19	WIL20	Average	St-d
Ca-rich willhendersonite												
SiO ₂	35.34	35.31	34.68	35.12	35.74	34.99	35.51	35.73	34.85	34.88	35.22	0.37
Al ₂ O ₃	29.41	29.31	29.55	29.16	28.89	29.13	29.45	28.87	29.46	29.44	29.27	0.24
K ₂ O	2.75	2.65	2.88	2.31	2.55	3.01	2.13	2.65	2.45	2.56	2.59	0.26
CaO	13.24	13.36	13.75	13.84	13.01	12.96	13.22	13.24	13.45	13.35	13.34	0.28
Na ₂ O	0.15	0.27	0.13	0.37	0.25	0.25	0.12	0.18	0.12	0.15	0.20	0.08
Fe ₂ O ₃	0.12	0.08	0.11	0.2	0.08	0.05	0.12	0.11	0.05	0.04	0.10	0.05
H ₂ O *	18.99	19.02	18.90	19.00	19.48	19.61	19.45	19.22	19.62	19.58	19.29	0.29
Total	81.01	80.98	81.10	81.00	80.52	80.39	80.55	80.78	80.38	80.42	80.79	0.27
Cation on the basis of 12 framework oxygens											Average	St-d
Si	3.05	3.05	3.05	3.04	3.13	3.05	3.07	3.09	3.03	3.04	3.06	0.03
Al	3.00	2.99	3.06	2.97	2.99	2.99	3.00	2.94	3.02	3.09	3.00	0.04
Fe ³⁺	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.00
ΣT	6.06	6.04	6.11	6.03	6.12	6.05	6.08	6.04	6.06	6.13	6.07	0.04
Ca	1.23	1.24	1.29	1.28	1.22	1.21	1.22	1.23	1.25	1.24	1.24	0.03
K	0.30	0.29	0.31	0.26	0.29	0.34	0.24	0.29	0.27	0.28	0.29	0.03
Na	0.03	0.05	0.02	0.06	0.04	0.04	0.02	0.03	0.02	0.03	0.03	0.01
ΣC	1.55	1.58	1.63	1.60	1.55	1.59	1.48	1.55	1.55	1.55	1.56	0.04
Total	7.61	7.62	7.74	7.63	7.68	7.64	7.56	7.59	7.60	7.68	7.63	0.06
E%	0.09	0.08	0.05	0.05	0.09	0.09	0.12	0.07	0.09	0.11		
Ca/(Ca + K)	0.80	0.81	0.81	0.83	0.81	0.78	0.84	0.81	0.82	0.81	0.81	0.02
R	0.50	0.51	0.50	0.51	0.51	0.50	0.51	0.51	0.50	0.50	0.51	0.00

Table 3. Representative chemical compositions of Ca-K willhendersonite from Lessini Mounts. * The H_2O content is calculated by difference to 100; Mg, Sr, and Ba were checked but were always below the detection limit; E% is the balance error of the electrical charges: $[Al - (K + 2Ca)]/(K + 2Ca)$; R is the tetrahedral content ($Si/(Si + Al)$) and St-d is standard deviation.

	WIL4	WIL7	WIL12	WIL13	WIL22	WIL23	WIL24	WIL27	WIL29	WIL31	Average	St-d
	Ca-K willhendersonite											
SiO ₂	34.81	34.45	34.86	34.91	34.23	34.57	35.02	34.96	35.12	34.82	34.78	0.28
Al ₂ O ₃	28.12	28.42	28.09	28.02	28.66	28.38	27.86	27.98	27.87	28.46	28.19	0.28
K ₂ O	8.11	8.45	8.66	8.12	7.99	8.13	8.55	8.71	8.05	8.44	8.32	0.27
CaO	10.75	10.42	10.25	10.77	11.02	10.79	10.35	10.16	10.22	10.46	10.52	0.29
Na ₂ O	0.04	0.05	0.02	0.04	0.01	0.06	0.08	0.04	0.04	0.01	0.04	0.02
Fe ₂ O ₃	0.05	0.01	0.02	0.04	0.05	0.01	0.03	0.06	0.01	0.01	0.03	0.02
H ₂ O *	18.12	18.20	18.10	18.10	18.04	18.06	18.11	18.09	18.69	17.80	18.13	0.22
Total	81.88	81.80	81.90	81.90	81.96	81.94	81.89	81.91	81.31	82.20	81.87	0.22

Table 3. Cont.

	WIL4	WIL7	WIL12	WIL13	WIL22	WIL23	WIL24	WIL27	WIL29	WIL31	Average	St-d
Cation on the basis of 12 framework oxygens											Average	St-d
Si	3.07	3.05	3.08	3.08	3.02	3.05	3.09	3.09	3.11	3.06	3.07	0.03
Al	2.92	2.96	2.92	2.91	2.98	2.95	2.90	2.91	2.91	2.95	2.93	0.03
Fe ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣT	5.99	6.01	6.00	5.99	6.00	6.00	5.99	6.00	6.01	6.01	6.00	0.01
Ca	1.02	0.99	0.97	1.02	1.04	1.02	0.98	0.96	0.97	0.99	0.99	0.03
K	0.91	0.95	0.98	0.91	0.90	0.91	0.96	0.98	0.91	0.95	0.94	0.03
Na	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.00
ΣC	1.93	1.95	1.95	1.94	1.94	1.94	1.96	1.95	1.89	1.93	1.94	0.02
Total	7.93	7.96	7.95	7.93	7.94	7.94	7.95	7.95	7.90	7.94	7.94	0.02
E%	−0.01	0.01	0.00	−0.01	0.00	0.00	−0.01	0.00	0.02	0.01		
Ca/(Ca + K)	0.53	0.51	0.50	0.53	0.54	0.53	0.50	0.49	0.52	0.51	0.51	0.01
R	0.51	0.51	0.51	0.51	0.50	0.51	0.52	0.51	0.52	0.51	0.51	0.00

5. Discussion and Conclusions

Alteration phenomena in the basaltic rocks from the Lessini Mounts resulted in distinctive secondary mineral assemblages representing a multi-stage hydrothermal alteration process [12]. The occurrence of secondary minerals, their frequency, and their associations may be significantly different on both the outcrop- and sample-scale, with variability that can be in the order of a few centimeters. In the earliest stages, clay and silica minerals precipitate along the vesicles' inner walls, followed by the fine-grained zeolites erionite, offretite, analcime, natrolite, heulandite, and stilbite. The final stage is marked by the large, well-shaped zeolites (phillipsite-harmotomo, gmelinite, chabazite) associated with rare zeolites yugawaralite and willhendersonite. In particular, as regards willhendersonite, it is important to remember that, in the world, only three finds of this zeolite are reported (Terni, Eifel, Styria), and the data available in the literature are very few (practically absent for that of Styria). The morphological and chemical data presented here aim to implement this rare zeolite knowledge, found for the first time in northern Italy.

Willhendersonite from the Lessini Mounts is morphologically very similar to that of the other three known localities. Crystals are colorless, transparent, and mainly tabular and flattened, and they are often twinned to form trellis-like intergrowths. The cleavages are perfect, well developed, and parallel to {100}, {010}, and {001}, as indexed on the triclinic cell.

The calculated cell parameters' values were found to be relatively consistent with literature data (Table 4). In particular, unit-cell values of willhendersonite from Lessini are very similar to the Mayen and Bellberg samples, while those from Terni and Styria show slightly lower unit-cell parameters. No significant differences were found in the unit-cell parameters with respect to the holotype willhendersonite studied by Tillmanns et al. [2].

Table 4. Unit-cell parameters of willhendersonite from the Lessini Mounts, compared with literature data. Values of estimated standard deviations are given in parentheses.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
Lessini (this work)	9.239(2)	9.221(2)	9.496(2)	92.324(2)	92.677(2)	89.992(2)	808.9(5)
Literature data							
Terni [1]	9.138	9.178	9.477	92.31	92.50	90.05	793.4
Terni [10]	9.180(3)	9.197(3)	9.440(3)	91.42(2)	91.72(2)	90.05(2)	796.4(5)
Styria [9]	9.16	9.17	9.49	92.3	92.9	90.4	795.4
Mayen [1]	9.21(2)	9.23(2)	9.52(2)	92.4(1)	92.7(1)	90.1(1)	807.7(30)
Mayen [2]	9.206(2)	9.216(2)	9.500(4)	92.34(3)	92.70(3)	90.12(3)	804.4(4)
Bellberg [11]	9.248(5)	9.259(5)	9.533(5)	92.313(5)	92.761(5)	89.981(5)	814.7(8)

Regarding the chemical composition, two different groups of crystals were distinguished based on the extra-framework cation content (Figure 4). The Ca-rich group (red circles in Figure 4) has a composition that straddles those observed in the Colle Fabbri

samples [10]. In particular, willhendersonite from the Lessini Mounts has a composition that includes the intermediate terms from Colle Fabbri (Will-int, [10]) but extends towards the Ca-richest terms, expanding the compositional range so far known in the literature.

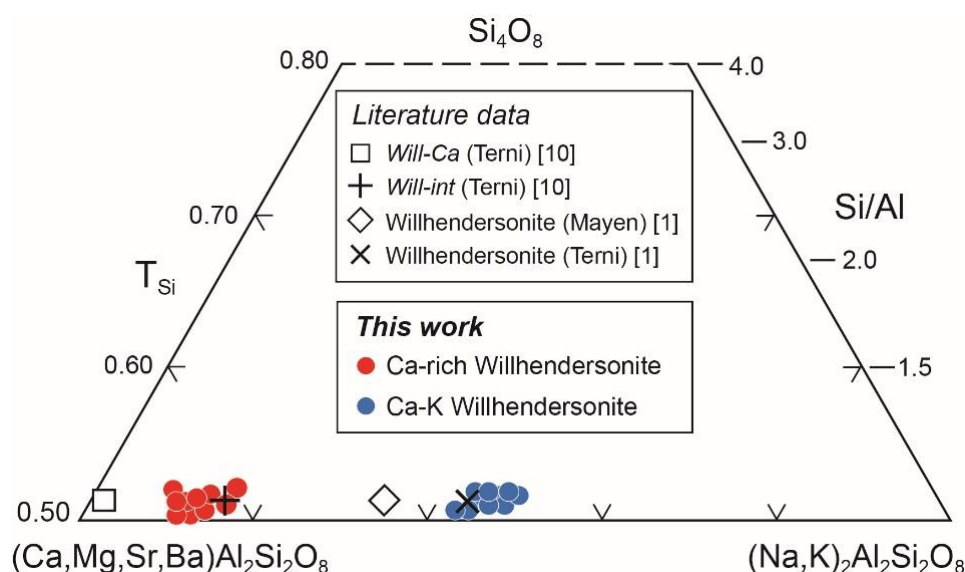


Figure 4. Compositional ternary diagram illustrating major variations of willhendersonite compositions. Red and blue circles are crystals from the Lessini Mounts. Components are: Si_4O_8 (molecular proportions $[\text{Si} - 2(\text{Ca} + \text{Mg} + \text{Sr} + \text{Ba}) - 2(\text{Na} + \text{K})]/4$), $(\text{Ca},\text{Mg},\text{Sr},\text{Ba})\text{Al}_2\text{Si}_2\text{O}_8$ (molecular proportions $\text{Ca} + \text{Mg} + \text{Sr} + \text{Ba}$), and $(\text{Na},\text{K})_2\text{Al}_2\text{Si}_2\text{O}_8$ (molecular proportions $(\text{Na} + \text{K})/2$).

The Ca-K crystals (blue circles in Figure 4), on the other hand, are characterized by comparable quantities of K and Ca and, consequently, are distributed in the central sector of the ternary diagram of Figure 4. Their composition comprises the San Venanzo samples [1] but extends towards richer terms in K, defining greater chemical variability in extra-framework cation content.

In the willhendersonite from the Lessini Mounts, the K content is low in the Ca-rich group (average of 0.29 apfu) and it is notably high in the Ca-K group (average 0.94 apfu). In comparison, the K content is significant in the samples from San Venanzo and Mayen (0.90 and 0.74 apfu, respectively) and very low in the sample from Colle Fabbri (0.03–0.30 apfu). In the Lessini samples, the Ca content has an average of 1.24 apfu in the Ca-rich group and 0.99 apfu in the Ca-K group, whereas the Ca content is notably high in the Colle Fabbri sample (1.43–1.28 apfu) and it is low in the samples from San Venanzo and Mayen (1.01 and 1.06 apfu, respectively).

The new chemical data of willhendersonite from the Lessini Mounts, together with the literature data on Mayen [1,2] and the occurrence of a Ca-pure willhendersonite reported in Vezzalini et al. [10], highlight the presence of a considerable compositional variability (probably not yet fully defined) of this zeolitic species. The existence of a continuous isomorphous series between Ca and K end-members, suggested by Vezzalini et al. [10], has been reinforced by the description of Lessini samples with intermediate compositions. This suggests a redefinition of willhendersonite as a series extending from a Ca end-member to compositions with equal proportions of Ca and K. According to [10], the absence of the K-pure willhendersonite end-member means that, at present, the series is incomplete. Further analyses are planned to investigate the distribution of this rare zeolite in the Lessini secondary minerals and to better understand the chemical variability of willhendersonite to define the existence of a Ca-K isomorphous series.

According to the literature data [12], the sampling area of willhendersonite (south-western sector of the Alpone valley, Figure 1) is characterized by the occurrence of other zeolites, all of which are of Ca-rich type (e.g., Ca-chabasite, Ca-phillipsite, Ca-gmelinite,

Ca-erionite, heulandite), followed by extensive crystallization of calcite. The presence of Ca-rich species in this area of the Lessini Mounts might suggest that the zeolite-forming fluids could have interacted with the underlying calcareous marine sedimentary rocks through which the basalts erupted. Hydrothermal fluids may have permeated the sedimentary and volcanic pile, leaching Ca out of the calcareous sedimentary rocks. Furthermore, as suggested by experimental works [28], with a likely high concentration of carbonate ions in solution, the zeolites' growth rate would increase in response to the increased dissolution of silica from the surrounding rocks. In this context, the composition of the underlying rocks through which the volcanics erupted seems to play an important role in zeolite formation.

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Data Availability Statement: Data is contained within the article. The data presented in this study can be seen in the content above.

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