



# Martinandresite, $\text{Ba}_2(\text{Al}_4\text{Si}_{12}\text{O}_{32})\cdot 10\text{H}_2\text{O}$ , a new zeolite from Wasenalp, Switzerland

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## Abstract

The new zeolite martinandresite, ideally  $\text{Ba}_2(\text{Al}_4\text{Si}_{12}\text{O}_{32})\cdot 10\text{H}_2\text{O}$ , was discovered in the armenite locality of Wasenalp near the Isenwegg peak, Ganter valley, Simplon region, Switzerland. The associated minerals are armenite, quartz, dickite, and chlorite. Martinandresite forms tan-coloured blocky crystals up to  $8\times 5\times 3.5$  mm, their aggregates up to 6 cm across, as well as cruciform twins up to 3.5 mm. The major form is {010}; the subordinate forms are {100} and {001}. Indistinct cleavage is observed, presumably on (010) and in a direction across (010). The Mohs' hardness is  $4\frac{1}{2}$ . Density measured by flotation in heavy liquids is  $2.482(5)$  g/cm<sup>3</sup>. Density calculated using the empirical formula is equal to  $2.495$  g/cm<sup>3</sup>. Martinandresite is optically biaxial, negative,  $\alpha = 1.500(2)$ ,  $\beta = 1.512(2)$ ,  $\gamma = 1.515(2)$  ( $\lambda = 589$  nm).  $2V$  (meas.) =  $55(10)^\circ$ . The IR spectrum is given. The chemical composition of martinandresite is (wt%; electron microprobe, H<sub>2</sub>O determined by the modified Penfield method): Na<sub>2</sub>O 0.37, K<sub>2</sub>O 0.12, BaO 21.55, Al<sub>2</sub>O<sub>3</sub> 15.03, SiO<sub>2</sub> 49.86, H<sub>2</sub>O 12.57, total 99.50. The empirical formula based on 16 atoms Si + Al *pfu* is  $\text{Na}_{0.17}\text{K}_{0.04}\text{Ba}_{2.00}(\text{Al}_{4.19}\text{Si}_{11.81}\text{O}_{32})\text{H}_{19.85}\text{O}_{9.93}$ . The crystal structure was determined using single-crystal X-ray diffraction data. The new mineral is orthorhombic, space group *Pmnm*, with  $a = 9.4640(5)$ ,  $b = 14.2288(6)$ ,  $c = 6.9940(4)$  Å,  $V = 941.82(8)$  Å<sup>3</sup> and  $Z = 1$ . The crystal structure of martinandresite is unique and is based on the Al–Si–O tetrahedral framework containing four-, six- and eight-membered rings of tetrahedra. Si and Al are disordered between the two independent tetrahedral sites. The strongest lines of the powder X-ray diffraction pattern [ $d$ , Å ( $I$ , %) ( $hkl$ )] are: 6.98 (74) (001), 6.26 (83) (011), 5.61 (100) (101), 3.933 (60) (220, 031), 3.191 (50) (112), 3.170 (62) (041), 3.005 (79) (231, 141). Martinandresite is named after Martin Andres (b. 1965), the discoverer of the armenite locality of Wasenalp.

**Keywords** New mineral · Martinandresite · Harmotome · Zeolite group · Crystal structure · IR spectroscopy · Wasenalp · Switzerland

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## Introduction

The interest in zeolites goes beyond the scope of mineralogy, because these solids not only occur naturally but are also produced industrially on a large scale and are used as ion exchangers, sorbents, catalysts and catalyst carriers. Each

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discovery of a zeolite mineral belonging to a novel structural type is of strong interest as a possible prototype of a material with useful properties.

The new zeolite-group mineral martinandresite (Cyrillic: *мартинандресит*) with the idealized formula  $\text{Ba}_2(\text{Al}_4\text{Si}_{12}\text{O}_{32}) \cdot 10\text{H}_2\text{O}$  was discovered at the armenite locality of Wasenalp near the Isenwegg peak, Ganter valley, Simplon region, Switzerland (for the locality see: Hetherington 2001; Andres 2009; Weiss 2016). This area is also the type locality of barium mica ganterite (Graeser et al. 2003; Graeser and Hetherington 2004). The geographical coordinates of Wasenalp are  $46^\circ 16' 6''\text{N}$ ,  $8^\circ 5' 9''\text{E}$ .

Zoisite-, celsian- and armenite-bearing gneisses of Wasenalp contain up to 15 wt% Ba and are cut by steep open veins (Alpine clefths) trending NNW–SSE. Within these rocks, late-stage hydrothermal fluids created a series of free-grown minerals, including clear quartz (rock crystal), calcite, brown dravite and clinzoisite, whitish due to the clear armenite (Weiss 2016), and martinandresite.

The new mineral is intimately associated with armenite, quartz, dickite, and chlorite. Some crystals are milky white due to fine inclusions of dickite crystals. Fluid inclusions studies of quartz and armenite showed (Hetherington 2001) that these veins opened at a lithostatic pressure of *ca.* 3 kbar at temperatures of 420–450 °C. Clear crystals of quartz and armenite grew at 280–300 °C and 2 kbar. Similar late-stage conditions might have prevailed during the crystallization of martinandresite.

Martinandresite is named after the Swiss mineral collector and amateur mineralogist Martin Andres (b. 1965), the discoverer of the armenite vein locality of Wasenalp. Martin Andres has collected samples of the new mineral. In June 2016, he generously provided a sample of this mineral to one of the authors (SW). Martin Andres is also the author of several popular publications on the minerals of Switzerland.

The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2017-038). The type material (a part of the holotype specimen) is deposited in the Geological Museum of Lausanne, Switzerland; the catalogue number is MGL 093284.

## Experimental methods

Five chemical analyses were carried out using an Oxford INCA Wave 700 electron microprobe (WDS mode, 20 kV, 600 pA, 300 nm beam diameter).  $\text{H}_2\text{O}$  was determined by the Alimarin method [the Penfield method was modified for small samples and involving selective sorption of  $\text{H}_2\text{O}$  on  $\text{Mg}(\text{ClO}_4)_2$  from gaseous products obtained by heating the mineral at 1080 °C in oxygen at 1 atm].  $\text{CO}_2$  was not analysed because of the absence of absorption

bands corresponding to vibrations of C–O bonds in the IR spectrum.

To obtain an IR absorption spectrum, martinandresite powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of  $4\text{ cm}^{-1}$ . 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Powder X-ray diffraction data were obtained using a Rigaku R-Axis Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using the Debye–Scherrer geometry ( $d=127.4\text{ mm}$ ). A  $\text{CoK}\alpha$  radiation was used.

Single-crystal XRD studies of martinandresite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using CrysAlis-Pro Version 1.171.37.35 (Agilent Technologies 2014). The data were corrected for the Lorentz factor and polarization effects.

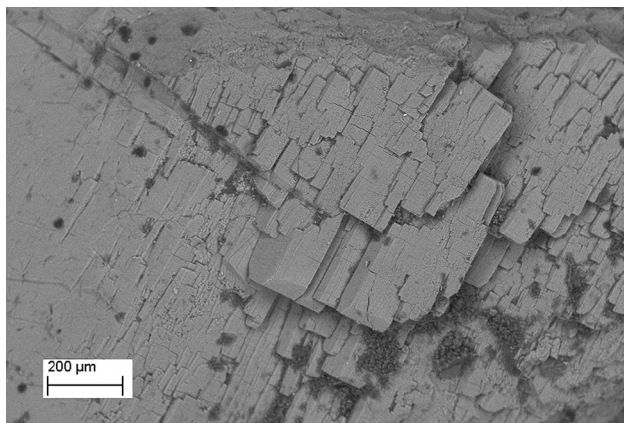
## Results

### General appearance and physical properties

Martinandresite forms aggregates up to 6 cm across consisting of 6–8 mm-sized blocky and rounded tan crystals, autoepitaxially covered by milk-white, cross-twinned plates up to 3.5 mm (Figs. 1, 2). Blocky crystals up to  $8 \times 5 \times 3.5\text{ mm}$  are observed (Fig. 2). These plates may form scaly to lamellar aggregates to 7 mm, visually resembling baryte and overgrowing blocky crystals (Fig. 1). More perfect platy crystals reach a maximum size of  $5 \times 3 \times 0.7\text{ mm}$ . Three pinacoids are definitely observed:  $\{010\}$  (the major



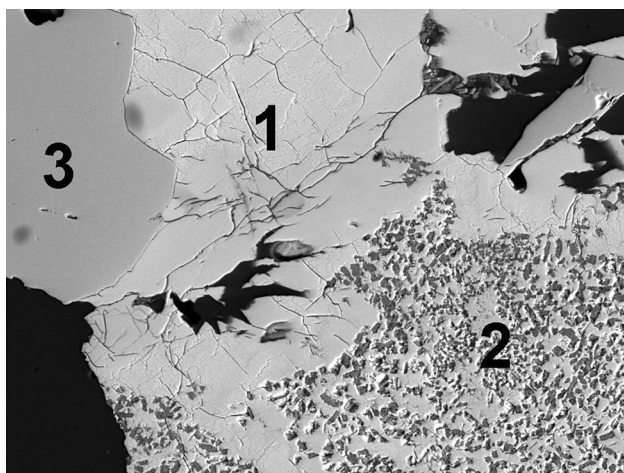
**Fig. 1** Aggregates of platy to lamellar martinandresite crystals. Field width 3 cm



**Fig. 2** Fragment of the surface of a martinandresite blocky crystal showing epitaxial overgrowth of platy crystals with two cleavages. SEM photo: C. Rewitzer

form), {100} and {001}. Non-indexed faces are also present on the crystals.

Martinandresite is transparent to translucent. The colour is white to tan, locally light green due to microscopic chlorite inclusions. White colour may be due to dickite inclusions (Fig. 3). The streak is white. The lustre is vitreous to porcelainous. Macroscopically, two directions of indistinct cleavage are observed, presumably on (010) and in a direction across (010) (Fig. 2). No cleavage is observed for small particles under the optical microscope. The fracture is uneven. Parting has not been observed. The Mohs' hardness is 4½. Density measured by flotation in heavy liquids (mixtures of bromoform with benzene) is 2.482(5) g/cm<sup>3</sup>. A density of 2.495 g/cm<sup>3</sup> was calculated



**Fig. 3** Pure martinandresite (1) and martinandresite with inclusions of dickite (2) and armenite (3). Polished section, BSE image. Field width 0.6 mm

using the empirical formula and unit-cell parameters were obtained from single-crystal X-ray diffraction (XRD) data.

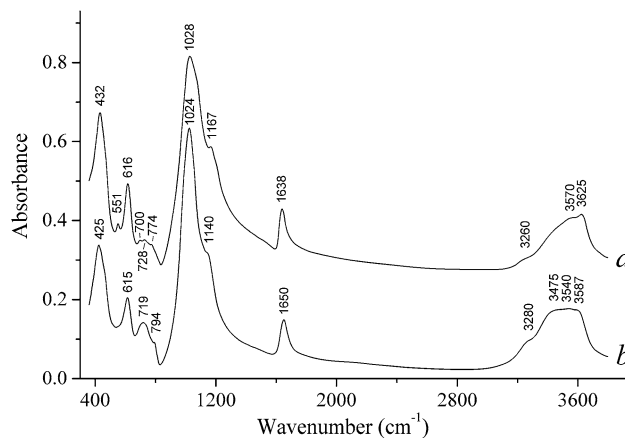
**Optical properties**

Under the microscope, martinandresite is nonpleochroic, colourless. It is optically biaxial, negative,  $\alpha = 1.500(2)$ ,  $\beta = 1.512(2)$ ,  $\gamma = 1.515(2)$  ( $\lambda = 589$  nm).  $2V$  (meas.) = 55(10)°,  $2V$  (calc.) = 53°. Dispersion of the optical axes is weak,  $r < v$ .

The mineral is non-fluorescent under both long- and short-wave UV radiation.

**Infrared absorption spectroscopy**

Absorption bands in the IR spectrum of martinandresite (Fig. 4) and their assignments are (cm<sup>-1</sup>; s—strong band, w—weak band, sh—shoulder): 3625, 3570sh, 3260sh (O–H stretching vibrations of H<sub>2</sub>O molecules), 1638



**Fig. 4** Powder IR spectrum of (a) martinandresite and (b) harmotome Ba<sub>1.90</sub>Na<sub>0.88</sub>K<sub>0.16</sub>(Al<sub>4.84</sub>Si<sub>11.16</sub>O<sub>32</sub>)·nH<sub>2</sub>O from Zlatolist, Eastern Rhodopes, Bulgaria

**Table 1** Chemical composition (in wt%) of martinandresite

Constituent	Average content	Range	Standard deviation	Probe standard deviation
Na <sub>2</sub> O	0.37	0.29–0.47	0.06	Albite
K <sub>2</sub> O	0.12	0.00–0.22	0.06	Orthoclase
BaO	21.55	21.13–22.08	0.43	BaSO <sub>4</sub>
Al <sub>2</sub> O <sub>3</sub>	15.03	14.72–15.34	0.23	Albite
SiO <sub>2</sub>	49.86	49.53–50.18	0.29	SiO <sub>2</sub>
H <sub>2</sub> O	12.57 ± 0.15			
Total	99.50			

**Table 2** Powder X-ray diffraction data of martinandresite

$I_{\text{obs}}$	$d_{\text{obs}}$ (Å)	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$ (Å)	$hkl$
44	7.86	33	7.880	110
74	6.98	70	6.994	001
83	6.26	76	6.277	011
100	5.61	100	5.625	101
7	5.22	7	5.231	111
41	4.975	36	4.988	021
8	4.723	6	4.732	200
3	4.402	2	4.412	121
33	4.232	27	4.240	130
60	3.933	48, 4	3.940, 3.925	220, 031
22	3.773	22	3.779	211
20	3.620	19	3.626	131
6	3.552	5	3.557	040
2	3.491	2	3.497	002
9	3.391	8	3.396	012
1	3.272	1	3.280	102
50	3.191	44	3.196	112
62	3.170	43	3.171	041
12	3.132	8	3.138	022
33	3.077	29	3.080	310
79	3.005	24, 60	3.021, 3.006	231, 141
23	2.974	21	2.979	122
4	2.873	4	2.876	301
49	2.816	41, 6, 6	2.819, 2.815, 2.812	311, 032, 202
24	2.723	23	2.725	150
45	2.664	50	2.666	321
22	2.628	7, 8	2.636, 2.634	051, 241
20	2.617	23	2.615	222
3	2.537	3	2.539	151
6	2.492	7	2.494	042
2	2.460	1	2.459	331
10	2.414	6, 6	2.419, 2.411	232, 142
7	2.366	1, 5	2.371, 3.666	060, 400
17	2.302	17, 1	2.303, 2.301	251, 013
6	2.261	7	2.264	103
17	2.236	1, 5, 6, 12	2.246, 2.245, 2.236, 2.236	061, 420, 341, 113
17	2.212	6, 10, 8	2.215, 2.214, 2.206	023, 411, 242
6	2.185	7	2.185	161
3	2.142	1, 2	2.150, 2.138	152, 421
3	2.121	2	2.120	260
8	2.096	10, 2, 3	2.100, 2.092, 2.091	332, 033, 203
5	2.042	6	2.043	133
3	2.027	2	2.026	431
10	2.004	12, 4	2.006, 2.000	223, 252
10	1.958	2, 2, 2, 11	1.970, 1.963, 1.960, 1.956	440, 062, 402, 342
9	1.921	10, 2	1.922, 1.914	162, 233
5	1.890	1, 8	1.896, 1.889	441, 422
10	1.829	8, 7	1.829, 1.827	361, 501
13	1.807	4, 1, 10, 3, 4, 4	1.813, 1.813, 1.809, 1.804, 1.803, 1.803	323, 262, 352, 271, 053, 243
7	1.778	12	1.779	080

**Table 2** (continued)

$I_{\text{obs}}$	$d_{\text{obs}}$ (Å)	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$ (Å)	$hkl$
6	1.759	4, 2, 4	1.761, 1.758, 1.757	451, 530, 072
2	1.723	1, 2	1.728, 1.724	172, 081
3	1.709	1, 3	1.716, 1.709	442, 370
2	1.696	3	1.696	181
6	1.674	5, 6	1.675, 1.671	460, 124
11	1.662	10, 8, 1, 6	1.663, 1.661, 1.660, 1.653	063, 403, 371, 512
4	1.641	4, 2	1.641, 1.640	034, 204
6	1.626	2, 2, 6, 2	1.629, 1.629, 1.625, 1.621	214, 461, 541, 522
8	1.577	9, 3	1.577, 1.576	600, 550
5	1.567	7, 2	1.565, 1.559	353, 190
5	1.541	3, 5, 2, 3	1.550, 1.542, 1.539, 1.535	234, 091, 601, 372
5	1.512	5, 3	1.512, 1.510	173, 462
6	1.507	5, 3	1.506, 1.503	471, 282
1	1.491	1	1.490	054
2	1.473	2, 2	1.471, 1.469	363, 503
4	1.466	2, 4	1.464, 1.462	631, 513
1	1.448	3	1.447	561
4	1.424	7, 3, 2	1.424, 1.421, 1.417	192, 254, 382
6	1.405	14, 3	1.405, 1.404	344, 533
3	1.395	3, 2, 2, 3	1.399, 1.399, 1.394, 1.392	414, 183, 0.10.1, 164
2	1.386	5	1.385	391
2	1.374	2, 4	1.376, 1.373	632, 025
2	1.362	2, 4	1.363, 1.362	2.10.0, 562
3	1.355	5, 3	1.355, 1.354	283, 651
3	1.337	2	1.347	354
4	1.332	10, 2, 2	1.333, 1.328, 1.326	642, 135, 074
1	1.302	1, 2, 2	1.308, 1.300, 1.296	444, 730, 193
4	1.276	5, 2, 6, 2, 6, 5	1.285, 1.278, 1.275, 1.274, 1.274, 1.270	623, 731, 3.10.1, 581, 315, 2.10.2
3	1.257	1, 1, 2, 7	1.261, 1.260, 1.256, 1.255	454, 633, 712, 245
3	1.245	1, 1, 6, 2	1.247, 1.244, 1.243, 1.242	084, 155, 741, 722
1	1.229	4	1.228	2.11.1
3	1.222	4	1.221	750
2	1.215	5	1.214	483
2	1.205	3, 1, 1	1.205, 1.203, 1.203	065, 1.11.2, 751
1	1.198	4	1.197	3.11.0

\*For the calculated pattern, only reflections with intensities  $\geq 1$  are given

\*\*For the unit-cell parameters calculated from single-crystal data (Table 3)

(bending vibrations of H<sub>2</sub>O molecules), 1167, 1028s (stretching vibrations of the tetrahedral framework), 774w, 728w, 700w, (mixed vibrations of the tetrahedral framework), 616, 551, 432 s (lattice modes involving predominantly bending vibrations of the tetrahedral framework and librational vibrations of H<sub>2</sub>O molecules).

There are distinct differences between the IR spectra of martinandresite and chemically-related zeolite harmotome in the wavenumber regions 1600–3700 cm<sup>-1</sup> (vibrations of H<sub>2</sub>O molecules) and 500–800 cm<sup>-1</sup>.

## Chemical composition

Analytical data for martinandresite are given in Table 1. Contents of other elements with atomic numbers > 8 are below detection limits.

The empirical formula of martinandresite (based on 16 atoms Si + Al *pfu*) is Na<sub>0.17</sub>K<sub>0.04</sub>Ba<sub>2.00</sub>(Al<sub>4.19</sub>Si<sub>11.81</sub>O<sub>32</sub>)H<sub>19.85</sub>O<sub>9.93</sub>. The simplified formula is Ba<sub>2</sub>(Al<sub>4</sub>Si<sub>12</sub>O<sub>32</sub>)·10H<sub>2</sub>O, which requires BaO 21.72, Al<sub>2</sub>O<sub>3</sub> 14.44, SiO<sub>2</sub> 51.08, H<sub>2</sub>O 12.76, total 100.00 wt%.

**Table 3** Crystal data, data collection information and structure refinement details for martinandresite

Formula	$\text{Na}_{0.14}\text{Ba}_{2.00}[\text{Si}_{11.86}\text{Al}_{4.14}\text{O}_{32}]\cdot 10\text{H}_2\text{O}$
Formula weight	1414.90
Temperature (K)	293(2)
Radiation and wavelength (Å)	MoK $\alpha$ ; 0.71073
Crystal system, space group, Z	Orthorhombic, <i>Pmnm</i> , 1
Unit-cell dimensions (Å)	$a = 9.4640(5)$ $b = 14.2288(6)$ $c = 6.9940(4)$
$V$ (Å <sup>3</sup> )	941.82(8)
Absorption coefficient $\mu$ (mm <sup>-1</sup> )	2.688
$F_{000}$	689
Crystal size (mm)	0.07 × 0.09 × 0.10
Diffractometer	Xcalibur S CCD
Absorption correction	Multi-scan empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm
$\theta$ range for data collection (°)	2.86–28.28
Index ranges	$-12 \leq h \leq 12$ , $-18 \leq k \leq 18$ , $-9 \leq l \leq 9$
Reflections collected	17,030
Independent reflections	1287 ( $R_{\text{int}} = 0.0925$ )
Independent reflections with $I > 2\sigma(I)$	1278
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on $F^2$
Number of refined parameters	88
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0527$ , $wR2 = 0.1156$
$R$ indices (all the data)	$R1 = 0.0531$ , $wR2 = 0.1158$
GoF	1.418
Largest diff. peak and hole (e/Å <sup>3</sup> )	1.21 (0.87 Å from Ba) and $-1.35$ (1.51 Å from Ba)
$wR2 = \Sigma w( F_{\text{ol}} ^2 -  F_{\text{cl}} ^2)^2 / \Sigma w F_{\text{ol}} ^2)^{1/2}$ ; $w = 1/[\sigma^2(F_{\text{ol}}) + (0.0233P)^2 + 6.3917P]$	
$P = ([\max \text{ of } (0 \text{ or } F_{\text{ol}}^2)] + 2F_{\text{c}}^2)/3$	

The Gladstone–Dale compatibility index (Mandarino 1981) calculated from the empirical formula and unit-cell parameters found from single-crystal XRD data is  $1 - (K_p/K_C) = 0.015$  (superior).

### X-ray diffraction data and crystal structure

Powder X-ray diffraction data for martinandresite are listed in the Table 2. Orthorhombic unit-cell parameters refined from the powder data are:  $a = 9.465(2)$ ,  $b = 14.234(2)$ ,  $c = 7.000(2)$  Å,  $V = 943.0(6)$  Å<sup>3</sup>.

According to the single-crystal XRD data, martinandresite is orthorhombic, with the space group *Pmnm* and unit-cell dimensions  $a = 9.4640(5)$ ,  $b = 14.2288(6)$ ,  $c = 6.9940(4)$  Å, and  $V = 941.82(8)$  Å<sup>3</sup>. A rather high value of  $R_{\text{int}}$  (9.25%) is probably caused by relatively low quality of even the best of tested crystals because of its slightly divergent character. The crystal structure was solved by direct methods and refined using the SHELX-97 software package (Sheldrick 2008) to  $R = 0.0527$  for 1278 unique reflections with  $I > 2\sigma(I)$ . The crystal data and the experimental details are

presented in Table 3, atom coordinates, thermal displacement parameters, site occupancies and bond-valence sums in Table 4, selected interatomic distances in Table 5.

The crystal structure of martinandresite is unique. It is based on the Al–Si–O tetrahedral framework containing four-, six- and eight-membered rings of tetrahedra (Fig. 5). There are two crystallographically non-equivalent *T* sites in the structure. Both are filled by Si and Al. No evidence for Al and Si ordering was found. The mean *T*–O distances for *T*(1) and *T*(2) sites are 1.630 and 1.634 Å, respectively. Four-membered tetrahedral rings are linked to form double crankshaft chains along the *a* axis. The chains are connected via common vertices of tetrahedral rings to form six- and eight-membered tetrahedral rings (Fig. 5). The system of channels in the structure of martinandresite contains three sets. Two sets are parallel to the *c* and to *a* axes and their openings are defined by eight-membered rings. Another set of channels is parallel to the *b* axis and its openings are defined by six-membered rings of tetrahedra.

Extra-framework cations and H<sub>2</sub>O molecules are located in the channels. Ba cations are placed at the intersection of

**Table 4** Atom coordinates, thermal displacement parameters ( $U_{eq}$  in Å<sup>2</sup>) and anisotropic thermal displacement parameters (Å<sup>2</sup>), site occupancy factors (s.o.f.), site multiplicities ( $Q$ ) and bond-valence sums (BVS) [bond-valence parameters were taken from Brese and O’Keeffe (1991)] for martinandresite

Site	$x/a$	$y/b$	$z/c$	$U_{eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	s.o.f.	$Q$	BVS
Ba	0.75	0.25	0.80553(11)	0.0213(2)	0.0208(4)	0.0162(3)	0.0269(4)	0.000	0.000	0.000	1	2	1.82
T(1)	0.08452(15)	0.51364(10)	0.3028(2)	0.0148(3)	0.0140(7)	0.0122(6)	0.0182(7)	-0.0005(5)	0.0011(6)	-0.0011(5)	Si <sub>0.741</sub> Al <sub>0.259</sub> *	8	4.01
T(2)	0.58758(16)	0.64032(9)	0.0213(2)	0.0147(3)	0.0142(7)	0.0067(6)	0.0231(7)	-0.0002(5)	0.0031(6)	0.0000(5)	Si <sub>0.741</sub> Al <sub>0.259</sub> *	8	3.97
O(1)	0.5	0.0	0.5	0.0458(19)	0.051(5)	0.051(4)	0.035(4)	0.001(3)	-0.018(4)	-0.009(4)	1	4	2.14
O(2)	0.5656(5)	-0.0812(3)	0.8248(7)	0.0339(11)	0.044(3)	0.022(2)	0.036(2)	0.0151(19)	0.002(2)	-0.001(2)	1	8	2.03
O(3)	0.0238(5)	0.6059(3)	0.1850(7)	0.0327(10)	0.033(2)	0.029(2)	0.035(2)	0.0042(19)	-0.009(2)	0.006(2)	1	8	2.09
O(4)	0.2500	0.1313(4)	0.9011(10)	0.0292(14)	0.020(3)	0.026(3)	0.042(4)	-0.004(3)	0.000	0.000	1	4	1.98
O(5)	0.2500	0.9604(5)	0.3435(10)	0.0331(16)	0.015(3)	0.035(3)	0.049(4)	0.012(3)	0.000	0.000	1	4	2.07
O(6)	0.5424(6)	0.75	0.9812(9)	0.0294(14)	0.031(4)	0.016(3)	0.041(4)	0.000	-0.007(3)	0.000	1	4	2.04
O(7)=H <sub>2</sub> O	0.4228(10)	0.75	0.5302(11)	0.051(2)	0.062(6)	0.057(5)	0.035(4)	0.000	-0.007(4)	0.000	1	4	0.21
O(8)=H <sub>2</sub> O	0.2500	0.8618(6)	0.8454(11)	0.051(2)	0.036(4)	0.070(6)	0.047(5)	0.015(4)	0.000	0.000	1	4	0.19
O(9)=H <sub>2</sub> O	0.75	0.726(3)	0.489(3)	0.127(18)	0.19(3)	0.12(5)	0.067(13)	-0.005(16)	0.000	0.000	0.5*	4	
Na	0.75	0.75	0.869(2)	0.08(4)**							0.072*	2	

An insignificant K admixture (~3%, according to electron microprobe data) is assumed to be incorporated in Ba site. Na site was located from difference Fourier synthesis. We assume that some additional Na cations were not localized due to their low occupancies. Na site was not taken into account for bond-valence analysis

\*Fixed during the refinement

\*\* $U_{iso}$

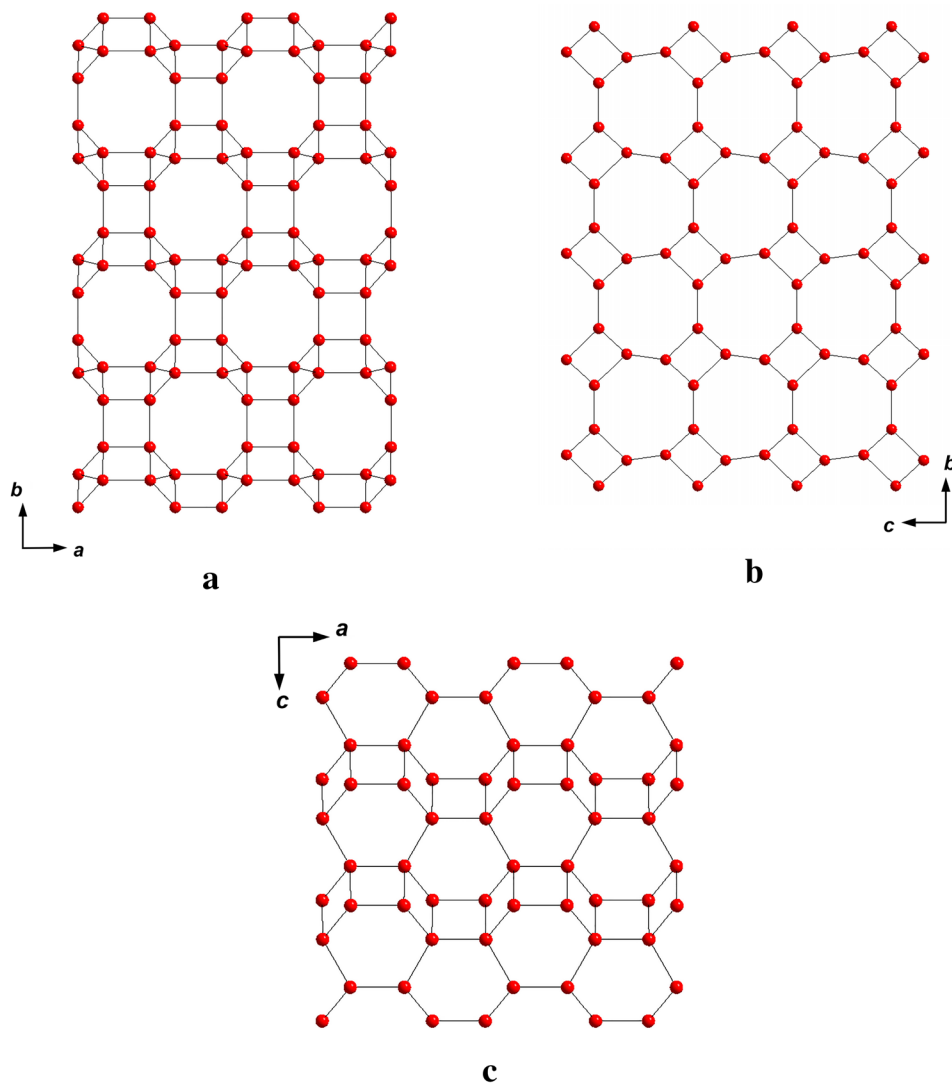
**Table 5** Selected interatomic distances (Å) in the structure of martinandresite

Ba		<i>T</i> (1)	
O(7)	2.861(8)×2	O(1)	1.6061(15)
O(8)	2.914(8)×2	O(2)	1.627(4)
O(3)	2.965(5)×4	O(5)	1.634(2)
O(6)	3.144(6)×2	O(3)	1.653(4)
O(5)	3.170(7)×2		
Na		<i>T</i> (2)	
O(6)	2.116(7)×2	O(2)	1.625(4)
O(4)	2.332(9)×2	O(3)	1.632(5)
O(9)	2.68(3)	O(4)	1.635(3)
O(2)	2.986(5)×4	O(6)	1.642(2)

the channels which are parallel to the *c* and to *a* axes and form twelve-fold polyhedra with Ba–O distances in the range from 2.861(8) to 3.170(7) Å (Table 5). The environment of

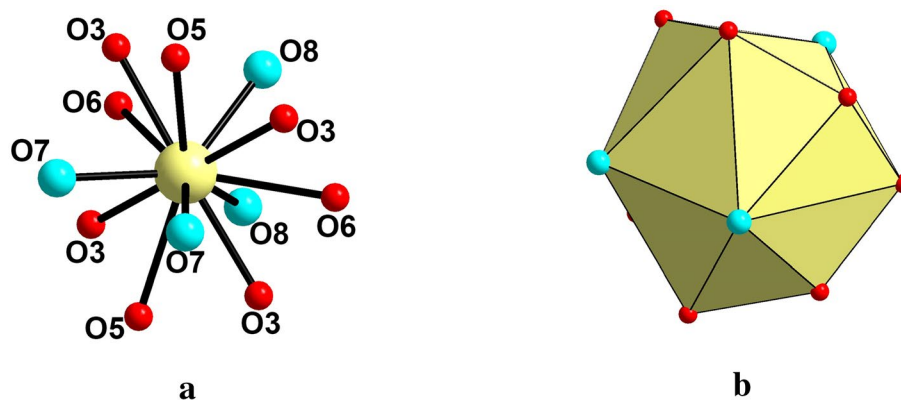
Ba cations and coordination in the Ba-centered polyhedron are shown in Fig. 6. Na site with a very small occupancy factor of 7% was found in the channels parallel to the *a* axis. Na cations form four short bonds with O atoms of the framework with the distances from 2.116(7) to 2.332(9) Å and one elongated bond 2.68(3) Å long with O(9) (oxygen atom of water molecule). Additionally, four bonds with Na–O distances of 2.986(5) Å could be included in the coordination sphere of Na.

The values of bond-valence sums (Table 4) show that all the oxygen atoms of the framework are saturated (the values vary in the range from 1.98 to 2.14). Analysis of interatomic distances allows to suppose the following rather weak hydrogen bonds involving three crystallographically non-equivalent water molecules [O(7), O(8) and O(9)]: O(7)⋯O(9), O(7)⋯O(8), O(8)⋯O(2), O(8)⋯O(8) and O(9)⋯O(4) with the corresponding O–O distances of 3.13(11), 3.17(11), 3.098(6), 3.18(18) and 3.05(3) Å, respectively.

**Fig. 5** Zeolite framework in the structure of martinandresite in three projections. *T* sites are shown as red circles



**Fig. 6** Environment of Ba cations (a) and coordination polyhedron of Ba (b) in the structure of martinandresite



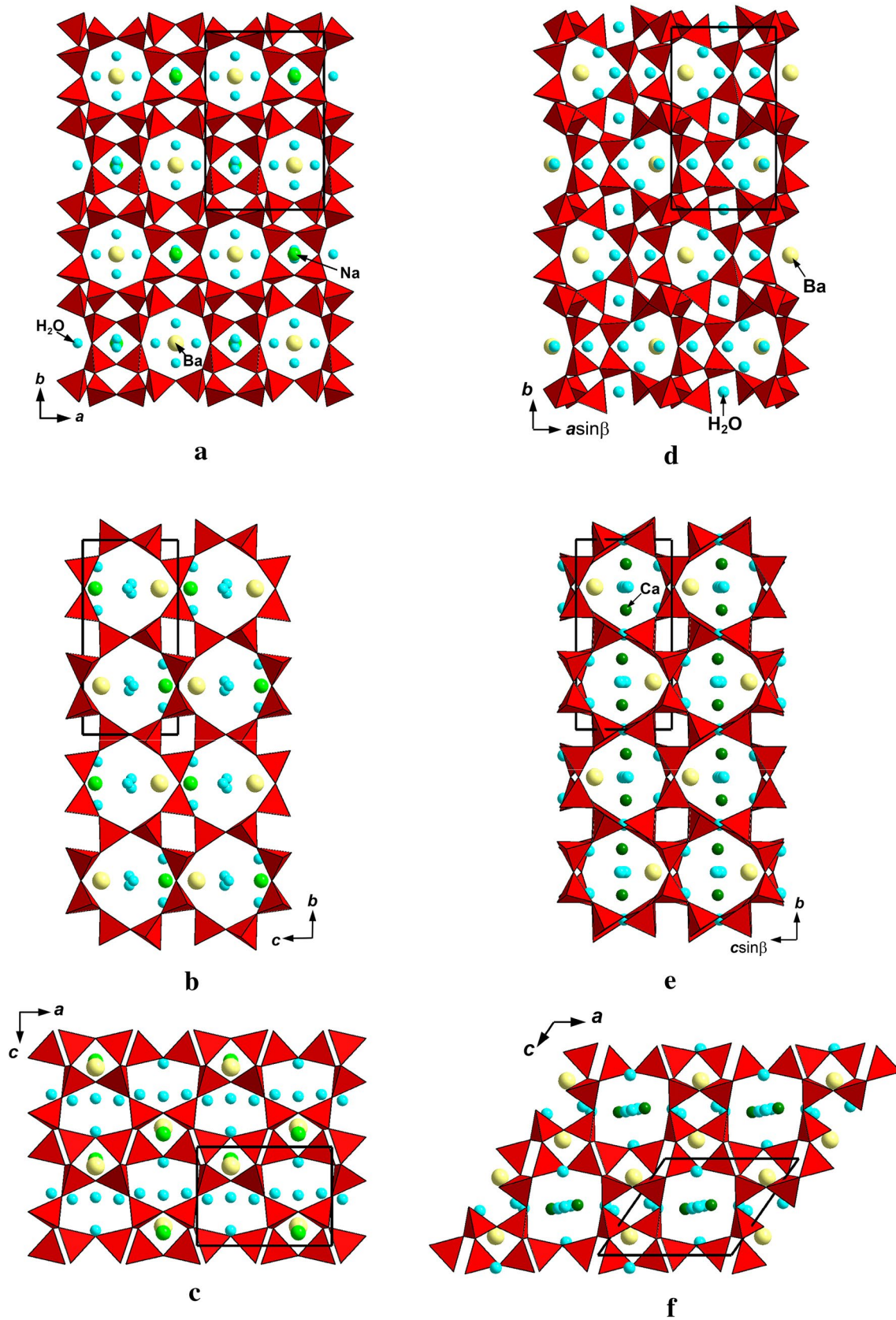
**Table 6** Comparative data for martinandresite and harmotome

Mineral	Martinandresite	Harmotome
Formula	Ba <sub>2</sub> (Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> )·10H <sub>2</sub> O	Ba <sub>2</sub> (Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> )·12H <sub>2</sub> O
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pmmn</i>	<i>P2<sub>1</sub>/m</i>
<i>a</i> (Å)	9.4640	9.87–9.88
<i>b</i> (Å)	14.2288	14.13–14.14
<i>c</i> (Å)	6.9940	8.69–8.71
$\beta$ (°)	90	124.7–124.8
<i>V</i> (Å <sup>3</sup> )	941.82	996.4–999.2
<i>Z</i>	1	1
Strong lines of the powder X-ray diffraction pattern <i>d</i> , Å ( <i>I</i> , %)	7.86 (44) 6.98 (74) 6.26 (83) 5.61 (100) 3.933 (60) 3.191 (50) 3.170 (62) 3.005 (79) 2.816 (49) 2.664 (45)	8.10 (40) 7.16 (50) 6.38 (100) 4.08 (60) 3.24 (60) 3.17 (60) 3.13 (80) 2.730 (60) 2.698 (60) 2.670 (70)
Wavenumbers of IR absorption bands (cm <sup>-1</sup> )	3625, 3570sh, 3260sh, 1638, 1167, 1028s, 774w, 728w, 700w, 616, 551, 432s	3587, 3540, 3474sh, 3280sh, 1652, 1140sh, 1024s, 794w, 719, 615, 425s
Optical data	Biaxial (–) $\alpha = 1.500$ $\beta = 1.512$ $\gamma = 1.515$ $2V = 55^\circ$	Biaxial (+) $\alpha = 1.503–1.508$ $\beta = 1.505–1.509$ $\gamma = 1.508–1.514$ $2V = 80^\circ$
Density (g cm <sup>-3</sup> )	2.482 (meas.) 2.495 (calc.)	2.41–2.47 (meas.) 2.448 (calc.)
Sources	This work	Sahama and Lehtinen (1967), Rinaldi et al. (1974) Perrotta (1976) and Stuckenschmidt et al. (1990)

## Discussion

Martinandresite is chemically close to harmotome, ideally Ba<sub>2</sub>[Al<sub>4</sub>Si<sub>12</sub>O<sub>32</sub>]·12H<sub>2</sub>O (Sadanaga et al. 1961; Rinaldi et al. 1974; Stuckenschmidt et al. 1990), which belongs to the phillipsite subgroup and is characterized by monoclinic symmetry, space group *P2<sub>1</sub>/m*. The unit-cell dimensions *a* and

*b* of martinandresite (9.46 and 14.23 Å, respectively) are close to those of harmotome (9.87–9.88 and 14.13–14.14 Å), while the *c* parameter is significantly different: 6.99 Å in orthorhombic martinandresite and 8.69–8.71 Å in monoclinic, with  $\beta = 124.8^\circ$ , harmotome (Table 6). The frameworks of both martinandresite and harmotome (as well as the other zeolites of the phillipsite subgroup) contain four- and



**Fig. 7** The crystal structures of martinandresite (a–c, left column) and harmotome (d–f, right column) drawn after Rinaldi et al. (1974)

eight-membered tetrahedral rings which form layers perpendicular to the *a* axis in martinandresite and approximately perpendicular to the *a* axis in harmotome (Rinaldi et al. 1974). Structural and metrical similarity of martinandresite and merlinoite (which shows close relation to the phillipsite structure type) is also observed. Merlinoite, ideally  $K_5Ca_2[Al_9Si_{23}O_{64}] \cdot 22H_2O$  and its varieties (Galli et al. 1979; Gatta et al. 2015 and references therein) are characterized by orthorhombic (pseudotetragonal) symmetry, space group *Immm* with the unit-cell dimensions  $a = 14.116(7)$ ,  $b = 14.229(6)$ ,  $c = 9.946(6)$  Å (Galli et al. 1979) and the presence of double crankshaft chains formed by four-membered tetrahedral rings with random (Si,Al) distribution running along the *c* axis. Thus, the framework containing four- and eight-membered tetrahedral rings with interconnecting eight-membered ring channels running parallel to all the three axes is formed (Gatta et al. 2015). However, six-membered tetrahedral rings that occur in the structure of martinandresite are absent in the representatives of the phillipsite structure type as well as in merlinoite and its varieties. The comparative data of martinandresite and harmotome are given in Fig. 7 and Table 6.

Despite harmotome and martinandresite having similar composition, their crystal structures are different. This fact has no unambiguous explanation. The structural differences may be a result of different conditions of crystallization (temperature, pressure and/or composition of hydrothermal solution). Another cause of the structural differences may be a different composition of extra-framework cations: martinandresite is close to the barium end-member, whereas most harmotome samples contain significant amounts of Na + K + Ca.

Among natural zeolites, double crankshaft chains formed by four-membered tetrahedral rings occur also in the frameworks of gismondine, ideally  $Ca_2[Al_4Si_4O_{19}] \cdot 9H_2O$  (Fischer and Schramm 1971) and in minerals of the gmelinite series [gmelinite-Ca,  $(Ca_{0.5}, Sr, K, Na)_8[Al_8Si_{16}O_{48}] \cdot 22H_2O$ , gmelinite-Na,  $(Na, K, Ca_{0.5})_8[Al_8Si_{16}O_{48}] \cdot 22H_2O$  (Galli et al. 1982), and gmelinite-K,  $(K, Ca_{0.5}, Na)_8[Al_8Si_{16}O_{48}] \cdot 22H_2O$  (Vezzalini et al. 1990)], where in the framework, there are 12-, 8-, 6- and 4-membered tetrahedral rings. It is worth to note that natural Ba analogue of gismondine was reported by Braithwaite et al. (2001), and Ba-substituted gmelinite was studied by Vigdorichik and Malinovskii (1986). A significant amount of Ba was also reported for merlinoite (Gatta et al. 2015 and references therein).

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