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Trabzonite, $Ca_4[Si_3O_9(OH)]OH$: crystal structure, revised formula, new occurrence and relation to killalaite

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ABSTRACT

The crystal structure of the rare skarn mineral trabzonite, $Ca_4[Si_3O_9(OH)]OH$, from the type locality near Ikizdere, Turkey and from the Upper Chegem caldera, Northern Caucasus, Kabardino Balkaria, Russia has been solved and refined using single crystal X ray data. This shows that the chemical formula should be modified from $Ca_4(Si_3O_{10})\cdot 2H_2O$, reported in the original trabzonite description, to an OH bearing composition. The crystal structure, which contains Si_3O_{10} trimers embedded in a framework of CaO_{6-8} polyhedra, has orthorhombic symmetry, space group *Ama*2, *a* 20.6, *b* 9.1, *c* 10.3 Å. The orthorhombic *A* centred cell is easily obtained by transformation from the original monoclinic cell of $P2_1/m$ symmetry. The revised formula means that trabzonite and foshagite are polymorphs; foshagite has wollastonite like silicate chains and in contrast to trabzonite it does not contain silanol groups.

The structure and composition of killalaite from both localities was also studied. Single crystal X ray structure refinement of killalaite from the Northern Caucasus confirmed it to be non stoichiometric with a composition between $Ca_6[Si_2O_6(OH)]_2(OH)_2$ and $Ca_7[Si_2O_7]_2(OH)_2$ (*Z* 2). Trabzonite, killalaite and dellaite form a series of modular structures which differ mainly in the degree of condensation of the SiO_4 units.

Keywords: trabzonite, killalaite, crystal structure, Raman spectroscopy, skarn mineralogy.

Introduction

There are strong similarities in the unit cell dimensions of dellaite, $Ca_6[Si_2O_7][SiO_4](OH)_2$; killalaite, $Ca_{6.4}[H_{0.6}Si_2O_7]_2(OH)_2$, which was originally described as $Ca_3Si_2O_7\cdot H_2O$ (Nawaz, 1974); and trabzonite, originally described as $Ca_4[Si_3O_{10}]\cdot 2H_2O$ (Sarp and Burri, 1987). All three skarn minerals have two axes of ~6.9 Å enclosing an angle of ~97–98º (Armbruster *et al.*, 2011). The length of the third axis is primarily dependent upon the size of variably condensed SiO_4 units. Killalaite only contains disilicate Si_2O_7 units (Taylor, 1977) whereas dellaite has alternate orthosilicate SiO_4 and disilicate Si_2O_7 units (Ganiev *et al.*, 1970; Armbruster *et al.*, 2011). Trisilicate Si_3O_{10} units were proposed for trabzonite by Sarp and Burri (1986, 1987). Killalaite and trabzonite were both originally described with H_2O bearing formulae, these are

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not present in dellaite, which only contains OH groups. A revised OH bearing formula, $Ca_{3.2}[H_{0.6}Si_2O_7](OH)$, was derived for killalaite from crystal structure data (Taylor, 1977) and it was therefore suggested that trabzonite also probably contained OH instead of H_2O (Armbruster *et al.*, 2011).

Trabzonite has only been described from a single locality (Sarp and Burri, 1986, 1987): "The mineral has been found near Ikizdere at NW of Varda Yaylasi (Rize) (near the border to Trabzon province) – Turkey and occurs in skarn produced by granitic intrusion in volcano sedimentary formations." Interestingly, neither trabzonite nor killalite have been reported in cements or as reaction products in kiln processes.

The predicted structural relations between trabzonite, dellaite and killalaite sparked our interest in a structural investigation of trabzonite. At the same time, we became aware of chemical analyses corresponding to trabzonite for a mineral from high temperature skarns in calcareous xenoliths in the ignimbrites of the Upper Chegem caldera, Northern Caucasus, Kabardino Balkaria, Russia (e.g. Galuskin *et al*., 2009). We also analysed killalaite from the same locality.

Sample description

An isolated grain of holotype trabzonite from the collection of the Natural History Museum in Geneva, Switzerland, from skarns near Ikizdere, Turkey, (NHM Geneva accession number 477/051) was used for structure refinement. At Ikizdere trabzonite occurs as a retrograde mineral in a skarn containing spurrite, rustumite, calcite, vesuvianite, hillebrandite, defernite, tobermorite, killalaite, garnet, perovskite, and molybdenite (Sarp and Burri, 1986, 1987). A small sample ($3 \times 2 \times 1$ cm) from the type locality (NHM Geneva accession number 435/78) was also made available to us. Unfortunately, this sample did not contain trabzonite; the mineral with a trabzonite like composition that was present in this sample was identified by Raman spectroscopy as foshagite. Foshagite develops after killalaite and is replaced by fukalite (Fig. 1).

Trabzonite is a widespread mineral in xenolith no. 1 (numbering is after Galuskin *et al.*, 2009) in ignimbrites of the Upper Chegem caldera, Northern Caucasus. The xenolith consists of skarned carbonate–silicate rocks. It also occurs in the endoskarn zone of xenolith no. 5, as spherulites composed of radiating orthorhombic crystals with {110}, {1$\bar{1}$0} and {111} crystal forms (Fig. 2*a*). Trabzonite from xenolith no. 3 replaces rankinite–pavlovskyite pseudomorphs after wollastonite. The latter mineral replaces quartz phenocrysts in the ignimbrite (Fig. 2*b*). Trabzonite also occurs in small cavities of cuspidine skarn surrounded by killalaite aggregates (Fig. 2*c*). Xenolith no. 7, which is about 10 m in diameter and located 1 km from xenolith no. 1 (Galuskin *et al.*, 2009) contains killalaite in altered larnite zones. In this xenolith, killalaite occurs as well developed crystals, terminated by {110}, {001} and {0*kl*}, associated with idiomorphic hydroxylellestadite (Fig. 2*d*).

Experimental

Chemical analyses were carried out using a CAMECA SX100 electron microprobe operating in wavelength dispersive spectrometry (WDS) mode with a 15 kV accelerating voltage, 10–20 nA beam current and 1–3 μm beam diameter (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). The following lines and standards were used for the trabzonite and killalaite analyses: Ca*K*α, wollastonite; Si*K*α, wollastonite; Mn*K*α, rhodochrosite; Mg*K*α, diopside; Na*K*α, albite; Al*K*α, orthoclase; S*K*α, baryte.

The Raman spectra of trabzonite and killalaite from the Northern Caucasus were recorded using a Dilor XY spectrometer (Bayerisches

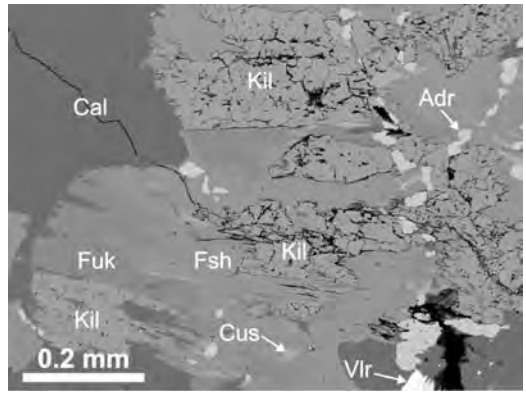

FIG. 1. Back scattered electron image of a skarn sample from Ikizdere northwest of Varda Yaylasi, Rize, Turkey showing foshagite (the dimorph of trabzonite) replacing killalaite and being replaced by fukalite. Mineral abbreviations are Adr, andradite; Cal, calcite; Cus, cuspidine; Fsh, foshagite; Fuk, fukalite; Kil, killalaite; Vrl, valeriite.

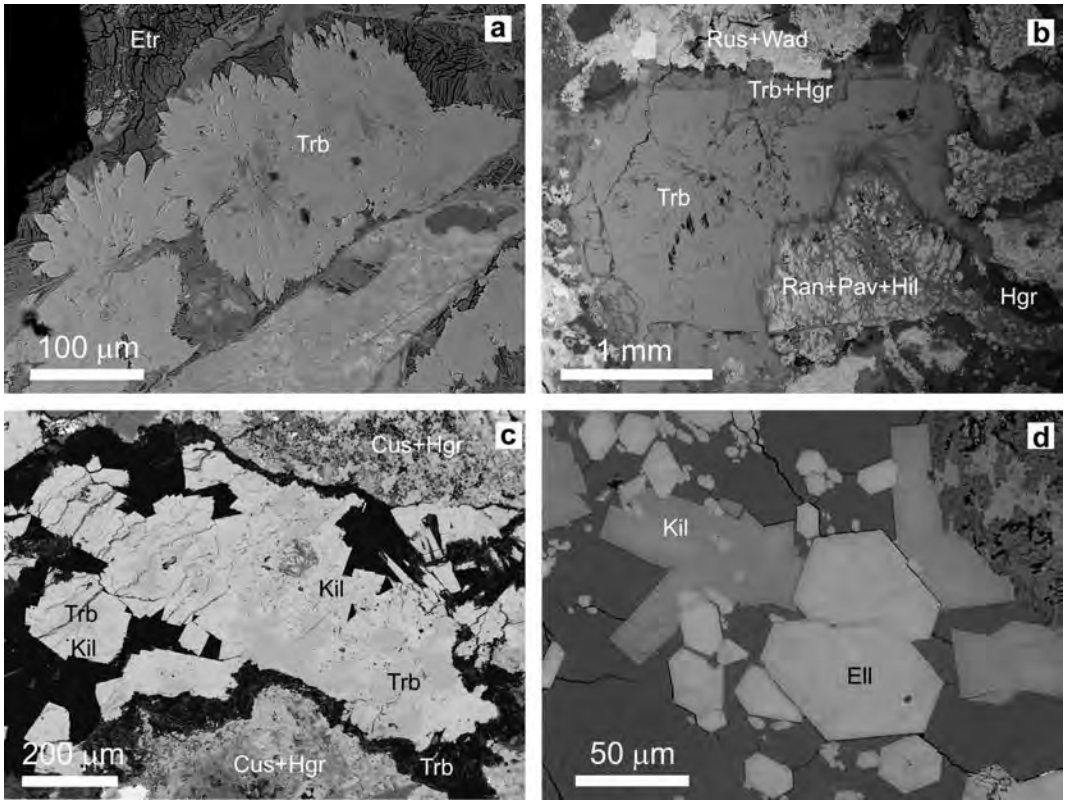

FIG. 2. Back scattered electron image of a skarn sample from the Upper Chegem caldera, Northern Caucasus. (*a*) Trabzonite spherulites in fractures of the endoskarn zone (from xenolith no. 5). (*b*) Incomplete pseudomorphic replacement of trabzonite after rankinite–pavlovskyite intergrowths (from xenolith no. 3). (*c*) Trabzonite surrounded by aggregates of killalaite (from xenolith no. 3). (*d*) Killalaite and hydroxylellestadite crystals in altered larnite skarn (from xenolith no. 7). Mineral abbreviations are Cus, cuspidine; Ell, hydroxylellestadite; Etr, ettringite; Hil, hillebrandite; Hgr, hydrogrossular; Kil, killalaite; Pav, pavlovskyite; Ran, rankinite; Rus, rusinovite; Trb, trabzonite; Wad, wadalite.

Geoinstitut, University of Bayreuth, Germany) equipped with a 1800 line mm^{-1} grating monochromator, a charge coupled device (CCD) Peltier cooled detector and an Olympus BX40 confocal microscope. The incident laser excitation was provided by a water cooled argon laser source operating at 514.5 nm. The power at the exit of a 100× objective lens varied from 30 to 50 mW. Raman spectra were recorded in backscatter geometry in the range 100–4000 cm^{-1} at a resolution of 2 cm^{-1}. Collection times of 20 s and accumulations of 5 scans were chosen.

The Raman spectra of killalaite and foshagite from Turkey were recorded using a WITec confocal CRM alpha 300 Raman microscope (Jagiellonian Centre for Experimental Therapeutics, Cracow) equipped with an air cooled solid state laser operating at 532 nm and a CCD detector which was cooled to −82ºC. The laser was coupled to the microscope via a single mode optical fibre with a diameter of 50 μm. A dry Olympus MPLAN (100×/0.90NA) objective was used. The scattered radiation was focussed onto a multi mode fibre (50 μm diameter) and monochromator. The power of the laser at the sample position was 44 mW. Some 15–20 scans with integration times of 10–15 s and a resolution of 3 cm^{-1} were collected and averaged. The monochromators of both spectrometers were calibrated using the Raman scattering line produced by a silicon plate (520.7 cm^{-1}).

Single crystal X ray studies were carried out on two trabzonite grains (a) from Ikizdere, Turkey and (b) from Chegem, Russia, using a Bruker APEX II SMART diffractometer (Mo$K\alpha$, λ 0.71073 Å). Experimental details are summarized in Table 1. Both grains were complex. The grain from Turkey consisted of two principal crystal lites, which were each divided into two by a small angular offset. This small offset did not allow the closely spaced diffraction patterns to be separated. The trabzonite grain from Russia consisted of at least six radially intergrown crystallites whose diffraction patterns were manually separated and a degree of overlap between the individual patterns could not be completely avoided. A 'single crystal' of killalaite from Northern Caucasus (Russia) was also studied, but this consisted of at least five individual crystallites in subparallel intergrowth with their *b* axes slightly inclined to one another. Diffraction peaks generated by the major crystallite were separated from those of the minor crystallites, but the possibility of overlap from several individuals could not be completely excluded.

TABLE 1. Parameters for X ray data collection and crystal structure refinement of trabzonite and killalaite.

	Trabzonite Ikizdere	Trabzonite Northern Caucasus	Killalaite Northern Caucasus
Crystal data			
Unit cell dimensions (Å)	a = 20.5805(17) b = 10.3240(8) c = 9.1053(8)	a = 20.6088(9) b = 10.3288(4) c = 9.1071(4)	a = 6.824(5) b = 15.465(5) c = 6.839(5) β = 97.692(5)°
Volume (Å^3)	1934.6(3)	1938.6(1)	715.2(8)
Space group	*Ama*2 (No. 40)	*Ama*2 (No. 40)	$P2_1/m$ (No. 11)
Z	8	8	2
Chemical formula	$Ca_4(Si_3O_9OH)(OH)$	$Ca_4(Si_3O_9OH)(OH)$	$Ca_{6.3}[H_{0.7}Si_2O_7]_2(OH)_2$
Measurement data			
Crystal shape	Aggregate	Spherulite	Aggregate
Crystal size (mm)	0.13 × 0.14 × 0.17	0.10 × 0.05 × 0.05	0.05 × 0.05 × 0.05
Diffractometer	APEX II SMART	APEX II SMART	APEX II SMART
X ray radiation	Mo$K\alpha$; λ = 0.71073 Å	Mo$K\alpha$; λ = 0.71073 Å	Mo$K\alpha$; λ = 0.71073 Å
X ray power	50 kV, 30 mA	50 kV, 30 mA	50 kV, 30 mA
Monochromator	Graphite	Graphite	Graphite
Temperature	293 K	293 K	293 K
Time per frame	120 s	60 s	120 s
Maximum θ value	30.5°	36.54°	30.54°
Index ranges	$-29 \leqslant h \leqslant 19$ $-13 \leqslant k \leqslant 14$ $-12 \leqslant l \leqslant 11$	$-33 \leqslant h \leqslant 30$ $-16 \leqslant k \leqslant 16$ $-14 \leqslant l \leqslant 15$	$-7 \leqslant h \leqslant 9$ $-22 \leqslant k \leqslant 19$ $-9 \leqslant l \leqslant 8$
Measured reflections	11,321	13,753	4987
Unique reflections	2899	4101	2035
Obs. reflections ($I > 2\sigma(I)$)	2410	2632	1460
Structure refinement			
Parameters used	178 + 6 restraints	178 + 6 restraints	139 + 3 restraints
R_{int}	0.0982	0.1103	0.0632
R_σ	0.0747	0.1342	0.0904
$R1$, $I > 2\sigma$(I)	0.0565	0.0635	0.0761
$R1$, all data	0.0724	0.1147	0.1082
w$R2$ (on F^2)	0.1475	0.1522	0.2087
GooF	1.010	0.974	1.004
$\Delta\rho_{min}$ ($-$e Å^{-3})	0.83 close to Ca5	1.31 close to H11	1.16 close to Ca4
$\Delta\rho_{max}$ (e Å^{-3})	1.18 close to Ca5	1.41 close to Ca6	1.55 close to Ca3

Diffraction data were collected using ω scans at different φ settings (φ−ω scan) (Bruker, 1999). Data were processed using *SAINT* (Bruker, 1999). An empirical absorption correction using *SADABS* (Sheldrick, 1996) was applied. The trabzonite structure was solved by direct methods (Sheldrick, 2008) with subsequent analyses of difference Fourier maps. The space group $P2_1/m$ and cell setting suggested by Sarp and Burri (1986, 1987) was used for structure solution. However, after successful structure determination for the crystal from Turkey, the structural data were checked for higher symmetry using the program *Platon* (Speck, 2001). This suggested an orthorhombic symmetry in space group *Ama*2. The original monoclinic unit cell with *a* 6.9, *b* 20.6, *c* 6.9 Å, β 97.2º was transformed by the matrix (0 −1 0, 1 0 1, −1 0 1) to an orthorhombic unit cell with *a* 20.6, *b* 9.1, *c* 10.3 Å. The trabzonite structure was refined using the program *SHELX97* (Sheldrick, 2008) for both crystals. The refinements including anisotropic atom displacement parameters summing up to 179 variables were carried out using neutral atom scattering factors. As *Ama*2 is a polar space group, twinning by the inversion centre was also considered. In the Russian sample twinning appeared insignificant but in the crystal from Turkey a twin ratio of 0.23(7)/77(7) was refined.

A corresponding strategy was applied to refine the structure of killalaite (139 variables) using the starting values of Taylor (1977) in space group $P2_1/m$. A twin of the type (0 0 1, 0 −1 0, 1 0 0), corresponding to interchange of *a* and *c* of very similar length, was refined (with a twin ration of 0.60/0.40). The low quality of the diffraction data did not allow us to address the existence of a possible superstructure as speculated by Taylor (1977).

To locate potential OH positions, bond valence calculations were performed using parameters for Ca^{2+} and O^{2-} from Brown and Altermatt (1985) and parameters for Si^{4+} and O^{2-} from Brese and O'Keefe (1991). The hydrogen sites were refined isotropically and restrained to be 0.96(2) Å from the corresponding oxygen atoms.

Results

The results of our electron microprobe analyses are summarized in Tables 2 and 3. The results of the crystal structure refinements including atom coordinates and isotropic equivalents (U_{eq}) of anisotropic atom displacement parameters for trabzonite and killalaite are listed in Tables 4 and 5, respectively. Anisotropic displacement parameters are summarized in Tables 6 and 7, and selected interatomic distances for trabzonite in Table 8. Structural data are also summarized in CIF files which are available at www.minersoc.org/pages/e journals/dep mat.html. Bond valence values are listed in Tables 9 and 10. The Raman spectra of trabzonite and killalaite are shown in Figs 3−6.

Discussion

The predictions made in our previous dellaite study (Armbruster *et al.*, 2011) concerning the structure and chemistry of trabzonite have turned out to be correct: (1) trabzonite (Fig. 7) belongs to the same group of modular structures as dellaite and killalaite, which differ in the degree of condensation of the SiO_4 units; (2) in common with dellaite and killalaite there are no H_2O molecules in trabzonite, only OH groups. There is also one surprising observation: the initial predictions about the structural relations were made on the basis of the strikingly similar unit cell dimensions with two axes of ~6.9 Å and an angle of ~98º between them but in the face centred orthorhombic structure (space group *Ama*2) of trabzonite these characteristic relations are no longer obvious.

After showing that trabzonite was orthorhombic, we tested the symmetry of the related mineral killalaite (Taylor, 1977) using corresponding projections. Although the cell dimensions of killalaite can easily be transformed into a face centred orthorhombic setting, we found convincing evidence that killalaite is truly monoclinic, with space group $P2_1/m$, in analyses of the distribution of Si and Ca polyhedra. According to Taylor's (1977) and our own structural data, killalaite appears to be non stoichiometric with a composition that is intermediate between the theoretical endmembers $Ca_6[Si_2O_6(OH)]_2(OH)_2$ and $Ca_7[Si_2O_7]_2(OH)_2$. If the Ca5 site is empty the first formula is valid and the corresponding structure is characterized by an additional silanol group, which maintains charge balance. If Ca5 is fully occupied, the second formula, which does not have an additional silanol group, is correct. In the two available structure refinements (Taylor, 1977 and this study) the Ca5 occupancies are 0.43(2) and 0.32(1), respectively. Both structure refinements are in good agreement, although the improved data quality in our study allowed better refinement of anisotropic

TABLE 2. Composition of trabzonite and killalaite from Ikizdere, Turkey.

	1	2	SD	Range	3	SD	Range
Composition (wt.%)							
SiO_2	42.44	42.51	0.25	41.95–42.76	39.12	0.77	37.07–39.98
Al_2O_3	0.05	n.d.	n.d.		n.d.		
MgO	0.14	n.d.	n.d.		n.d.		
CaO	52.76	53.58	0.39	53.23–54.05	56.46	0.68	54.83–57.46
MnO	0.04	n.d.	n.d.		0.09	0.07	0.0–0.23
Na_2O	0.32	n.d.	n.d.		n.d.		
SO_3	n.d.	n.d.	n.d.		0.16	0.08	0.03–0.37
H_2O*	4.25	4.37			4.31		
Total	100.00	100.46			100.14		
Formula (a.p.f.u.)							
Ca	3.980†	4.022†			6.303‡		
Na	0.044						
Mg	0.015						
Mn^{2+}	0.002				0.008		
X	4.041	4.022			6.311		
Si	2.988	2.978			4.076		
Al	0.004						
S^{6+}					0.013		
Z	2.992	2.978			4.089		
OH	1.996	2.044			2.998		

1, trabzonite composition from original analysis by Sarp and Burri (1987), with data normalized to 100 wt.%.
2, foshagite (mean of 8 analyses) with killalaite.
3, killalaite (mean of 23 analyses).
* Water content calculated on the basis of charge balance.
† Formula calculated on the basis of 11 oxygen atoms,
‡ Formula calculated on the basis of 16 oxygen atoms.
The abbreviation n.d. is not detected; a.p.f.u. is atoms per formula unit; *X* is the sum Ca + Mg + Mn + Na; *Z* is the sum Si + Al + S.

displacement parameters (Table 7) and prominent H sites were located, as discussed below.

Trabzonite (Fig. 7) has a herringbone arrangement of SiO_4 trimers with Si1–O4–Si2 and Si2–O3–Si3 angles of 143º and 132º, respectively. Along the *b* axis the trimers are separated by CaO_{6-8} polyhedra (Ca1, Ca2, Ca4, Ca6). The SiO_4 trimers meet at a spine running parallel to *b* formed by $Ca3O_7$ and $Ca5O_8$ polyhedra. The OH groups OH11 and OH12 are also part of this backbone. Projections along [011] (Fig. 8) show that the silicate trimers are not straight but form arc like arrangements.

Although both of the analyses indicate it has close to endmember composition (Tables 2 and 3), there are significant differences in the cell dimensions of trabzonite from the Northern Caucasus (Russia) and from Turkey (Table 1). These differences are probably an artefact produced by the radial intergrowth of the crystal lites, which produces strongly distorted and overlapping diffraction patterns.

The crystal chemistry, including hydrogen bonding, of dellaite has recently been reviewed (Armbruster *et al.*, 2011). In contrast to trabzonite and killalaite, dellaite does not contain silanol groups. The dellaite structure is very similar to that of killalaite, with the major difference being that killalaite only contains disilicate units, whereas dellaite is made up of alternating SiO_4 and Si_2O_7 units.

The main objective of the present study was to solve the structure of trabzonite. Therefore, all of the crystals or crystal aggregates selected for X ray diffraction were chosen to be pure trabzonite on the basis of microscopic inspection

TABLE 3. Chemical composition of trabzonite and killalaite from the altered xenoliths of the Upper Chegem caldera.

	1	SD	Range	2	SD	Range	3	SD	Range	4	SD	Range	5	SD	Range
Composition (wt %)															
SiO_2	41 45	0 38	40 80–42 16	41 03	0 51	40 11–41 84	40 72	0 57	39 09–41 59	37 97	0 57	36 77–38 72	37 38	0 05	37 37–37 56
Al_2O_3	0 45	0 07	0 33–0 57	0 52	0 10	0 34–0 70	0 63	0 17	0 31–0 84	n d			n d		
MgO	n d			n d			0 15	0 05	0 07–0 24	n d			n d		
CaO	52 52	0 35	51 89–52 99	52 63	0 57	51 74–54 08	52 38			56 36	0 50	35 26–57 03	56 42	0 36	55 62–56 75
Na_2O	n d			n d			n d			0 02	0 02	0–0 05	n d		
SO_3	n d			n d			n d			0 11	0 04	0–0 125	n d		
H_2O*	4 33			4 40			4 44			4 47			4 59		
Total	98 75			98 58			98 32			98 93			98 39		
Formula (a p f u)															
Ca	4 009†			4 027†			4 017†			6 378‡			6 426‡		
Mg	0 000			0 000			0 016			0 000			0 000		
Na	0 000			0 000			0 000			0 004			0 000		
X	4 009			4 027			4 033			6 382			6 426		
Si	2 953			2 930			2 914			4 010			3 974		
Al	0 038			0 044			0 053			0 000			0 000		
S^{6+}	0 000			0 000			0 000			0 008			0 000		
Z	2 991			2 973			2 967			4 018			3 974		
OH	2 056			2 097			2 118			3 148			3 254		

1, trabzonite (mean of 16 analyses) from spherulites found in cracks of altered ignimbrite (Fig 2*a*, xenolith no 5)
2, trabzonite (mean of 17 analyses) from rusinovite zone of skarn (Fig 2*b*, xenolith no 3)
3, trabzonite (mean of 23 anlyses) in cavities of altered larnite-cuspidine skarn (Fig 2*c*, xenolith no 3)
4, killalaite (mean of 13 anlyses) in cavities of altered larnite-cuspidine skarn (Fig 2*c*, xenolith no 3)
5, killalaite (mean 13) in association with hydroxylellestadite (Fig 2*d*, xenolith no 7)
* Water content calculated on the basis of charge balance
† Formula calculated on the basis of 11 oxygen atoms,
‡ Formula calculated on the basis of 16 oxygen atoms
The abbreviations n d is not detected; a p f u is atoms per formula unit; *X* is the sum Ca + Mg + Na; *Z* is the sum Si + Al + S

TABLE 4. Atom coordinates and U_{eq} (Å^2) values for trabzonite from Ikizdere, Turkey.

Site	Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ca1	Ca	0.35412(6)	0.09773(11)	0.05961(15)	0.0113(3)
Ca2	Ca	0.36296(6)	0.09381(11)	0.43914(14)	0.0105(2)
Ca3	Ca	0.25	0.11905(16)	−0.2611(2)	0.0146(4)
Ca4	Ca	0.50	0.0	0.6235(2)	0.0124(4)
Ca5	Ca	0.25	−0.16686(16)	−0.05094(19)	0.0118(3)
Ca6	Ca	0.50	0.0	0.21685(18)	0.0107(3)
Si1	Si	0.37313(8)	−0.11729(14)	−0.2419(2)	0.0089(3)
Si2	Si	0.49671(8)	0.21342(14)	−0.09381(18)	0.0083(3)
Si3	Si	0.37396(8)	−0.19912(14)	0.2484(2)	0.0098(3)
O1	O	0.4747(2)	0.1420(4)	0.4274(5)	0.0118(8)
O2	O	0.4642(2)	0.1475(4)	0.0456(5)	0.0137(9)
O3	O	0.4417(2)	0.2172(4)	0.7699(5)	0.0146(9)
O4	O	0.4463(2)	−0.1172(4)	−0.1639(5)	0.0140(9)
O5	O	0.3897(2)	−0.0476(4)	0.2382(5)	0.0120(8)
O6	O	0.3386(2)	−0.2573(4)	−0.2348(5)	0.0117(8)
O7	O	0.3312(2)	−0.2560(4)	0.1179(5)	0.0105(8)
O8	O	0.3262(2)	−0.0170(4)	−0.1541(5)	0.0108(8)
O9	O	0.3881(2)	0.9311(4)	0.5932(5)	0.0139(9)
OH10	O	0.3297(2)	0.7773(4)	0.3999(5)	0.0146(9)
OH11	O	0.2500	0.0154(7)	0.1062(7)	0.0189(14)
OH12	O	0.2500	0.0504(6)	0.4835(8)	0.0189(14)
H10	H	0.348(5)	0.819(9)	0.485(7)	0.050
H11	H	0.25	0.019(13)	0.211(2)	0.050
H12	H	0.25	−0.040(4)	0.457(17)	0.050

Restraints (Å): H10−OH10: 0.96(2), H10−O9: 1.6(2), H11−OH11: 0.96(2), H11−OH12: 2.5(2), H12−OH12: 0.96(2), and origin of polar space group.

TABLE 5. Atom coordinates and U_{eq} (Å^2) values and occupancy for killalaite from Northern Caucasus.

Site	Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}	Occupancy
Ca1	Ca	0.3324(3)	−0.09374(11)	0.9295(3)	0.0217(4)	1
Ca2	Ca	0.7197(3)	−0.10117(13)	0.3315(3)	0.0297(5)	1
Ca3	Ca	0.0084(5)	0.25	0.3351(4)	0.0300(7)	1
Ca4	Ca	0.9196(5)	0.25	0.8314(4)	0.0332(8)	1
Ca5	Ca	0.5216(11)	0.25	0.4815(11)	0.013(2)	0.320(11)
Si1	Si	0.8142(4)	−0.08700(14)	0.8382(4)	0.0205(5)	1
Si2	Si	0.7798(4)	0.08307(13)	0.5996(4)	0.0159(5)	1
O1	O	0.6784(9)	−0.0583(4)	0.0010(8)	0.0182(12)	1
O2	O	0.6904(11)	−0.1461(5)	0.6641(10)	0.0306(15)	1
O3	O	0.0039(10)	−0.1438(4)	0.9203(9)	0.0212(13)	1
O4	O	0.6701(12)	0.0487(5)	0.3904(10)	0.0379(19)	1
O5	O	0.6296(10)	0.1308(4)	0.7326(11)	0.0270(14)	1
O6	O	0.9547(10)	0.1509(4)	0.5740(10)	0.0235(13)	1
O7	O	0.8861(11)	−0.0004(5)	0.7243(12)	0.0386(19)	1
OH8	O	0.2761(19)	0.25	0.763(2)	0.055(4)	1
OH9	O	0.6614(15)	0.25	0.1541(16)	0.029(2)	1
H2	H	0.555(9)	−0.131(13)	0.67(3)	0.050	0.68
H8	H	0.418(4)	0.25	0.77(3)	0.050	1
H9	H	0.54(2)	0.25	0.22(4)	0.050	0.68

Restraints (Å): H2−O2: 0.96(2), H8−OH8: 0.96(2), H9−OH9: 0.96(2).

TABLE 6. Anisotropic displacement parameters (Å^2) for trabzonite from Ikizdere, Turkey.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.0105(6)	0.0120(5)	0.0114(6)	0.0006(4)	−0.0023(5)	−0.0006(4)
Ca2	0.0101(5)	0.0101(5)	0.0112(6)	0.0010(4)	0.0007(4)	0.0014(4)
Ca3	0.0095(8)	0.0164(7)	0.0178(9)	0.0064(7)	0.000	0.000
Ca4	0.0091(8)	0.0183(9)	0.0098(8)	0.000	0.000	−0.0026(6)
Ca5	0.0083(7)	0.0120(7)	0.0152(9)	0.0036(6)	0.000	0.000
Ca6	0.0108(8)	0.0114(7)	0.0101(8)	0.000	0.000	0.0003(6)
Si1	0.0090(7)	0.0081(6)	0.0095(7)	0.0003(6)	0.0008(7)	0.0001(5)
Si2	0.0077(7)	0.0078(6)	0.0094(7)	0.0002(6)	0.0002(6)	−0.0013(5)
Si3	0.0105(7)	0.0094(6)	0.0096(7)	0.0002(7)	−0.0011(6)	−0.0008(5)
O1	0.015(2)	0.0100(18)	0.0104(19)	0.0004(16)	−0.0028(19)	−0.0005(15)
O2	0.016(2)	0.0138(19)	0.011(2)	0.0040(16)	0.0036(17)	0.0002(17)
O3	0.014(2)	0.0156(18)	0.014(2)	−0.0002(16)	−0.0014(18)	0.0029(16)
O4	0.008(2)	0.0143(18)	0.019(2)	0.0015(16)	−0.0055(18)	0.0000(16)
O5	0.013(2)	0.0093(16)	0.0132(19)	0.0004(18)	−0.0027(19)	−0.0014(15)
O6	0.014(2)	0.0088(16)	0.012(2)	0.0001(16)	−0.0008(17)	−0.0003(15)
O7	0.008(2)	0.014(2)	0.0096(19)	−0.0012(16)	−0.0048(16)	−0.0017(16)
O8	0.009(2)	0.0100(17)	0.014(2)	0.0003(15)	0.0002(16)	0.0007(15)
O9	0.013(2)	0.017(2)	0.012(2)	0.0042(16)	0.0003(17)	−0.0026(17)
OH10	0.014(2)	0.015(2)	0.014(2)	−0.0011(16)	0.0047(17)	−0.0011(17)
OH11	0.014(3)	0.021(3)	0.021(4)	−0.004(3)	0.000	0.000
OH12	0.016(3)	0.016(3)	0.025(4)	−0.002(3)	0.000	0.000

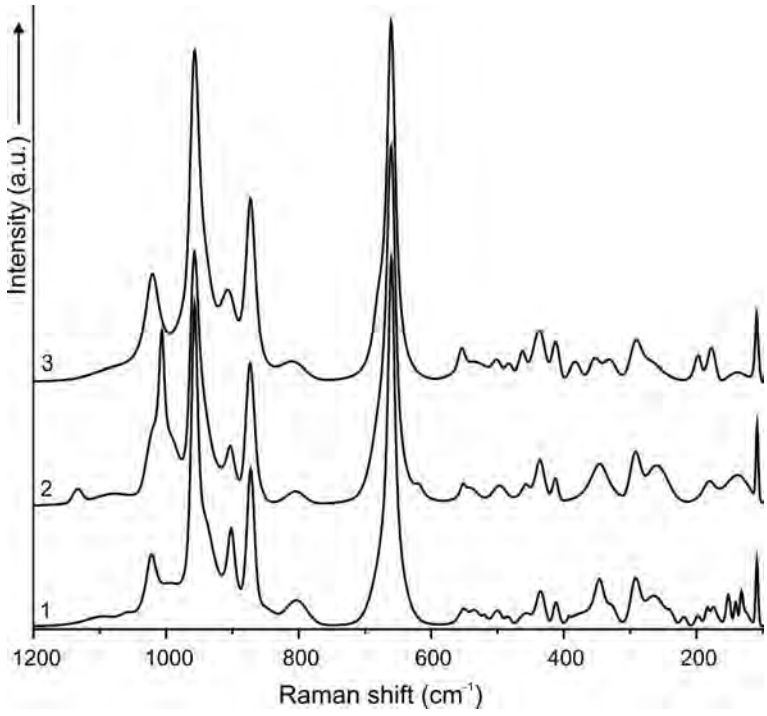

FIG. 3. Raman spectra of trabzonite from the Upper Chegem caldera, Northern Caucasus. Spectra are as follows: (1) a pseudomorph (Fig. 2*b*); (2) a spherulite (Fig. 2*a*); (3) an aggregate with killalaite (Fig. 2*c*).

TABLE 7. Anisotropic displacement parameters (Å^2) for killalaite from Northern Caucasus.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.0213(11)	0.0167(8)	0.0268(10)	−0.0026(6)	0.0020(7)	−0.0027(6)
Ca2	0.0272(12)	0.0315(10)	0.0306(11)	0.0131(8)	0.0049(8)	0.0075(8)
Ca3	0.062(2)	0.0104(10)	0.0190(13)	0.000	0.0088(12)	0.000
Ca4	0.067(2)	0.0116(11)	0.0197(14)	0.000	0.0005(13)	0.000
Ca5	0.013(4)	0.008(3)	0.018(4)	0.000	0.000(3)	0.000
Si1	0.0209(14)	0.0170(10)	0.0236(13)	0.0039(9)	0.0027(10)	0.0025(9)
Si2	0.0191(13)	0.0106(9)	0.0180(12)	0.0011(8)	0.0023(9)	−0.0009(8)
O1	0.019(3)	0.016(3)	0.020(3)	−0.002(2)	0.003(2)	0.003(2)
O2	0.023(4)	0.044(4)	0.024(3)	−0.002(3)	−0.001(3)	−0.009(3)
O3	0.030(4)	0.012(3)	0.021(3)	0.001(2)	0.003(3)	0.002(2)
O4	0.050(5)	0.037(4)	0.025(4)	−0.005(3)	0.000(3)	−0.022(4)
O5	0.027(4)	0.021(3)	0.035(4)	−0.002(3)	0.009(3)	0.006(3)
O6	0.031(4)	0.015(3)	0.025(3)	0.003(2)	0.005(3)	−0.006(2)
O7	0.028(4)	0.024(3)	0.068(5)	0.018(3)	0.018(4)	0.007(3)
OH8	0.040(7)	0.013(5)	0.102(11)	0.000	−0.022(7)	0.000
OH9	0.026(5)	0.018(4)	0.044(6)	0.000	0.008(4)	0.000

TABLE 8. Bond distances (Å) for trabzonite from Ikizdere, Turkey.

Ca1	O2	2.326(5)	Ca2	O9	2.248(4)
Ca1	O5	2.330(5)	Ca2	O6	2.263(5)
Ca1	OH11	2.344(3)	Ca2	O1	2.355(4)
Ca1	O8	2.349(5)	Ca2	O7	2.341(5)
Ca1	OH10	2.409(5)	Ca2	OH12	2.402(2)
Ca1	O6	2.417(5)	Ca2	O5	2.404(5)
	Mean	**2.363**		Mean	**2.336**
Ca3	2 × O8	2.320(4)	Ca4	2 × O1	2.368(5)
Ca3	2 × O7	2.382(5)	Ca4	2 × O9	2.425(5)
Ca3	OH12	2.432(7)	Ca4	2 × O4	2.536(5)
Ca3	2 × OH10	2.740(5)	Ca4	2 × O3	2.871(5)
	Mean	**2.474**		Mean	**2.550**
Ca5	OH11	2.364(7)			
Ca5	2 × O8	2.394(4)	Ca6	2 × O2	2.301(5)
Ca5	2 × O7	2.451(5)	Ca6	2 × O5	2.331(4)
Ca5	2 × O6	2.646(4)	Ca6	2 × O1	2.469(5)
Ca5	OH12	2.937(7)		mean	**2.367**
	Mean	**2.535**			
Si1	O8	1.626(5)	Si2	O2	1.588(5)
Si1	O6	1.612(4)	Si2	O1	1.616(4)
Si1	O9	1.612(5)	Si2	O4	1.664(5)
Si1	O4	1.666(5)	Si2	O3	1.680(5)
	Mean	**1.629**		Mean	**1.637**
Si3	O7	1.590(5)			
Si3	O5	1.601(4)			
Si3	OH10	1.671(5)			
Si3	O3	1.652(5)			
	Mean	**1.629**			

and electron microprobe analyses. In the crystals that were used there was no indication (such as streaking or unindexed reflections) that could be interpreted as evidence of polysomatic inter growth between trabzonite and killalaite or dellaite. Figure 2*c* shows intergrowths between trabzonite and killalaite in the skarns from the Upper Chegem caldera, but these were not studied by X ray diffraction.

Hydrogen bonding in trabzonite

Unfortunately, the poor quality of the diffraction data for trabzonite (for crystals from both localities) does not allow the residual electron density peaks, representing H positions in difference Fourier maps, to be determined. The only hydrogen bond that could be located directly was at H11. However, the bond valence calcula tions (Table 9) give important information about the pattern of hydrogen bonding. The position of OH11 and OH12, the O sites with the lowest bond valence sums, are very similar to the corre sponding OH arrangement in dellaite. The third OH group, necessary for charge balance, is at OH10, a position with a bond strength sum of 1.3 vu (valence units). This bond strength sum is considerably greater than at the other two OH groups, which have 1.06 vu at OH11 and 0.97 vu at OH12, indicating that the proton at OH10 is engaged in strong hydrogen bonding. Bond valence calculations (Table 9) indicate that O9, which is 2.65 Å from OH10, has a valence sum of only 1.80 vu. Thus O9 is the most probable acceptor of the hydrogen bond, with OH10 as the donor. After defining the corresponding soft constraints the hydrogen sites were successfully refined; the OH10 site is the tetrahedral corner of Si3 and forms a silanol group. A similar silanol OH group has also been identified in the structure of killalaite (see below and Taylor, 1977).

Hydrogen bonding in killalaite

The pattern of hydrogen bonding in killalaite derived from our structural data is incomplete, but some major features can be identified. The two stoichiometries (a) $Ca_6[Si_2O_6(OH)]_2(OH)_2$ and (b) $Ca_7[Si_2O_7]_2(OH)_2$) which limit the composition of killalaite must be distinguished in a discussion of hydrogen bonding. If Ca5 is empty as in stoichiometry (a) the oxygen site O2 with the lowest valence sum (Table 10) is a silanol group. In this case H2 forms a strong hydrogen bond with

TABLE 9. Bond valence values for trabzonite from Ikizdere, Turkey.

Site	Ca1	Ca2	Ca3	Ca4	Ca5	Ca6	Si1	Si2	Si3	Σ
O1		0 35		0 33 2 × ↑		0 26 2 × ↑		1 02		1 96
O2	0 38					0 40 2 × ↑		1 11		1 89
O3				0 09 2 × ↑				0 86	0 93	1 88
O4				0 21 2 × ↑			0 89	0 90		2 00
O5	0 37	0 31				0 37 2 × ↑			1 07	2 12
O6	0 30	0 45			0 16 2 × ↑		1 03			1 94
O7		0 37	0 33 2 × ↑		0 27 2 × ↑				1 09	2 06
O8	0 36		0 39 2 × ↑		0 32 2 × ↑		0 99			2 06
O9		0 47		0 29 2 × ↑			1 04			1 80
OH10	0 30		0 12 2 × ↑						0 88	1 30
OH11	0 36 2 × →				0 34					1 06
OH12		0 31 2 × →	0 28		0 07					0 97
Σ	2 07	2 26	1 94	1 85	1 91	2 06	3 95	3 89	3 97	

TABLE 10. Bond valence values for killalaite from Northern Caucasus, Russia.

Site	Ca1	Ca2	Ca3	Ca4	Ca5	Si1	Si2	Σ
O1	0.30 0.31	0.37				1.06		2.03
O2		0.30	0.18 2 × ↑		0.41 2 × ↑	0.95		1.84 (1.43)
O3	0.34		0.32 2 × ↑	0.34 2 × ↑		1.06		2.06
O4	0.41	0.32					1.03	1.76
O5	0.35	0.30		0.13 2 × ↑	0.20 2 × ↑		0.97	1.95 (1.75)
O6		0.35	0.40 2 × ↑	0.34 2 × ↑			1.02	2.11
O7		0.04 0.04				0.92	0.91	1.91
O8		0.32 2 × →		0.21	0.13			0.98 (0.85)
O9	0.25 2 × →		0.23	0.06	0.21			1.00 (0.79)
Σ	1.96	2.04	2.01	1.89	1.55	3.99	3.93	

Note: values in parentheses are calculated for empty Ca5.

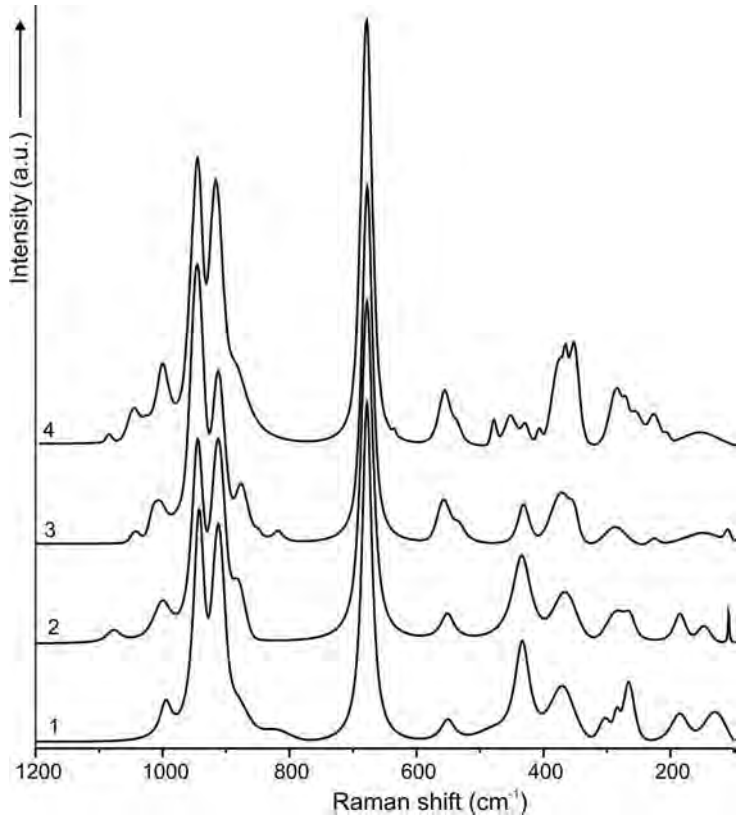

FIG. 4. Raman spectra of killalaite: (1) on a cross section approximately perpendicular to *z* from the Upper Chegem caldera, Northern Caucasus (Fig. 2*d*); (2) on a cross section approximately parallel to *z* from the Upper Chegem caldera, Northern Caucasus (Fig. 2*d*); (3) intergrowths with trabzonite from the Upper Chegem caldera, Northern Caucasus (Fig. 2*c*); (4) on a specimen from Ikizdere, Turkey (Fig. 1).

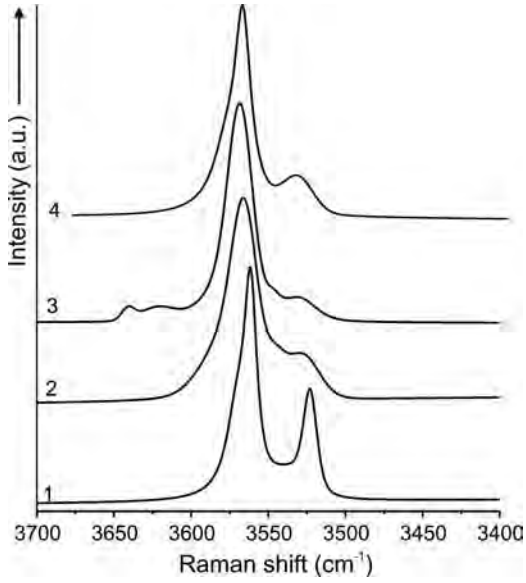

FIG. 5. Raman spectra of killalaite in the OH region: (1) on a cross section approximately perpendicular to *z* from the Upper Chegem caldera, Northern Caucasus (Fig. 2*d*); (2) on a cross section approximately parallel to *z* from the Upper Chegem caldera, Northern Caucasus (Fig. 2*d*); (3) intergrowths with trabzonite from the Upper Chegem caldera, Northern Caucasus (Fig. 2*c*); (4) specimen from Ikizdere, Turkey (Fig. 1).

O4 as an acceptor (H2···O4: 2 Å). If hydrogen bonds are not included in the sum, O4 has a bond valence sum of only 1.76 vu and does not bond to Ca5. The OH8 and OH9 sites are clearly identified by their low bond valence sums (Table 10) as OH groups, independent of the occupancy at Ca5. We located H8 forming a hydrogen bond with O5 as the acceptor (H8···O5: 2.4 Å) as O5 is also characterized by a low bond valence sum (Table 10), particularly if Ca5 is vacant. Refined H9, linked to OH9, seems only to exist if Ca5 is empty because the Ca5−H9 distance is only 1.8 Å; H9 then forms a weak hydrogen bond with O2 as the acceptor (H9···O2: 2.5 Å). Potential H9a, populated if Ca5 is occupied, could not be found. A possible acceptor of this hydrogen bond is O3, which is 2.9 Å from O9.

Assignment of Raman bands

The Raman spectra of killalaite, $Ca_{6.3}[H_{0.7}Si_2O_7]_2(OH)_2$, from Russia and Turkey and trabzonite, $Ca_4[Si_3O_9(OH)](OH)$, from Russia are similar at first glance, but they can be differentiated by characteristic differences (Figs 3 and 4). The bands observed in the region 100−450 cm^{-1} for both minerals are mainly related to lattice vibrations of SiO_4 tetrahedra and stretching vibrations of Ca−O bonds. The most intense bands at 660 and 678 cm^{-1}, of trabzonite and killalaite, respectively, are due to *b*(Si−O−Si) bending and *s*(Si−O_{br}) stretching vibrations. The strong band at 912 cm^{-1} in the spectrum of killalaite is related to *s*(Si−O) vibrations of the oxygen atoms bridging the SiO_4 tetrahedra in $[Si_2O_7]$ groups. A corresponding band is observed at ~900 cm^{-1} in other disilicates, e.g. rusinovite $Ca_{10}[Si_2O_7]_3Cl_2$ and rankinite $Ca_3[Si_2O_7]$ (Galuskin *et al*., 2011). The killalaite spectrum differs from the spectra of these disilicates in the presence of additional bands associated with stretching vibrations of OH groups, and in the presence of bands that can be attributed to silanol modes. We believe that the Si−OH stretching vibration in killalaite is at 945 cm^{-1}. In the spectrum of trabzonite strong bands at 957, 902 and 872 cm^{-1} correspond to the *s*(Si−O) vibrations. The band at 957 cm^{-1} is related to the stretching vibrations of the Si−OH bond. The strong trabzonite band (Fig. 3, spectrum 2) at 1006 cm^{-1} with a shoulder at 1020 cm^{-1} can be assigned to *s*(Si−O) stretching modes of terminal oxygen atoms of the trimeric unit $[Si_3O_9(OH)]^{7-}$. This is in agreement with recent data for pavlovskyite, $Ca_8[Si_3O_{10}][SiO_4]_2$ and kilchoanite, $Ca_6[Si_3O_{10}][SiO_4]$ (Galuskin *et al.*, 2012). There is no corresponding band in the spectrum of killalaite (Fig. 4).

In the high wavenumber region, there are three bands at 3523, 3561 and 3570 cm^{-1} in killalaite (Fig. 5) and two bands at 3576 and 3602 cm^{-1} in the trabzonite spectra (Fig. 6), corresponding to *s*(O−H) stretching vibrations. Single crystal X ray diffraction shows that killalaite and trabzonite are similar structures and contain the same types of OH groups. Both minerals have three OH groups, one Si−OH silanol group and two OH groups in which oxygen is not connected to Si.

The interpretation of the Raman spectrum of killalaite in the OH region is complicated by the partially occupied (~32%) Ca5 site as this site influences the nature and arrangement of the OH groups. First consider the situation if Ca5 is empty: a weak bifurcated hydrogen bond O9−H9···2 × O2 (O9−O2 3.37 Å) is expected. The Raman band at 3570 cm^{-1} is probably related

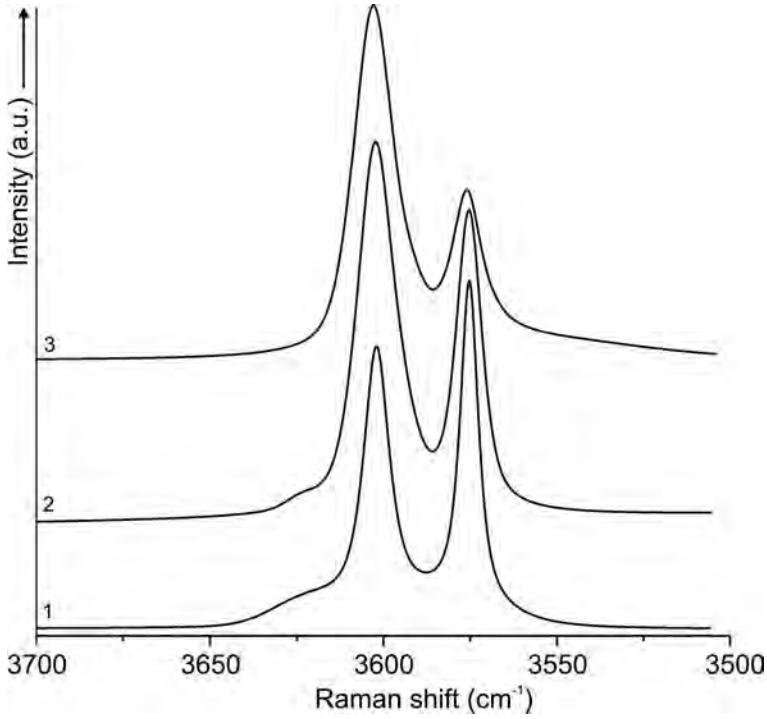

FIG. 6. Raman spectra of trabzonite in the OH region: (1) a pseudomorph (Fig. 2*b*); (2) a spherulite (Fig. 2*a*); (3) an aggregate with killalaite (Fig. 2*c*).

to this hydrogen bond. If the Ca5 site is occupied, the O9−H9a bond is probably in the opposite direction (although this was not verified by structure refinement) and therefore the configuration becomes O9−H9a···2 × O3 (O9−O3 2.92 Å). This configuration probably produces the Raman band at ~3523 cm^{-1}. The band at 3565 cm^{-1} corresponds to the configuration O8−H8···2 × O5 (O8−O5 3.07 Å). The OH2 silanol group (which is only populated if the Ca5 site is empty) forms a strong hydrogen bond O2−H2···O4 with (O2−O4 2.86 Å) in killalaite. This hydrogen bond should produce a Raman stretching vibration near 3470 cm^{-1}, but it is not present in the killalaite spectrum. It may be that the geometry of the hydrogen bond (bending) and cooperative effects (disorder due to partial occupation of Ca5) shift the band position towards higher frequencies (3532 cm^{-1}).

In the case of trabzonite, the bands at 3602 and 3575 cm^{-1} are related to hydrogen bonding in the hydroxyl groups OH12 (in the configuration O12−H12···2 × O6 with O12−O6 3.35 Å) and OH11 (in the configuration O11−H11···2 × O6 with O11−O6 3.31 Å), respectively. A Raman band relating to hydrogen bonding of the silanol group (O10−H10···O9 with O10−O9 2.66 Å) is expected at a frequency of 2730 cm^{-1} but not observed in the Raman spectrum. Our trabzonite structure refinement and bond valence calculations (Table 9) support a strong hydrogen bond of the type O10−H10···O9, and therefore there must be a reason for the failure in locating a corresponding band in the Raman spectrum. Strong or very strong hydrogen bonds have the tendency to be particularly polarized and to produce very diffuse bands at low frequencies (e.g. Nyfeler *et al.*, 1997). If unpolarized spectra are recorded in random orientation these bands are easily overlooked.

Structural relations between trabzonite and other trisilicates in the CSH system

A recent review of trisilicate minerals by Wierzbicka Wieczorek *et al.* (2010) lists the calcium silicates rosenhahnite, $Ca_3[Si_3O_8(OH)_2]$

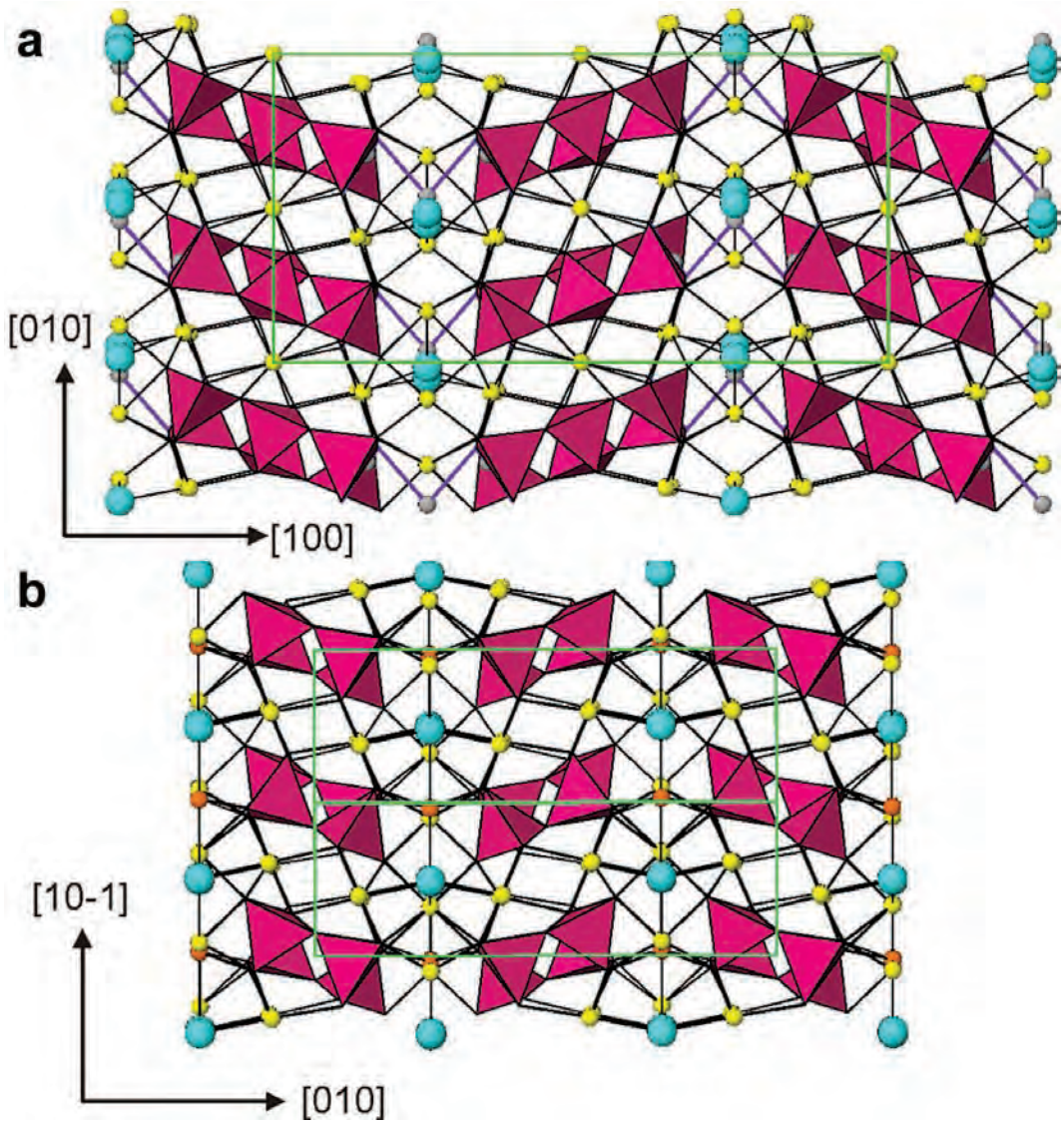

FIG. 7. Comparison of the crystal structures of trabzonite and killalaite. (*a*) The crystal structure of trabzonite which contains red SiO_4 tetrahedra connected as trimers. The Ca sites are represented by yellow spheres, OH sites are light blue with grey hydrogen atoms, hydrogen bonds are indicated in lilac. (*b*) The crystal structure of killalaite projected along [101], with colours as above. The partially occupied site Ca5 is shown in orange.

(Wan *et al.*, 1977) and kilchoanite, $Ca_6[Si_3O_{10}][SiO_4]$ (Taylor, 1971). Recently, we have also identified trisilicate groups in the structure of pavlovskyite, $Ca_8[SiO_4]_2[Si_3O_{10}]$ (Galuskin *et al.*, 2012). Wierzbicka Wieczorek *et al.* (2010) rank trisilicates according to the Si–Si–Si angles, which range between 82.5 and 165.5º. Trabzonite has a Si–Si–Si angle of 126.6º, which is close to the corresponding angle of 127.2º for rosenhahnite (Fig. 8) whereas kilchoanite and pavlovskyite have a considerably more twisted Si–Si–Si arrangement with an angle of 98.1º. It is interesting to note that the cell dimensions of rosenhahnite (Wan *et al.*, 1977) have two axes of ~6.9 Å; the angle between them is 94.8º which is more acute than in

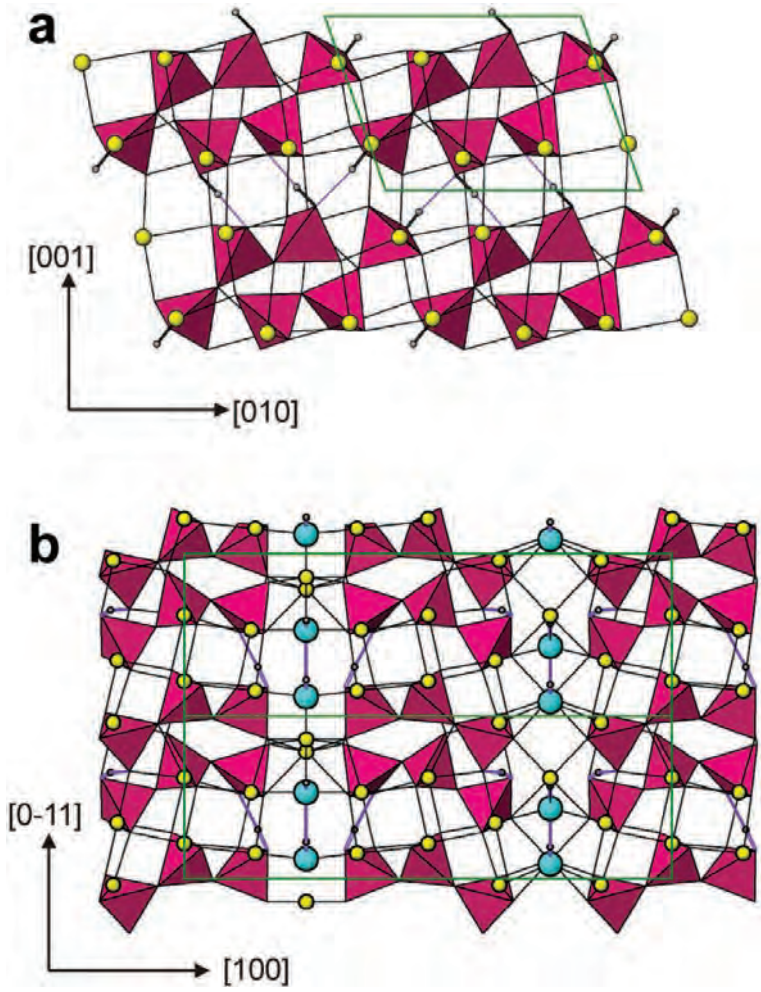

FIG. 8. Comparison of the crystal structures of rosenhahnite and trabzonite. (*a*) The crystal structure of rosenhahnite (Wan *et al.*, 1977) projected along the *a* axis, with red SiO_4 tetrahedra connected as trimers. The Ca sites are represented by yellow spheres, hydrogen atoms in silanol groups are small grey spheres, hydrogen bonds are indicated in lilac. (*b*) The crystal structure of trabzonite projected along [011], with colours as above. The OH groups, other than those in silanol groups, are shown as light blue spheres.

killalaite, dellaite and trabzonite (in the mono clinic setting) which have angles of 97–98º. In rosenhahnite (Fig. 8) all of the OH groups are of the silanol type, and in contrast to killalaite and trabzonite, the structure has no central backbone formed by CaO_x polyhedra. Thus, the herringbone pattern of trisilicate units (Fig. 7) is not present in rosenhahnite. The absence of a central backbone is also responsible for the low Ca:Si ratio, which is 1:1 in rosenhahnite, whereas trabzonite has 4:3 and killalaite between 3:2 and 7:4.

Using the new formula for trabzonite derived in this paper, foshagite and trabzonite have the same chemical composition and should be considered polymorphs. The density of trabzonite calculated from structural data is 2.79 g cm^{-3}, whereas foshagite is 2.74 g cm^{-3} (Gard and Taylor, 1960). To better distinguish between the two minerals, the formula of foshagite can be written $Ca_4[Si_3O_9](OH)_2$ to emphasize the fact that is a chain silicate with a wollastonite like *Dreier Einfachketten* and without silanol groups (Gard

and Taylor, 1960). The Ca coordination in foshagite is described as sixfold (Gard and Taylor, 1960) whereas trabzonite has Ca4 and Ca5 with eightfold, Ca3 with sevenfold, and Ca1, Ca2 and Ca6 with sixfold coordination (Table 8), this may explain the difference in density.

Foshagite is believed to be stable above 260ºC, and up to at least 500ºC between 120 to 210 MPa (Speakman, 1968). However, Hong and Glasser (2004) synthesized foshagite at saturated steam pressure above 130ºC and considered it to be the stable phase. Foshagite replacing vesuvianite in xenoliths of the Rustenburg Layered Suite (South Africa) was estimated (Buik *et al*., 2000) to have formed between ~250 and 400ºC. However, this temperature estimate is strongly influenced by the experimental study of Speakman (1968). Henry (1999) described a skarn from Chesney Vale, Victoria, Australia, including foshagite (asso ciated with vesuvianite and calcite), xonotlite, prehnite and tobermorite. These minerals were interpreted as a retrograde assemblage that formed below 400ºC. In the skarns at Crestmore, California, USA, the type locality for foshagite (Eakle, 1925), foshagite occurs as veins in vesuvianite boulders. Unfortunately, the rarity of trabzonite, which only occurs at the two localities described in this paper, does not allow a temperature range for its formation to be given. The mineral assemblages in which it occurs suggest a late stage retrograde formation.

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 '-x, y-1/2, -z'

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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O6 O 0.9548(10) 0.1509(4) 0.5742(10) 0.0235(13) Uani 1 1 d . . .
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OH9 O 0.6613(15) 0.2500 0.1539(16) 0.029(2) Uani 1 2 d SD . .
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H8 H 0.418(4) 0.2500 0.77(3) 0.050 Uiso 1 2 d SD . .
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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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