

Chlorine content and crystal chemistry of dellaite from the Birkhin gabbro massif, Eastern Siberia, Russia

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ABSTRACT

Dellaite crystals of close to end-member composition, $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$, and with ~1.5 wt.% Cl, yielding $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_{1.75}\text{Cl}_{0.25}$ have been found in skarns within the gabbroid rocks of the Birkhin complex (Eastern Siberia, Russia). The greatest Cl content analysed in a dellaite domain in this skarn is 5.2 wt.% Cl corresponding to 0.8 Cl p.f.u. Dellaite occurs in altered merwinite-larnite-bredigite-gehlenite skarns and also in calcio-olivine skarns with residual larnite. The crystal structures of Cl-free and Cl-bearing (~1.5 wt.% Cl) dellaite have been refined, including hydrogen positions, from single-crystal X-ray data to $R_1 = 3.7$ and 3.8%, respectively. In addition, both dellaite varieties were studied by Raman spectroscopy indicating stronger hydrogen bonds for the Cl-bearing sample, which agrees with the structural data. Cl is strongly selective and enriches at one (O6) of the two OH positions allowing for the formation of a stronger hydrogen bond $\text{O8}\cdots\text{H8}\cdots\text{Cl6}$ compared to $\text{O8}\cdots\text{H8}\cdots\text{O6}$. Raman spectra of the domain with ~0.8 Cl p.f.u. confirm the general enhancement of a low-frequency band in the OH range suggesting the dominance of the $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bond systems.

Dellaite and killalaite, $\text{Ca}_{3.2}(\text{H}_{0.6}\text{Si}_2\text{O}_7)(\text{OH})$, have related modular structures, differentiated only by the Si_2O_7 units in killalaite and alternating Si_2O_7 and SiO_4 units in dellaite. The similarity in cell dimensions and chemical composition suggests that trabzonite, $\text{Ca}_4\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, with Si_3O_{10} trimers also belongs to the same family of structures.

KEYWORDS: dellaite, crystal structure, Cl content, Raman spectroscopy, skarn mineralogy.

Introduction

$\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$ ($\text{C}_6\text{S}_3\text{H}$) was synthesized and named “phase Y” by Della M. Roy (1958) and further characterized by Dent-Glasser and

Roy (1959). The same authors determined the triclinic cell dimensions and predicted from the chemical formula a crystal structure consisting of Si_2O_7 and SiO_4 entities. $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$ was synthesized in equilibrium with α' - Ca_2SiO_4 and H_2O above ~800°C and 1000 bar H_2O pressure. Dent-Glasser *et al.* (1961) showed that products synthesized by Flint *et al.* (1938), Jander and Franke (1941) and Funk (1958) were identical to the “phase Y” by Roy (1958). Thus 350°C and

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160 bar were the lowest temperature and pressure conditions under which $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$ had been produced. The crystal structure of this compound was solved by Ganiev *et al.* (1970) and refined by Safronov *et al.* (1981). The structure of $\text{C}_6\text{S}_3\text{H}$ is triclinic, space group $P\bar{1}$ with $a = 6.825(2)$, $b = 6.931(1)$, $c = 12.907(5)$ Å, $\alpha = 90.68(2)$, $\beta = 97.57(3)$, $\gamma = 98.12(2)^\circ$.

The first description of $\text{C}_6\text{S}_3\text{H}$ as a mineral goes back to Agrell (1965) reporting new minerals from contact-metamorphosed Jurassic limestones at Kilchoan on the Ardnamurchan peninsula on the northwest coast of Scotland. He distinguished two metamorphic events at Kilchoan characterized by: (1) a high $\text{CO}_2/\text{H}_2\text{O}$ ratio, and (2) a high $\text{H}_2\text{O}/\text{CO}_2$ ratio. The second event produced kilchoanite, $\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$, rustumite, $\text{Ca}_{10}(\text{SiO}_4)(\text{Si}_2\text{O}_7)_2\text{Cl}_2(\text{OH})_2$ (Howie and Ilyukhin, 1977), and dellaite, $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$. The latter was named in honour of Della M. Roy for synthesizing and characterizing the synthetic analogue. In this context it should be mentioned that rustumite is named after Rustum Roy, Della's husband. Dellaite at Ardnamurchan was found in late-stage replacement veins in which dellaite is assumed to have formed from kilchoanite and spurrite. The stability field of dellaite and calcite bordering spurrite and H_2O was assumed to be $<400^\circ\text{C}$ for CO_2 pressure and $<620^\circ\text{C}$ for H_2O pressure, assuming $P_{\text{tot}} = 345$ bar. Sarp *et al.* (1982a) described a dellaite-bearing skarn in the northeast of Turkey (Rize region, Eastern Pontides). Monticellite, spurrite and rustumite are primary, high-temperature ($\sim 700^\circ\text{C}$) skarn minerals, which were transformed by retrograde hydration to dellaite, hillebrandite, foshagite, defernite and other secondary reaction products. A third detailed report on dellaite was provided by Shimazaki *et al.* (2008) for an occurrence at Akagane mine, Iwate Prefecture, Honshu island (Japan), where high-temperature skarns were formed along the contact between gabbro and limestone. Dellaite formed secondary veinlets or interstitial aggregates associated with calcite and clintonite (brittle mica) within a bicchulite, $\text{Ca}_2(\text{Al}_2\text{SiO}_6)(\text{OH})_2$ (sodalite-group mineral), vesuvianite skarn.

In addition to these scarce natural occurrences of dellaite, the synthetic analogue has important bearing in the field of cement research: $\alpha\text{-Ca}_2[\text{SiO}_3(\text{OH})](\text{OH})$ (no mineral analogue) was transformed by heating in air to $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$ (dellaite), which coexists

with $\gamma\text{-Ca}_2\text{SiO}_4$ (calcio-olivine) up to $560\text{--}620^\circ\text{C}$ (Garbev *et al.*, 2008). A hydrothermal experiment with $\gamma\text{-Ca}_2\text{SiO}_4$ (calcio-olivine) as the starting material indicated (Speakman *et al.*, 1967) that at 600°C and H_2O pressure >170 bar, dellaite is a stable phase.

The thermal stability of three hydrous CSH minerals with the same C/S ratio of 2/1 has been studied under hydrothermal conditions (Hu *et al.*, 2006): $\alpha\text{-Ca}_2[\text{SiO}_3(\text{OH})](\text{OH})$ (no mineral analogue), $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$ (dellaite), and $\text{Ca}_2(\text{SiO}_3)(\text{OH})_2$ (hillebrandite). $\alpha\text{-C}_2\text{SH}$ is stable at low temperature and starts to decompose at 180°C to jaffeite and finally to dellaite at 350°C . Hillebrandite was stable below 350°C but at higher temperature it transformed to dellaite. Dellaite was reversibly transformed to hillebrandite below 300°C .

Due to structural similarities with dellaite, information about killalaite, $\text{Ca}_3\text{Si}_2\text{O}_7\cdot\text{H}_2\text{O}$, is given here. Killalaite was described as a new mineral from Killala Bay, Co. Sligo, Ireland, in limestones thermally metamorphosed by basalt-dolerite dykes (Nawaz, 1974). Additional occurrences are reported from Carneal, Co. Antrim, Northern Ireland (Nawaz, 1977) and in Turkey, from the Güneyce-Ikizdere region, Trabzon Province (Sarp *et al.*, 1982b), the same locality from which dellaite has also been described. A doleritic dyke at Kushiro, Hiroshima Prefecture, Japan, transformed impure argillaceous limestone to a gehlenite-spurrite skarn (Takechi *et al.*, 2000) bearing secondary jennite and killalaite (Kusachi *et al.*, 1984). The crystal structure of killalaite (Taylor, 1977) was refined from strong reflections only yielding a monoclinic cell with $a = 6.807$, $b = 15.459$, $c = 6.811$ Å, $\beta = 97.76^\circ$, space group $P2_1/m$, $Z = 4$ and composition $\text{Ca}_{3.2}(\text{H}_{0.6}\text{Si}_2\text{O}_7)(\text{OH})$. Additional weak reflections indicated a B -centred monoclinic cell with doubled a and c dimensions.

Trabzonite, $\text{Ca}_4\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, has been described (Sarp and Burri, 1986) from the same locality in Turkey (Güneyce-Ikizdere region) from which dellaite and killalaite were also reported. The crystal structure has not been solved but the crystals are monoclinic, space group $P2_1$ or $P2_1/m$, $a = 6.895(2)$, $b = 20.640(3)$, $c = 6.920(2)$ Å, $\beta = 98^\circ$, $Z = 4$ (Sarp and Burri, 1986) and the cell dimensions parallel to (010) are similar to those of killalaite.

In the present study, the structure, chemistry and hydrogen bonding of dellaite found in the high-temperature skarn within the Birkhin gabbro

massif, Eastern Siberia, Russia are discussed. In addition, the structural relations between dellaite, killalaite and trabzonite are highlighted. The sample locality and skarn paragenesis at the Birkhin gabbro massif are described by Lazic *et al.* (2011).

Mineral association

Dellaite from the Birkhin gabbro massif, Eastern Siberia, Russia, formed during the regressive stage of alteration of high-temperature skarns. It is a common mineral in skarned carbonate-silicate

xenoliths within the gabbroid rocks. Dellaite occurs in altered merwinite-larnite-bredigite-gehlenite skarns and also in calcio-olivine (γ - Ca_2SiO_4) skarn with residual larnite (β - Ca_2SiO_4). In kilchoanite ($\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$) skarns, dellaite is rare. Dellaite containing little Cl occurs as merwinite-dellaite aggregates replacing merwinite-larnite symplectites (Fig. 1a). In addition, dellaite is found in selvages around galuskinite ($\text{Ca}_7(\text{SiO}_4)_3(\text{CO}_3)$) veins (Lazic *et al.*, 2011), where dellaite partially replaces pavlovskyite ($\text{Ca}_8(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})$) (Fig. 1b). Dellaite with ~ 0.1 Cl p.f.u. is replaced by

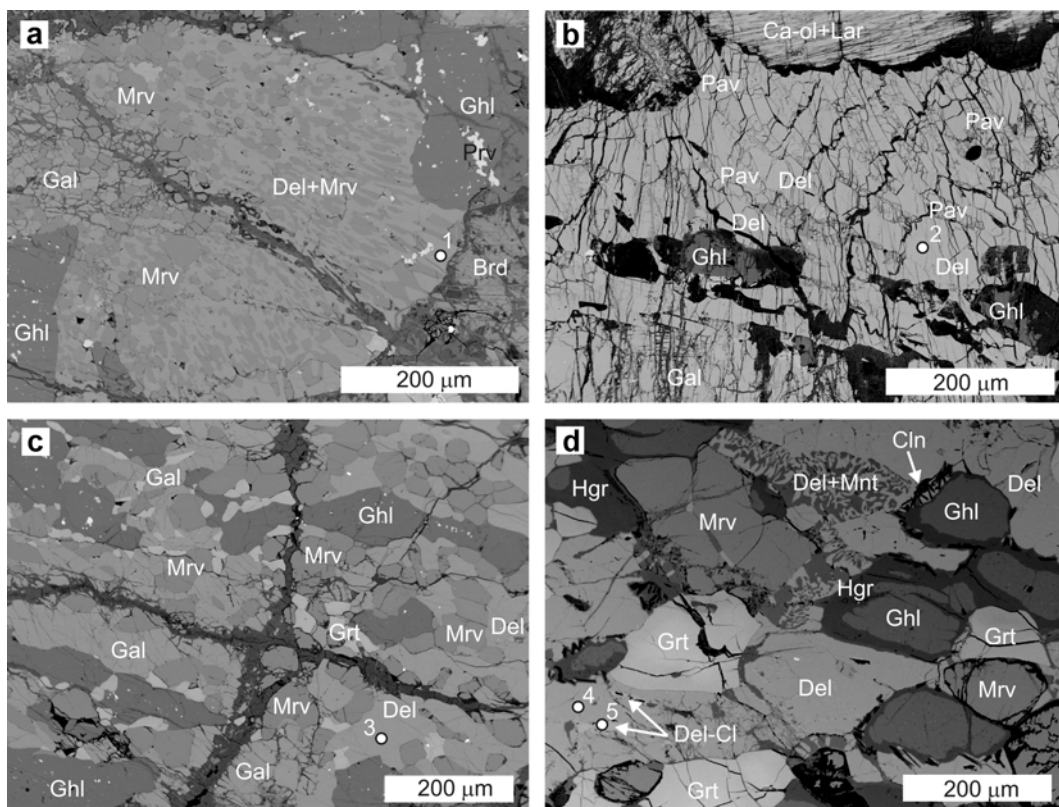


FIG. 1. Backscattered electron (BSE) images of skarns containing dellaite from the Birkhin gabbro massif: (a) dellaite-merwinite aggregate from an altered merwinite-bredigite-gehlenite skarn; dellaite forms after merwinite-larnite symplectite; (b) dellaite together with pavlovskyite forms selvages around galuskinite veins in calcio-olivine (larnite) skarns; (c) dellaite replaced by galuskinite in altered merwinite skarn; (d) section containing high-Cl dellaite, characterized by light BSE contrast. High-Cl dellaite forms domains in low-Cl dellaite. Sample from altered merwinite-gehlenite skarn characterized by the development of monticellite-dellaite symplectites after merwinite. Abbreviations: Del – dellaite, Del-Cl – Cl-bearing dellaite, Gal – galuskinite, Mrv – merwinite, Ghl – gehlenite, Prv – perovskite, Brd – bredigite, Ca-ol – calcio-olivine, Pav – pavlovskyite, Lar – larnite, Grt – andradite-grossular garnet, Hgr – hydrogrossular, Mnt – monticellite, Cln – clintonite. 1–5 – points studied by Raman spectroscopy; corresponding compositions are given in Table 2.

galuskinite and occurs in fine-grained skarns with primary merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$), gehlenite and Ti-Zr-bearing garnet (Fig. 1c). Dellaite with a large Cl content is found in merwinite-gehlenite symplectites after merwinite (Fig. 1d). In this association within dellaite containing ~ 0.2 Cl p.f.u., a dellaite domain with ~ 0.8 Cl p.f.u. was analysed. This high-Cl domain was striking due to

the lighter colour in images produced by back-scattered electrons (BSE).

Experimental methods

Chemical analyses were carried out using an electron microprobe CAMECA SX100, (WDS mode, 15 kV, 10–20 nA, $\sim 1 \mu\text{m}$ beam diameter). Natural and synthetic standards were employed.

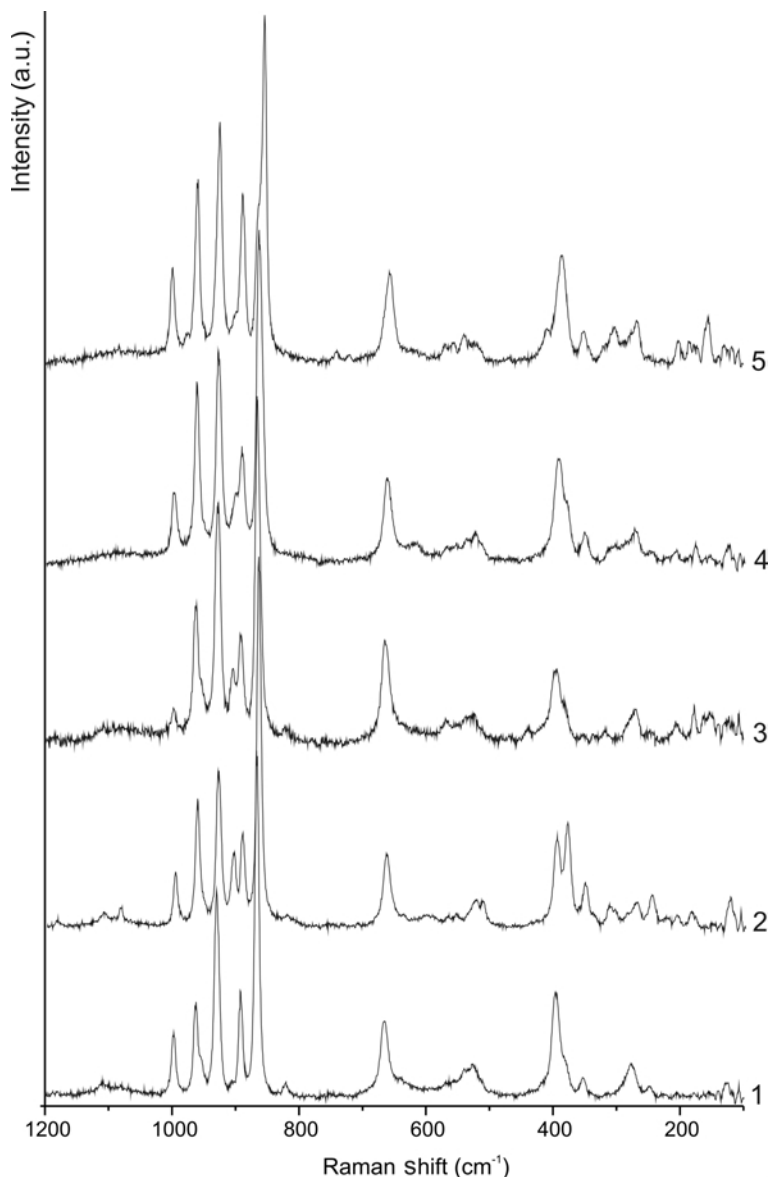


FIG. 2. Raman spectra of dellaite in the 1200–100 cm^{-1} range. The numbering scheme corresponds to chemical compositions in Table 2 and marked spots in Fig. 1.

The following lines and standards were used for the dellaite analyses: Ca- $K\alpha$, Si- $K\alpha$ – wollastonite; Cl- $K\alpha$ – tugtupite; F- $K\alpha$ – fluorphlogopite; Fe- $K\alpha$ – hematite; Mn- $K\alpha$ – rhodochrosite; Ti- $K\alpha$ – rutile; Mg- $K\alpha$ – diopside; Na- $K\alpha$ – albite.

Raman spectra of crystals of Cl-free and Cl-bearing dellaite (Figs 2–4) were recorded using a Dilor XY spectrometer equipped with a 1800 line mm^{-1} grating monochromator, a charge-coupled device (CCD), Peltier-cooled detector (1024×256) 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 end of the

$100\times$ objective lens varied from 30 to 50 mW. Raman spectra were recorded in backscatter geometry in the range $100\text{--}4000\text{ cm}^{-1}$ with resolution of 2 cm^{-1} . Collection times of 20 s and accumulations of five scans were chosen. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}). Fitting of the Raman spectra was done by means of *GRAMS* software for spectroscopy by Thermo Scientific, using mixed Lorentzian + Gaussian functions.

Single-crystal X-ray studies were carried out on two grains of Birkhin dellaite (Cl-free and Cl-bearing with $\sim 1.5\text{ wt.}\%$ Cl) using a Bruker

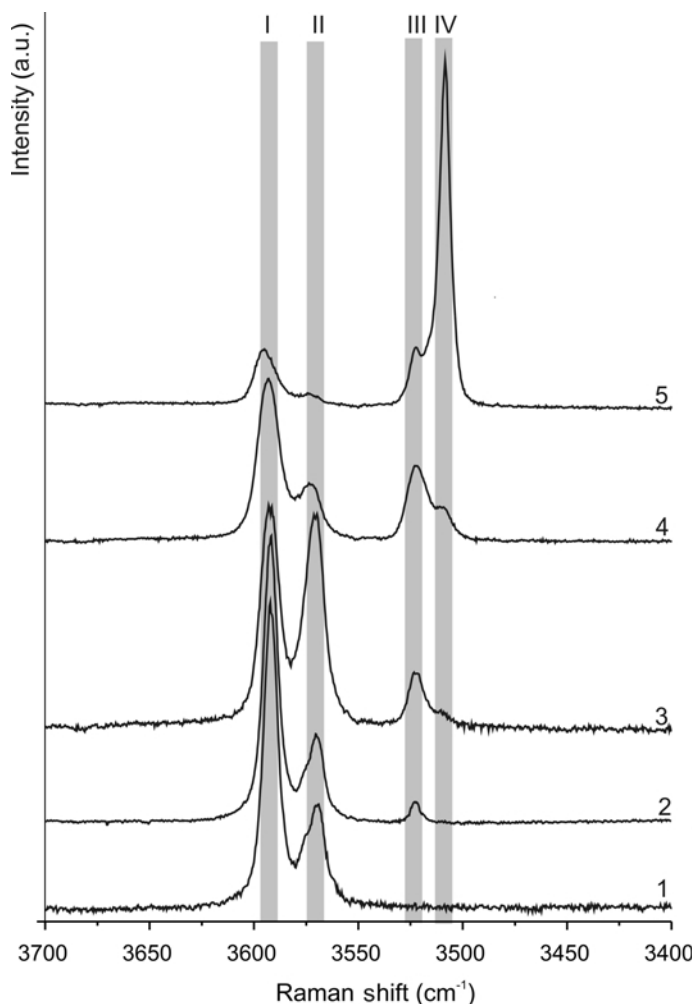


FIG. 3. Raman spectra of dellaite in the OH range between 3700 and 3400 cm^{-1} . The numbering scheme corresponds to the chemical compositions in Table 2 and marked spots in Fig. 1.

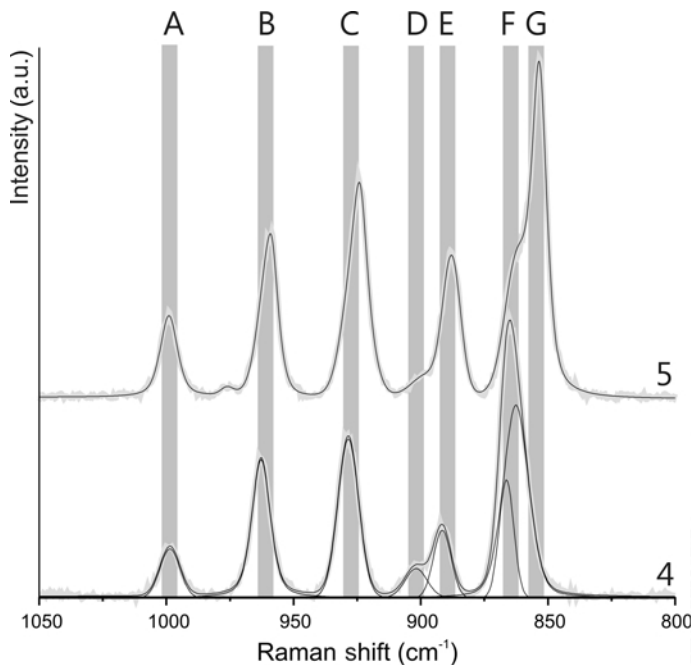


FIG. 4. Raman spectra of dellaite in the 1050–800 cm^{-1} range. The numbering scheme corresponds to the chemical compositions in Table 2 and marked spots in Fig. 1.

APEX II SMART diffractometer (Mo- $K\alpha$, $\lambda = 0.71073$ Å). Experimental details are summarized in Table 1. Diffraction data were collected with 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 structure was solved by direct methods with subsequent analyses of difference-Fourier maps. The dellaite structures were refined using the program *SHELX97* (Sheldrick, 2008) to $R_1 = 3.7\%$ and $R_1 = 3.8\%$, respectively. The refinements including anisotropic atom-displacement parameters summing up to 207 variables (Cl-free: $6169 F_o > 4\sigma(F_o)$; Cl-bearing: $2562 F_o > 4\sigma(F_o)$), were carried out with neutral-atom scattering factors. Hydrogen sites were refined isotropically and restrained to $0.96(2)$ Å from the oxygen donors. In the case of Cl-bearing dellaite, split positions of O6/Cl6 were refined isotropically.

Results

The results of the electron-microprobe analyses are summarized in Table 2. Compositions with four different levels of Cl content are distin-

guished. The points at which the analyses were made are marked with numbers in Fig. 1.

The results of the crystal-structure refinement including atomic coordinates and isotropic equivalents (U_{eq}) of anisotropic atom-displacement parameters are listed in Table 3, anisotropic-displacement parameters in Table 4, and selected interatomic distances in Table 5. Bond-valence parameters according to Brown and Altermatt (1985) are summarized in Table 6.

Raman spectra for dellaite with variable Cl content are displayed in Figs 2–4 and summarized in Table 7. The points at which spectroscopic data were collected are indicated with numbers in Fig. 1. The general appearance in the 1000–100 cm^{-1} region of the dellaite spectra with different Cl contents is similar (Fig. 2). Differences are noted in the region of OH-vibrations (Fig. 3) where there are four bands in the spectra of dellaite with ~ 0.2 Cl p.f.u.: I – 3593 cm^{-1} , II – 3571 cm^{-1} , III – 3523 cm^{-1} and IV – 3512 cm^{-1} . Dellaite with ≤ 0.1 Cl p.f.u. is characterized by only two intensive bands I and II. Band IV at $\sim 3509 \text{ cm}^{-1}$ (Table 7, Fig. 3) is intensive for dellaite with ~ 0.8 Cl p.f.u. only.

CRYSTAL CHEMISTRY OF DELLAITE

TABLE 1. Parameters for XRD data collection and crystal-structure refinement.

	Cl-free dellaite	Cl-bearing dellaite
Crystal data		
Chemical formula	$\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$	$\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_{1.75}\text{Cl}_{0.25}$
Crystal shape	prism	prism
Crystal size (mm)	$0.08 \times 0.13 \times 0.14$	$0.03 \times 0.04 \times 0.07$
Unit-cell parameters ($\text{\AA}$, °)	$a = 6.8155(1)$ $b = 6.9363(1)$ $c = 12.8904(3)$ $\alpha = 90.652(1)$ $\beta = 97.659(1)$ $\gamma = 98.195(1)$	$a = 6.8126(7)$ $b = 6.9416(7)$ $c = 12.9412(13)$ $\alpha = 90.582(2)$ $\beta = 97.552(1)$ $\gamma = 98.251(2)$
Volume ($\text{\AA}^3$)	597.495(19)	600.14(11)
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	2
Intensity measurement		
Diffractometer	APEX II SMART	APEX II SMART
X-ray radiation	Mo- $K\alpha$ $\lambda = 0.71073$ $\text{\AA}$	Mo- $K\alpha$ $\lambda = 0.71073$ $\text{\AA}$
X-ray power	50 kV, 30 mA	50 kV, 30 mA
Monochromator	Graphite	Graphite
Temperature	293 K	293 K
Time per frame (s)	45	60
Max. θ range for data collection	43.98	31.5
Index ranges	$-13 \leq h \leq 12$ $-13 \leq k \leq 12$ $-24 \leq l \leq 25$	$-9 \leq h \leq 9$ $-9 \leq k \leq 10$ $-16 \leq l \leq 16$
No. of measured reflections	16667	4826
No. of unique reflections (R_{int})	8302(0.028)	3290(0.026)
No. of observed reflections ($I > 2\sigma(I)$)	6169	2562
Refinement of the structure		
No. of parameters used in refinement	207 + 2 restraints	207 + 2 restraints
R_σ	0.0481	0.0545
R_1 , $I > 2\sigma(I)$	0.0370	0.0383
R_1 , all data	0.0581	0.0545
wR_2 (on F^2)	0.0866	0.0928
GoF	0.986	1.016
$\Delta\rho_{\text{min}}$ ($\text{e}/\text{\AA}^3$)	-1.14 close to Ca4	-0.65 close to Ca6
$\Delta\rho_{\text{max}}$ ($\text{e}/\text{\AA}^3$)	1.08 close to Ca1	0.85 close to Ca3

In spectra of Cl-bearing dellaite obtained for points 4 and 5 (Fig. 1d) having the same orientation, a slight shift towards lower frequencies in the 1000–800 cm^{-1} region was observed (Fig. 4). In particular the band near 860 cm^{-1} , which occurs in the spectrum of dellaite with 0.2 Cl p.f.u. at 863 cm^{-1} , is shifted to ~853 cm^{-1} in the spectrum of dellaite with 0.8 Cl p.f.u. (Fig. 4). This may indicate weakening of Si–O bonds in orthosilicate tetrahedra of Cl-rich dellaite.

Discussion

Dellaite, killalaite and trabzonite have in common that two unit-cell dimensions are ~6.8–6.9 $\text{\AA}$ enclosing an angle of ~98°. The third axis is different. The structural drawings of dellaite and killalaite (Fig. 5) indicate that the length of the third axis (c in dellaite and b in killalaite) is mainly determined by condensation of SiO_4 entities and space requirements of the interspace filled with CaO_x polyhedra. In dellaite, Si_2O_7

TABLE 2. Chemical composition of deliaite from skarns of the Birkin massif.

	1			2			3			4			5		
	Mean 14	s.d.	Range	Mean 7	s.d.	Range	Mean 15	s.d.	Range	Mean 23	s.d.	Range	Mean 11	s.d.	Range
TiO ₂ wt. %	0.03	0.04	0–0.12	0.02	0.03	0–0.06	0.04	0.04	0–0.13	0.02	0.02	0–0.09	tr		
SiO ₂	33.52	0.26	32.95–33.83	33.58	0.58	33.10–34.24	33.35	0.24	32.82–33.72	33.26	0.17	32.90–33.63	32.67	0.18	32.39–32.97
CaO	61.93	0.29	61.53–62.46	62.04	0.29	61.79–62.57	61.4	0.33	60.86–62.06	61.64	0.45	60.53–62.53	60.82	0.53	59.69–61.49
FeO	0.06	0.04	0–0.13	0.19	0.15	0.06–0.46	0.05	0.04	0–0.16	0.05	0.05	0–0.16	0.05	0.05	0–0.14
MnO	0.09	0.06	0–0.20	0.04	0.04	0–0.11	0.06	0.05	0–0.18	0.04	0.03	0–0.08	0.02	0.03	0–0.09
MgO	0.05	0.02	0.02–0.09	0.08	0.12	0–0.32	0.04	0.01	0.02–0.06	0.06	0.02	0.03–0.10	tr		
Na ₂ O	0.03	0.02	0–0.06	0.02	0.02	0–0.04	tr			tr			tr		
F	0.28	0.16	0–0.54	0.09	0.07	0–0.15	0.27	0.15	0–0.51	0.18	0.14	0–0.54	tr		
Cl	0.05	0.03	0.02–0.11	0.08	0.08	0.03–0.25	0.67	0.13	0.50–0.85	1.40	0.14	1.11–1.63	5.22	0.26	4.68–5.44
H ₂ O	3.19	0.08	3.08–3.33	3.28	0.070	3.19–3.38	3.01	0.08	2.90–3.15	2.87	0.07	2.71–2.91	1.94	0.09	1.80–2.09
–O=F+Cl	0.13			0.06			0.27			0.39			1.18		
Total	99.10			99.36			98.63			99.13			99.54		
Ca*	5.963			5.958			5.961			5.975			5.991		
Mg	0.007			0.011			0.005			0.008					
Na	0.005			0.003											
Fe ²⁺	0.005			0.014			0.004			0.004			0.004		
Mn ²⁺	0.007			0.003			0.005			0.003			0.002		
X	5.986			5.989			5.975			5.990			5.996		
Si	3.012			3.010			3.022			3.009			3.004		
Ti ⁴⁺	0.002			0.001			0.003			0.001					
Z	3.014			3.011			3.025			3.010			3.004		
OH	1.912			1.961			1.819			1.734			1.187		
Cl	0.008			0.012			0.103			0.215			0.813		
F	0.080			0.026			0.077			0.051					

Notes: 1 – deliaite, replacing lamite in merwinite-larnite symplectite, from altered merwinite skarn (Fig. 1a), 2 – deliaite forming together with pavlovskite selvages around galuskinite veins in calcio-olivine skarn (Fig. 1b), 3 – deliaite from altered merwinite skarn (Fig. 1c), 4, 5 – high-Cl deliaite from altered merwinite skarn with development of monticellite-deliaite symplectites after merwinite (Fig. 1d). tr – trace content. * – calculated on the basis of 9 cations and 13 O.

TABLE 3a. Atom coordinates, U_{eq} ($\text{\AA}^2$) values, and occupancies for Cl-free dellaite.

Site	Atom	x	y	z	U_{eq}
Ca1	Ca	0.08078(4)	0.19501(4)	0.10167(2)	0.01175(5)
Ca2	Ca	0.19107(4)	0.20688(4)	0.48981(2)	0.01202(5)
Ca3	Ca	0.89363(4)	0.46847(5)	0.29036(2)	0.01160(5)
Ca4	Ca	0.55859(5)	0.03393(4)	0.32091(2)	0.01210(5)
Ca5	Ca	0.31655(4)	0.19088(4)	0.87633(2)	0.01045(5)
Ca6	Ca	0.59254(4)	0.47476(4)	0.70369(2)	0.01015(5)
Si1	Si	0.61470(6)	0.28863(6)	0.09768(3)	0.00786(7)
Si2	Si	0.81039(6)	0.28402(6)	0.88458(3)	0.00744(6)
Si3	Si	0.71566(6)	0.29857(6)	0.50878(3)	0.00753(6)
O1	O	0.61764(16)	0.48774(16)	0.16476(8)	0.01056(17)
O2	O	0.39215(16)	0.18998(17)	0.05336(9)	0.01277(19)
O3	O	0.61669(16)	0.18463(16)	0.80559(8)	0.01069(17)
O4	O	0.74537(16)	0.15293(16)	0.17621(8)	0.01106(17)
O5	O	0.98600(16)	0.14945(16)	0.91036(9)	0.01181(18)
OH6	O	0.23019(19)	0.16600(18)	0.30036(9)	0.0162(2)
O7	O	0.84627(17)	0.12816(17)	0.48669(10)	0.0146(2)
OH8	O	0.19208(17)	0.20696(17)	0.68570(9)	0.01360(19)
O9	O	0.52307(16)	0.21540(16)	0.56576(8)	0.01119(17)
O10	O	0.74708(18)	0.33538(18)	0.99990(9)	0.0145(2)
O11	O	0.64136(17)	0.36964(17)	0.39136(8)	0.01223(18)
O12	O	0.83545(16)	0.48247(16)	0.58191(8)	0.01078(17)
O13	O	0.11403(16)	0.51184(16)	0.16863(8)	0.01025(17)
H6	H	0.195(5)	0.045(3)	0.282(3)	0.051(10)
H8	H	0.083(4)	0.113(4)	0.683(2)	0.045(9)

TABLE 3b. Atomic coordinates, U_{eq} values, and occupancies for Cl-bearing dellaite.

Site	Atom	x	y	z	U_{eq}	Occupancy
Ca1	Ca	0.07780(11)	0.19575(10)	0.09934(6)	0.01086(16)	1
Ca2	Ca	0.18816(11)	0.21087(10)	0.49388(6)	0.01389(17)	1
Ca3	Ca	0.89386(10)	0.46554(11)	0.28978(6)	0.01003(16)	1
Ca4	Ca	0.56112(11)	0.03221(10)	0.32089(6)	0.01060(16)	1
Ca5	Ca	0.31574(10)	0.19225(10)	0.87654(6)	0.00886(15)	1
Ca6	Ca	0.59179(10)	0.47259(10)	0.70343(5)	0.00864(15)	1
Si1	Si	0.61338(14)	0.28801(13)	0.09718(8)	0.00662(19)	1
Si2	Si	0.80890(14)	0.28349(13)	0.88451(7)	0.00601(19)	1
Si3	Si	0.71427(13)	0.29736(13)	0.50829(7)	0.00578(19)	1
O1	O	0.6176(3)	0.4862(3)	0.16456(18)	0.0084(5)	1
O2	O	0.3910(4)	0.1896(4)	0.05319(19)	0.0105(5)	1
O3	O	0.6154(3)	0.1853(3)	0.80662(18)	0.0087(5)	1
O4	O	0.7434(4)	0.1515(3)	0.17546(19)	0.0091(5)	1
O5	O	0.9847(4)	0.1496(3)	0.91059(19)	0.0098(5)	1
Cl6	Cl	0.1899(8)	0.1406(7)	0.3002(4)	0.0132(8)	0.252(8)
OH6	O	0.2344(8)	0.1702(7)	0.3005(4)	0.0132(8)	0.748(8)
O7	O	0.8426(4)	0.1252(3)	0.4851(2)	0.0133(5)	1
OH8	O	0.1917(4)	0.2084(4)	0.6868(2)	0.0160(11)	0.966(8)
Cl8	Cl	0.1917(4)	0.2084(4)	0.6868(2)	0.0160(11)	0.034(8)
O9	O	0.5212(4)	0.2156(3)	0.56584(19)	0.0098(5)	1
O10	O	0.7460(4)	0.3359(4)	0.99966(19)	0.0127(5)	1
O11	O	0.6411(4)	0.3710(4)	0.39196(19)	0.0108(5)	1
O12	O	0.8375(4)	0.4795(3)	0.58140(19)	0.0101(5)	1
O13	O	0.1151(4)	0.5122(3)	0.16844(18)	0.0084(5)	1
H6	H	0.238(11)	0.040(4)	0.280(5)	0.05(2)	0.75*
H8	H	0.080(7)	0.111(8)	0.682(5)	0.09(3)	0.97*

* Occupancies fixed to those of the oxygens of the corresponding OH groups.

TABLE 4a. Anisotropic displacement parameters, U_{ij} ($\text{\AA}^2$), for Cl-free dellaite.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.01179(11)	0.00962(12)	0.01384(12)	−0.00299(8)	0.00468(9)	−0.00088(9)
Ca2	0.01053(11)	0.01064(12)	0.01462(12)	0.00275(9)	0.00181(9)	0.00028(9)
Ca3	0.00861(11)	0.01672(13)	0.00922(10)	−0.00048(9)	0.00239(8)	−0.00005(9)
Ca4	0.01715(13)	0.00823(11)	0.01085(11)	−0.00095(8)	0.00417(9)	−0.00044(9)
Ca5	0.01159(11)	0.00971(11)	0.01031(10)	−0.00009(8)	0.00466(8)	−0.00048(9)
Ca6	0.01043(11)	0.01190(12)	0.00880(10)	0.00044(8)	0.00298(8)	0.00234(9)
Si1	0.00845(15)	0.00782(16)	0.00741(14)	−0.00060(11)	0.00247(11)	0.00031(12)
Si2	0.00768(15)	0.00700(16)	0.00773(14)	−0.00016(11)	0.00275(11)	−0.00023(12)
Si3	0.00792(15)	0.00707(16)	0.00770(14)	−0.00057(11)	0.00258(11)	0.00009(12)
O1	0.0120(4)	0.0096(4)	0.0103(4)	−0.0015(3)	0.0031(3)	0.0011(3)
O2	0.0103(4)	0.0152(5)	0.0120(4)	−0.0017(3)	0.0018(3)	−0.0011(4)
O3	0.0111(4)	0.0094(4)	0.0107(4)	−0.0004(3)	0.0013(3)	−0.0011(3)
O4	0.0120(4)	0.0099(4)	0.0113(4)	0.0012(3)	0.0015(3)	0.0017(3)
O5	0.0100(4)	0.0107(4)	0.0153(4)	0.0005(3)	0.0025(3)	0.0024(3)
O6	0.0226(6)	0.0139(5)	0.0127(5)	−0.0006(4)	0.0037(4)	0.0035(4)
O7	0.0116(5)	0.0095(5)	0.0238(5)	−0.0010(4)	0.0062(4)	0.0020(4)
O8	0.0144(5)	0.0129(5)	0.0131(4)	−0.0007(4)	0.0030(4)	−0.0004(4)
O9	0.0104(4)	0.0113(4)	0.0118(4)	0.0006(3)	0.0044(3)	−0.0013(3)
O10	0.0172(5)	0.0161(5)	0.0107(4)	−0.0005(3)	0.0075(4)	−0.0008(4)
O11	0.0138(4)	0.0143(5)	0.0089(4)	0.0016(3)	0.0029(3)	0.0017(4)
O12	0.0116(4)	0.0089(4)	0.0112(4)	−0.0015(3)	0.0021(3)	−0.0015(3)
O13	0.0113(4)	0.0091(4)	0.0101(4)	0.0007(3)	0.0037(3)	−0.0016(3)

TABLE 4b. Anisotropic displacement parameters, U_{ij} , for Cl-bearing dellaite.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.0097(3)	0.0107(3)	0.0124(4)	−0.0020(3)	0.0037(3)	0.0006(3)
Ca2	0.0081(3)	0.0124(3)	0.0200(4)	0.0070(3)	−0.0018(3)	0.0005(3)
Ca3	0.0061(3)	0.0169(4)	0.0068(4)	0.0014(3)	0.0007(3)	0.0006(3)
Ca4	0.0140(4)	0.0101(3)	0.0070(4)	0.0009(3)	0.0016(3)	−0.0009(3)
Ca5	0.0090(3)	0.0102(3)	0.0075(4)	0.0017(3)	0.0029(3)	−0.0001(2)
Ca6	0.0078(3)	0.0128(3)	0.0059(4)	0.0020(3)	0.0016(3)	0.0029(2)
Si1	0.0053(4)	0.0088(4)	0.0056(5)	0.0005(3)	0.0010(3)	0.0002(3)
Si2	0.0049(4)	0.0080(4)	0.0051(5)	0.0008(3)	0.0011(3)	0.0002(3)
Si3	0.0048(4)	0.0072(4)	0.0053(5)	0.0009(3)	0.0004(3)	0.0009(3)
O1	0.0089(11)	0.0111(11)	0.0059(13)	0.0007(9)	0.0011(9)	0.0031(9)
O2	0.0068(11)	0.0142(12)	0.0088(13)	0.0001(10)	0.0001(9)	−0.0035(9)
O3	0.0071(11)	0.0120(12)	0.0063(12)	0.0011(9)	−0.0003(9)	−0.0004(9)
O4	0.0078(11)	0.0096(11)	0.0098(13)	0.0016(9)	−0.0003(9)	0.0025(9)
O5	0.0061(11)	0.0100(11)	0.0131(13)	0.0015(10)	−0.0010(9)	0.0023(9)
O7	0.0110(12)	0.0090(11)	0.0208(15)	0.0006(10)	0.0032(11)	0.0031(9)
O8	0.0181(16)	0.0179(16)	0.0119(17)	0.0015(10)	0.0020(10)	0.0016(10)
Cl8	0.0181(16)	0.0179(16)	0.0119(17)	0.0015(10)	0.0020(10)	0.0016(10)
O9	0.0081(11)	0.0117(12)	0.0091(13)	0.0013(10)	0.0017(10)	−0.0010(9)
O10	0.0139(13)	0.0185(13)	0.0063(13)	0.0009(10)	0.0057(10)	0.0002(10)
O11	0.0102(12)	0.0160(13)	0.0064(13)	0.0023(10)	0.0010(9)	0.0024(10)
O12	0.0117(12)	0.0109(12)	0.0065(13)	0.0003(9)	0.0009(9)	−0.0024(9)
O13	0.0093(12)	0.0118(12)	0.0034(12)	0.0009(9)	0.0001(9)	0.0001(9)

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TABLE 5. Bond distances (Å) and bond valences (v.u.) for dellaite with and without ~0.25 Cl p.f.u.

Site 1	Site 2	Bond distance for Cl-free dellaite (Å)	Bond distance for Cl-bearing dellaite (Å)	Site 1	Site 2	Bond distance for Cl-free dellaite (Å)	Bond distance for Cl-bearing dellaite (Å)
Ca1	O2	2.2947(11)	2.296(3)	Ca5	O2	2.2717(11)	2.277(2)
Ca1	O13	2.3213(11)	2.330(2)	Ca5	O1	2.2926(11)	2.295(3)
Ca1	O5	2.3670(12)	2.373(3)	Ca5	O5	2.3307(11)	2.332(3)
Ca1	O5	2.4696(11)	2.447(3)	Ca5	O3	2.3537(11)	2.345(2)
Ca1	O4	2.5760(11)	2.579(3)	Ca5	O4	2.4340(11)	2.435(2)
Ca1	O6	2.6480(12)	2.698(5)	Ca5	O8	2.4996(12)	2.498(3)
Ca1	O10	2.7762(12)	2.759(3)			<2.364>	<2.364>
		<2.493>	<2.497>				
Ca1	Cl6		2.659(5)	Ca6	O11	2.2820(11)	2.286(2)
				Ca6	O1	2.3956(11)	2.405(2)
Ca2	O7	2.3293(12)	2.331(3)	Ca6	O13	2.4048(11)	2.411(2)
Ca2	O7	2.3303(12)	2.334(3)	Ca6	O12	2.4243(11)	2.444(3)
Ca2	O9	2.3350(11)	2.332(2)	Ca6	O3	2.4288(11)	2.424(3)
Ca2	O12	2.3753(11)	2.388(3)	Ca6	O9	2.4661(11)	2.459(2)
Ca2	O6	2.5089(12)	2.581(5)	Ca6	O6	2.6140(13)	2.594(5)
Ca2	O8	2.5241(12)	2.494(3)			<2.431>	<2.432>
		<2.401>	<2.410>	Ca6	Cl6		2.881(6)
			2.550(5)				
Ca2	Cl6		2.293(2)	Si1	O2	1.5998(12)	1.598(3)
Ca3	O12	2.2878(11)	2.310(3)	Si1	O1	1.6174(11)	1.616(2)
Ca3	O13	2.3064(11)	2.332(3)	Si1	O4	1.6506(11)	1.654(3)
Ca3	O11	2.3242(12)	2.339(2)	Si1	O10	1.6544(12)	1.656(3)
Ca3	O1	2.3329(11)	2.443(3)			<1.631>	<1.631>
Ca3	O8	2.4314(12)	2.624(2)				
Ca3	O4	2.6223(11)	<2.390>	Si2	O3	1.6190(11)	1.612(2)
		<2.384>	<2.390>	Si2	O5	1.6229(11)	1.623(2)
				Si2	O13	1.6276(11)	1.629(3)
Ca4	O3	2.3005(11)	2.314(2)	Si2	O10	1.6509(12)	1.655(3)
Ca4	O9	2.3312(11)	2.476(3)			<1.630>	<1.630>
Ca4	O11	2.4507(12)	2.474(3)				
Ca4	O4	2.4797(11)	2.531(5)	Si3	O7	1.6219(12)	1.626(2)
Ca4	O6	2.5201(13)	2.546(3)	Si3	O9	1.6266(11)	1.631(3)
Ca4	O8	2.5557(12)	2.721(5)	Si3	O12	1.6288(11)	1.631(2)
Ca4	O7	2.7064(12)	<2.484>	Si3	O11	1.6353(11)	1.633(3)
		<2.478>	<2.484>			<1.628>	<1.630>
Ca4	Cl6		2.472(5)				

units extending parallel to *c* alternate with SiO₄ units. In killalaite only Si₂O₇ units are aligned parallel to *b* (Fig. 5). This allows a very simplified estimation of the length of the longest axis. If we assume along this direction a space requirement of 2.2 Å for a single tetrahedron and 3.3 Å for the Ca polyhedral interspace, cell dimensions of 13.2 (dellaite) and 15.4 Å (killalaite) are calculated, which are close to the values observed. If we assume trimers of Si₃O₁₀ units extending parallel to *c* for trabzonite and a corresponding polyhedral arrangement as in dellaite and killalaite, the simplified model predicts 19.8 Å for the *b* axis,

which is not far from the observed value of 20.64 Å (Sarp and Burri, 1986). If such a close relationship exists between dellaite, killalaite, and trabzonite, the chemical formula of trabzonite having 2 H₂O must be questioned. Instead, the existence of OH-groups seems more likely.

Structure refinements on dellaite (Cl-free, this study) confirm the hydrogen positions located for the synthetic analogue (Safronov *et al.*, 1981). O6–H6 and O8–H8 represent the two OH groups. O6 and O8 are both four-coordinated by Ca. O6 is strongly underbonded, accepting only 0.78 v.u. (Table 6) from the nearest Ca neighbours. This

TABLE 6a. Bond valences (v.u.) for Cl-free dellaite according to Brown and Altermatt (1985).

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	Sum
Ca1		0.41		0.19	0.34 0.26	0.16				0.11			0.38	1.85
Ca2						0.23	0.38 0.38	0.22	0.37			0.33		1.91
Ca3	0.37			0.17				0.29			0.38	0.42	0.40	2.03
Ca4			0.41	0.25		0.22	0.14	0.20	0.37		0.27			1.86
Ca5	0.42	0.44	0.35	0.28	0.37			0.24						2.10
Ca6	0.31		0.29			0.17			0.26		0.43	0.29	0.31	2.06
Si1	1.06	1.12		0.97						0.96				4.11
Si2			1.06		1.05					0.97			1.03	4.11
Si3							1.05		1.04		1.01	1.03		4.13
Sum	2.16	1.97	2.11	1.86	2.02	0.78	1.95	0.95	2.04	2.04	2.09	2.07	2.12	

TABLE 6b. Bond valences (v.u.) for Cl-bearing dellaite according to Brown and Altermatt (1985).

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	Sum
Ca1		0.41		0.19	0.33 0.25	0.14				0.12			0.38	1.82
Ca2						0.19	0.37 0.37	0.24	0.37			0.32		1.86
Ca3	0.37			0.17				0.28			0.37	0.41	0.40	2.00
Ca4			0.39	0.25		0.22	0.13	0.21	0.38		0.25			1.83
Ca5	0.41	0.43	0.36	0.28	0.37			0.24						2.09
Ca6	0.31		0.29			0.18			0.27		0.42	0.28	0.30	2.05
Si1	1.07	1.12		0.96						0.96				4.11
Si2			1.08		1.05					0.96			1.03	4.12
Si3							1.04		1.03		1.02	1.03		4.12
Sum	2.16	1.96	2.12	1.86	2.00	0.73	1.91	0.97	2.05	2.04	2.06	2.04	2.11	

low bond-strength sum at O6 suggests strong donor–hydrogen interactions. In fact, there is only a very weak hydrogen bond with O3 as acceptor. The distance O6–O3 is 3.15 Å and H6···O3 is 2.53 Å. The bond strength sum (without H) at O8 is 0.95 v.u. (Table 6) and the shortest potential hydrogen bond has O6 as acceptor with H8···O6 of 2.7 Å and an O6–O8 separation of 3.61 Å. In accordance with these distances, Raman spectra of Cl-free dellaite display (Fig. 3, No. 1) two O–H stretching frequencies at ~3593 and 3570 cm⁻¹, respectively, underlining the nature of these weak hydrogen bonds (Libowitzky, 1999).

In the structurally related killalaite, hydrogen positions have not been determined but O8 and O9 were identified as donors of hydrogen bonds (Taylor, 1977). The potential donor acceptor distances of O8···O5 of 3.05 Å and O9···O2 of

3.25 Å in killalaite (Taylor, 1977) are also rather long, indicating only very weak hydrogen bonds. If the Ca5 site (occupancy: 0.43(2) according to Taylor (1977)) is locally empty, there is also an additional silanol-type of OH group with O2 as the donor.

Structure refinements on Cl-bearing dellaite (~1.5 wt.% Cl) indicated a strong selectivity for Cl on a position replacing O6 with Cl occupancy of 0.252(8). However, substantial O6/Cl6 disorder did not allow a complete separation of O6 and Cl6 leading to a O6–Cl6 distance of 0.34 Å. Most importantly, Cl6 shifts parallel to *a* towards H8 and acts as an acceptor of a H8···Cl6 (2.38 Å) hydrogen bond (Fig. 6). Thus the hydrogen bond is considerably stronger than in the Cl-free mineral. The Cl occupancy at the second OH site (O8) converged only to 0.034(8) Cl, which is

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TABLE 7. Observed Raman bands (cm^{-1}) for dellaite with variable Cl content. Sample numbers correspond to electron-microprobe analyses in Table 2 and to the analysis points marked in Fig. 1. Roman numerals refer to Fig. 3, and the uppercase letter symbols to Fig. 4.

Symbol	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
I	3592	3592	3592	3593	3595
II	3573	3573	3573	3574	3577
III		3523	3523	3522	3523
IV			3512	3510	3509
A	998	998	998	999	999
					976
B	963	963	963	963	959
	956		957		
C	930	930	928	928	925
		926			
D		907	904	902	897
E	892	893	891	892	888
F		867		866	862
G	867	860	865	863	853
	821	824	821		
					741
					721
	666	665	664	663	657
	652		642		
		604		622	619
		569	568	559	560
	551	555		539	540
	528	527	530	524	523
		513			
			439		
	411				409
	397	397	395	393	
		385			386
	382	381		379	
	354	353		352	351
		311	318	309	
					303
		284		289	
	278	272	273	272	270
	248	248		247	
		224		210	
		208	206		203
		184	178	178	181
			156	155	156
	127	124	122	126	124
			107		

at the limit of significance. Raman spectra of Cl-bearing dellaite (analysis 4 in Table 2) display intensity reduction of the O–H stretching frequencies (type I and II in Fig. 3). In addition, a new vibration occurs at 3523 cm^{-1} with a

shoulder at 3512 cm^{-1} . Thus the hydrogen bonding system becomes enhanced with increasing Cl content. There is also a significant increase in the unit-cell volume with incorporation of Cl. Cl-free dellaite has $597.5(1)\text{ \AA}^3$

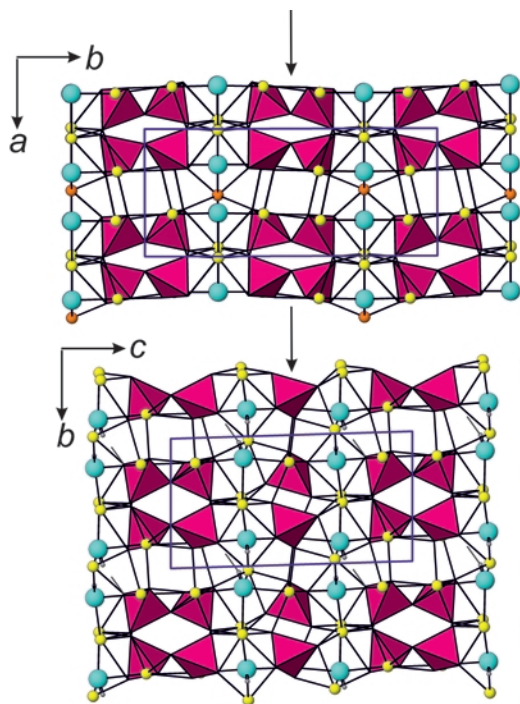


FIG. 5. (*upper*) Crystal structure of killalaite (Taylor, 1977) projected along *c*. SiO_4 tetrahedra are red and form Si_2O_7 dimers extending parallel to *b*. Fully occupied Ca sites are yellow; partly occupied Ca5 is orange. Blue spheres represent the oxygen sites of OH groups, H positions are shown by small grey spheres, solid black lines are Ca–O bonds. (*lower*) Crystal structure of dellaite (this study) projected along *a*. Si_2O_7 dimers alternate along *c* with SiO_4 units. Colours and symbols as above. Vertical arrows indicate the most obvious structural differences between killalaite and dellaite.

whereas $600.1(1) \text{ \AA}^3$ has been refined for dellaite with 1.5 wt.% Cl.

The intensity distribution in the OH-region of the Raman spectrum of dellaite with 0.8 Cl p.f.u. (Fig. 3, No. 5) is rather puzzling. With increase of Cl content, the sideband type IV in spectrum 4 (Fig. 3) increases and becomes the dominant OH Raman band in spectrum 5 (Fig. 3). Note spectra numbers 4 and 5 have been measured for the same crystal orientation. Unfortunately, it was not possible to extract a domain-producing spectrum no. 5 (Fig. 3) for crystal-structure analysis. Thus the interpretation of the Raman spectrum is somewhat speculative. We predict two models

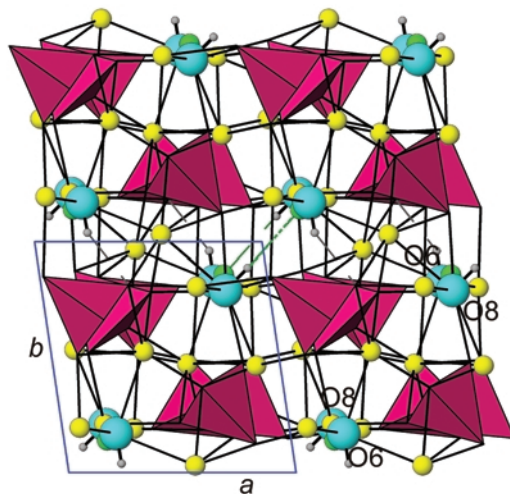


FIG. 6. Crystal structure of Cl-bearing dellaite (this study) projected parallel to *c*: red tetrahedra represent alternating Si_2O_7 dimers and SiO_4 groups (Fig. 5). Ca sites are yellow; blue spheres represent the oxygen sites of OH groups; H positions are shown by small grey spheres; solid black lines are Ca–O bonds. Cl replacing O6 is shown as a small green sphere. Dashed green lines represent O8–H8...Cl6 hydrogen bonds.

for a hypothetical dellaite composition with 1 Cl p.f.u.: (1) O6 is completely replaced by Cl6; thus there is only one enhanced hydrogen bond O8–H8...Cl6 producing one Raman band (probably type IV in Fig. 3). (2) After ~0.5 Cl p.f.u. are substituted at O6, forming the hydrogen bond O8–H8...Cl6, Cl also substitutes for O8 (up to 0.5 Cl p.f.u.). Thus a second type of enhanced (low-frequency) hydrogen bond is formed: O6–H6...Cl8. This would explain the doublet type III/IV for dellaite with ~0.8 Cl p.f.u. (Fig. 3, no. 5) and the more pronounced band type III in spectrum no. 4 (Fig. 3).

Unfortunately, only Shimazaki *et al.* (2008) analysed dellaite explicitly for Cl and found 0.2 wt.%. It would be interesting to know the Cl content of dellaite from Kilchoan on the Ardnamurchan peninsula (Agrell, 1965) where dellaite occurs together with rustumite for which the Cl content (7.59 wt.% according to stoichiometric formula) was unknown when first described by Agrell (1965). In addition, the skarns with dellaite, killalaite and trabzonite in northeast Turkey (Rize region, Eastern Pontides) described by Sarp (1982*a,b*) and Sarp and Burri

(1986) carry rustumite and also defernite (3.3 wt.% Cl). It is not unlikely that dellaite exists with >50% Cl replacing O6. Such dellaite would even qualify as a new mineral species.

The new discovery of significant Cl in dellaite confirms the difficulty in distinguishing Cl-rich dellaite from rustumite based on chemical data. Both minerals have the same CaO/SiO₂ ratio of 2/1. Stoichiometric rustumite is composed of (wt.%): 60.03 CaO, 32.16 SiO₂, 1.93 H₂O, 7.59 Cl whereas our most Cl-rich dellaite (Table 2, no. 5) has (wt.%): 60.82 CaO, 33.26 SiO₂, 1.94 H₂O, 5.22 Cl. In this study, distinction between rustumite and dellaite was assured by Raman spectroscopy of the grains analysed chemically (Figs 2–4). The Raman spectrum in the 1200–100 cm⁻¹ region of rustumite is significantly different from that of dellaite. Only four strong lines are recognized in the rustumite spectrum (cm⁻¹): 914, 812, 648 and 380 (authors' unpublished data on F-bearing rustumite from Lakargi, Caucasus).

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References

- Agrell, S.O. (1965) Polythermal metamorphism of limestones at Kilchoan, Ardnamurchan. *Mineralogical Magazine*, **34**, 1–15.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica*, **B41**, 244–247.
- Bruker (1999) *SMART and SAINT-Plus*. Versions 6.01. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dent-Glasser, L. and Roy, D.M. (1959) Further studies on 6CaO·3SiO₂·H₂O. *American Mineralogist*, **44**, 447–451.
- Dent-Glasser, L.S., Funk, H., Hilmer, W. and Taylor, H.F.W. (1961) The identity of some dicalcium silicate hydrates. *Journal of Applied Chemistry*, **11**, 186–190.
- Flint, E.P., McMurdie, H.F. and Wells, L.S. (1938) Formation of hydrated calcium silicates at elevated temperatures and pressures. *Journal of Research, National Bureau of Standards*, **21**, 617–638.
- Funk, H. (1958) Chemische Untersuchungen von Silicaten. XXII. Über Produkte der Wassereinwirkung auf verschiedene Formen des Ca₂SiO₄ bei 120° bis 350° C und ihre Bildungsbedingungen. *Zeitschrift für anorganische und allgemeine Chemie*, **297**, 103–120.
- Ganiev, R.M., Ilyukhin, V.V. and Belov, N.V. (1970) Crystal structure of cement phase Y = Ca₆[Si₂O₇][SiO₄](OH)₂. *Doklady Akademii Nauk SSSR*, **190**, 831–834 (in Russian).
- Garbev, K., Gasharova, B., Beuchle, G., Kreis, S. and Stemmermann, P. (2008) First observation of α-Ca₂[SiO₃(OH)](OH)-Ca₆[Si₂O₇][SiO₄](OH)₂ phase transformation upon thermal treatment in air. *Journal of the American Ceramic Society*, **91**, 263–271.
- Howie, R.A. and Ilyukhin, V.V. (1977) Crystal structure of rustumite. *Nature*, **269**, 231.
- Hu, X., Yanagisawa, K., Onda, A. and Kajiyoshi, K. (2006) Stability and phase relations of dicalcium silicate hydrate under hydrothermal conditions. *Journal of the Ceramic Society of Japan*, **114**, 174–179.
- Jander, W. and Franke, B. (1941) Die Bildung von Calciumhydrosilikaten aus Calciumoxyd und Kieselsäuregel bei 300° und 350°C und hohen Drucken. III. Mitteilung über hydrothermale Reaktionen. *Zeitschrift für anorganische und allgemeine Chemie*, **247**, 161–179.
- Kusachi, I., Henmi, C. and Henmi, K. (1984) The occurrences of killalaite and associated minerals from Kushiuro-Uenotani outcrop, Tojo, Hiroshima. *Koubutsu-Gakkai Kou'en-Youshi*, **100** (in Japanese).
- Lazic, B., Armbruster, T., Savelyeva, V.B., Zadov, A.E., Pertsev, N.N. and Dzierzanowski, P. (2011) Galuskinite, Ca₇(SiO₄)₃(CO₃), a new skarn mineral from the Birkhin gabbro massif, Eastern Siberia, Russia. *Mineralogical Magazine*, **75**, in press.
- Libowitzky, E. (1999) Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, **130**, 1047–1059.
- Nawaz, R. (1974) Killalaite, a new mineral from Co. Sligo, Ireland. *Mineralogical Magazine*, **39**, 544–548.
- Nawaz, R. (1977) A second occurrence of killalaite. *Mineralogical Magazine*, **41**, 546–548.
- Roy, D.M. (1958) Studies in the system CaO-Al₂O₃-SiO₂-H₂O IV; phase equilibria in the high-lime portion of the system CaO-SiO₂-H₂O. *American Mineralogist*, **43**, 1009–1028.
- Safronov, A.N., Nevsky, N.N., Ilyukhin, V.V. and Belov, N.V. (1981) The refinement of the crystal structure of the cement phase Y-C₆S₃H. *Doklady*

- Akademii Nauk SSSR*, **256**, 1387–1389 (in Russian).
- Sarp, H. and Burri, G. (1986) Trabzonite $\text{Ca}_4\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ a new hydrated silicate. *Schweizerische Mineralogische Petrographische Mitteilungen*, **66**, 453.
- Sarp, H., Deferne, J. and Sarman, E. (1982a) Second occurrence of killalaite in a skarn from the Güneyce-Ikizdere region (eastern Pontids, Turkey). *Archives des Sciences Geneve*, **35**, 275–278.
- Sarp, H., Deferne, J. and Sarman, E. (1982b) Metamorphisme polythermal de Güneyce-Ikizdere (Pontides Orientales, Turquie) et quelques precisions sur les conditions de formation de la defernite. *Archives des Sciences Geneve*, **35**, 279–288.
- Sheldrick, G.M. (1996) *SADABS*. University of Göttingen, Germany.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.
- Shimazaki, H., Miyawaki, R., Yokoyama, K., Matsubara, S. and Bunno, M. (2008) Occurrence and new data of dellaite from the Akagane mine, Japan. *Journal of Mineralogical and Petrological Sciences*, **103**, 385–389.
- Speakman, K., Taylor, H.F.W., Bennett, J.M. and Gard, J.A. (1967) Hydrothermal reactions of γ -dicalcium silicate. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, 1052–1060.
- Takechi, Y., Kusachi, I., Nakamuta, Y. and Kase, K. (2000) Nickel-bearing djerfisherite in gehlenite-spurrite skarn at Kushiro, Hiroshima Prefecture, Japan. *Resource Geology*, **50**, 179–184.
- Taylor, H.F.W. (1977) The crystal structure of killalaite. *Mineralogical Magazine*, **41**, 363–369.