







Article

Qeltite – the first terrestrial high-temperature mineral with a langasite-type structure from the pyrometamorphic rocks of the Hatrurim Complex

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Abstract

Qeltite (IMA2021–032), ideally $\text{Ca}_3\text{Ti}(\text{Fe}_2\text{Si})\text{Si}_2\text{O}_{14}$, was found in gehlenite–rankinite–wollastonite paralava from a pyrometamorphic rock of the Hatrurim Complex at Nabi Musa locality, Judean Desert, West Bank, Palestine. It generally occurs as light-brown flattened crystals up to 40–50 μm in length and less than 5 μm in thickness. Its aggregates reach 100–200 μm in size. Its empirical crystal chemical formula based on 14 O is: $(\text{Ca}_{2.96}\text{Sr}_{0.02}\text{Mn}_{0.01})_{\Sigma 2.99}\text{Ti}^{4+}(\text{Fe}_{1.59}\text{Si}_{0.60}\text{Al}_{0.43}\text{Ti}_{0.38}\text{Cr}_{0.01})_{\Sigma 3.01}(\text{Si}_{1.99}\text{P}_{0.01})_{\Sigma 2}\text{O}_{14}$. The strongest reflections in its calculated X-ray diffraction pattern are $[d, \text{Å}, (I, \%), hkl]$: 3.12, (100), 111; 2.85, (61), 201; 2.85, (48), 021; 2.32, (45), 211; 6.93, (31), 100; and 1.81, (30), 212. Qeltite is trigonal and crystallises in the noncentrosymmetric $P321$ space group, with $a = 8.0077(5) \text{ Å}$, $c = 4.9956(4) \text{ Å}$, $V = 277.42(4) \text{ Å}^3$ and $Z = 1$. Its microhardness VHN_{25} is 708(17) kg/mm^2 and its hardness on the Mohs scale is ~ 6 . Its calculated density is 3.48 g/cm^3 . It was found in fine-grained mineral aggregates within coarse-grained main minerals of rankinite–gehlenite paralava with subordinate wollastonite, Ti-bearing andradite and kalsilite. In these aggregates, the mineral is associated with khesinite, paqueite and pseudowollastonite, indicating a high-temperature genesis ($\sim 1200^\circ\text{C}$). Its crystallisation can be compared with the crystallisation of minerals containing refractory inclusions in meteorites.

Keywords: qeltite; new mineral; structure; Raman; langasite; pyrometamorphic rock; Hatrurim Complex

(Received 9 February 2024; accepted 26 April 2024; Accepted Manuscript published online: 2 May 2024; Associate Editor: Elena Zhitova)

Introduction

In gehlenite paralava of the Hatrurim Complex, spreading across the territories of Israel and Palestine, a whole series of new minerals with a langasite-type structure (Belokoneva *et al.*, 1980; Mill *et al.*, 1982; Kaminskii *et al.*, 1983; Mill and Pisarevsky, 2000; Andreev, 2006) has been recently discovered (Galuskina *et al.*, 2023), some of which have a composition close to garnet of the andradite–schorlomite series, which has complicated their correct identification. One of the first, qeltite, $\text{Ca}_3\text{Ti}(\text{Fe}_2\text{Si})\text{Si}_2\text{O}_{14}$, has been studied by us and approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2021–032, Galuskina *et al.*, 2021). Qeltite is the Fe–Si analogue of paqueite, $\text{Ca}_3\text{Ti}(\text{Al}_2\text{Ti})\text{Si}_2\text{O}_{14}$ (IMA2013–53), recently described from the Allende CV3

carbonaceous chondrite (Ma *et al.*, 2022) and later detected in contact facies of phosphide-bearing gehlenite paralava of the Hatrurim Complex in the wadi Zohar, Hatrurim Basin, Israel (Galuskin *et al.*, 2022).

Langasite phases comprise synthetic family compounds with the general formula $A_3BC_3D_2O_{14}$, where $A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}^{2+}, \text{Na}$ and K ; $B = \text{Ti}^{4+}, \text{Sb}^{5+}, \text{Nb}^{5+}, \text{Ta}^{5+}$ and Te^{6+} ; $C = \text{Fe}^{3+}, \text{Co}^{2+}, \text{Mn}^{2+}, \text{Ga}, \text{Al}$ and Ti^{4+} ; $D = \text{Si}, \text{Ge}^{4+}, \text{P}^{5+}, \text{V}^{5+}$ and As^{5+} (Mill, 2009; Lyubutin *et al.*, 2011; Markina *et al.*, 2019; Scheuermann *et al.*, 2000). The name of this family comes from the names of the chemical elements in lanthanum gallium silicate $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ – one member of the family (Andreev, 2004). The first phase of the langasite-type structure with composition $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ was synthesised in 1979 (Mill and Pisarevsky, 2000). Industry requests for piezoelectric materials for middle-band monolithic BAW (bulk acoustic wave) devices prompted the synthesis of these compounds at scale (Mill and Pisarevsky, 2000). The high piezoelectric and electromechanical constants of these materials (higher than those of quartz), and the absence of phase transformation up to the melting point (e.g. 1470°C) make these materials attractive for practical applications (Tichý

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Cite this article: Galuskina I.O., Stachowicz M., Vapnik Y., Zeliński G., Woźniak K. and Galuskin E. (2024) Qeltite – the first terrestrial high-temperature mineral with a langasite-type structure from the pyrometamorphic rocks of the Hatrurim Complex. *Mineralogical Magazine* 1–10. <https://doi.org/10.1180/mgm.2024.38>

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et al., 2010). At present, more than 200 synthetic compounds belonging to the langasite family are known (Markina *et al.*, 2019). These compounds are interesting not only for basic investigations but also for many applications due to functional properties such as piezoelectricity, optical nonlinearity and multiferroicity. The langasite family phases have been examined intensively in the context of their applications in bulk and surface acoustic wave devices, as well as in the field of lasers, photorefractive media, nonlinear optics and electrooptics (Markina *et al.*, 2019).

In Nature, until now only one phase with the langasite-type structure that was formed at high temperatures – paqueite – had been found, and that mineral was found in a meteorite (Ma *et al.*, 2022). Some low-temperature mineral phases belonging to the langasite family, such as the dugganite-group minerals (trigonal, *P321*) dugganite, $\text{Pb}_3\text{Zn}_3(\text{AsO}_4)_2(\text{TeO}_6)$, $a = 8.460(2)$ Å, $c = 5.206(2)$ Å (Williams, 1978; Lam *et al.* 1998); joëlbruggerite, $\text{Pb}_3\text{Zn}_3(\text{Sb}^{5+}, \text{Te}^{6+})\text{As}_2\text{O}_{13}(\text{OH}, \text{O})$, $a = 8.4803(17)$ Å, $c = 5.2334(12)$ Å (Mills *et al.*, 2009); and kuksite, $\text{Pb}_3\text{Zn}_3(\text{PO}_4)_2(\text{TeO}_6)$, $a = 8.39$ Å, $c = 5.18$ Å, formed in oxidised ore, pyrite-bearing, metasomatites with gold–telluride mineralisation (Kim *et al.*, 1990) or in the oxidation zone of silver–lead and silver–polymetallic ores (Williams, 1978; Mills *et al.* 2009). The structure of chermnykhite, $\text{Pb}_3\text{Zn}_3(\text{VO}_4)_2(\text{TeO}_6)$, which belongs to the dugganite group, needs re-investigation, as along with the structure of kuksite, it was defined as orthorhombic ($a = 8.58(3)$ Å, $b = 14.86(5)$ Å and $c = 5.18(3)$ Å, Kim *et al.*, 1990). The structure of joëlbruggerite should also be clarified, as the OH position was incorrectly determined as a result of a bond valence sum miscalculation (Mills *et al.*, 2009). By analogy with the formula of langasite, which was adapted to paqueite and qeltite, the crystal chemical formula of minerals of the dugganite group should be written as follows: (for example, for dugganite) $\text{Pb}_3\text{Te}^{6+}\text{Zn}_3\text{As}_2^{5+}\text{O}_{14}$.

There is another interesting mineral, taikanite, $\text{Sr}_2\text{BaMn}_2^{3+}(\text{Si}_4\text{O}_{12})\text{O}_2$, which was found in oxidised manganese ore (Kalinin *et al.*, 1985). The structure of taikanite is monoclinic (*C121*), $a = 14.600(2)$ Å, $b = 7.759(4)$ Å, $c = 5.142(1)$ Å, $\beta = 93.25(2)^\circ$ and derived from structures of the langasite type $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$, where the *A* site is split and occupied by Ba and Sr, and one of the tetrahedral sites *D* changes into an octahedral one and is occupied by Mn^{3+} (Armbruster *et al.*, 1993).

In this paper we described qeltite – one of the terrestrial minerals with a langasite-type structure which has been discovered in paralava of the Hatrurim pyrometamorphic Complex. The mineral is named after the Wadi Qelt in the close vicinity of the qeltite type locality Nabi Musa, Judean Desert, Palestine. Type material was deposited in the mineralogical collection of the Fersman Mineralogical Museum, Leninskiy pr., 18/k2, 115162 Moscow, Russia, catalogue numbers 5695/1.

Experimental methods

The crystal morphology, optical properties and chemical composition of qeltite and associated minerals were studied using an optical microscope, a Phenom XL analytical scanning electron microscope (Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Sosnowiec, Poland), and an electron microprobe analyser (Cameca SX100, Micro-Area Analysis Laboratory, Polish Geological Institute – National Research Institute, Warsaw, Poland). The microprobe chemical analyses were performed in wavelength-dispersive spectroscopy mode at acceleration voltage 15 kV, beam current 20 nA and beam

diameter 1 µm. The following lines and standards were used: $\text{MgK}\alpha$ – diopside; $\text{SiK}\alpha$ and $\text{ZrL}\alpha$ – zircon; $\text{AlK}\alpha$ and $\text{KK}\alpha$ – orthoclase; $\text{CaK}\alpha$ – wollastonite; $\text{SrL}\alpha$ – celestine; $\text{NbL}\alpha$ – metallic Nb; $\text{BaL}\beta$ – baryte; $\text{TiK}\alpha$ – rutile; $\text{VK}\alpha$ – metallic V; $\text{CrK}\alpha$ – Cr_2O_3 ; $\text{MnK}\alpha$ – rhodonite; $\text{FeK}\alpha$ – pentlandite; $\text{NiK}\alpha$ – nickeline; $\text{CuK}\alpha$ – chalcopyrite; and $\text{ZnK}\alpha$ – ZnS.

Raman spectra of qeltite were recorded on a WITec alpha 300R Confocal Raman Microscope (Department of Earth Science, University of Silesia, Poland) equipped with an air-cooled solid laser (488 nm) and a CCD camera operating at -61°C . The laser radiation was coupled to a microscope through a single-mode optical fibre with a diameter of 3.5 µm. An air Zeiss LD EC Epiplan–Neofluar DIC-100/0.75NA objective was used. Raman-scattered light was focused by a broad-band single mode fibre with effective pinhole size of ~ 30 µm and a monochromator with 1800 gr/mm. The power of the laser at the sample position was ~ 20 mW. Integration times of 3 s with an accumulation of 20 scans and a resolution of 2 cm^{-1} were chosen. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}).

Single-crystal X-ray diffraction (SCXRD) studies were carried out with a four-circle SuperNova diffractometer with $\text{AgK}\alpha$ radiation ($\lambda = 0.56087\text{ Å}$), equipped with an Eos CCD detector (Agilent). The detector-to-crystal distance was 66.0 mm. $\text{AgK}\alpha$ radiation ($\lambda = 0.0560\text{ Å}$) was used at 65 kV and 0.6 mA. Crystals were attached to a non-diffracting MiTeGen micromount support. A frame-width of 1° in ω scans and a frame time of 90 s were used for data collection. Reflection intensities were corrected for Lorentz, polarisation and absorption effects and converted to structure factors using *CrysAlisPro* 1.171.40.67a (Rigaku Oxford Diffraction, 2019) software. Observed unit-cell parameters are consistent with trigonal symmetry. The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.729$) suggested space group symmetry was *P321*. The crystal showed significant systematic absences, violations of the glide planes and screw axes. Further examination of the structural model of lower, *P3* symmetry led to a model equivalent to a *P321* structure. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Prince, 2004). The following curves were used: Ca at the *A* site; Ti at the *B* site; Fe vs. Si at the *C* site; Si at the *D* site and O at the O1–O3 sites. The *A*, *B*, *D* and O sites were found to be fully occupied by Ca, Ti, Si and O, respectively. The *C* site has a mixed (Fe, Si) occupancy. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material.

Powder X-ray diffraction data for qeltite could not be measured, therefore we present a calculated powder pattern ($\text{CuK}\alpha$ radiation, Debye–Scherrer geometry), based on the obtained structure model in Supplementary Table S1.

Qeltite occurrence and description

Qeltite was found in gehlenite–rankinite paralava within the pyrometamorphic Hatrurim Complex, which is a unique geological object described in numerous publications by different authors (Bentor *et al.*, 1963a, 1963b; Gross, 1977; Vapnik *et al.*, 2007; Geller *et al.*, 2012; Novikov *et al.*, 2013; Galuskina *et al.*, 2014), so here we provide only a brief characterisation.

Rocks of the Hatrurim Complex are represented mainly by spurrite and fluorapatite marbles, gehlenite, larnite and spurrite rocks, which form large areas in the immediate surroundings of

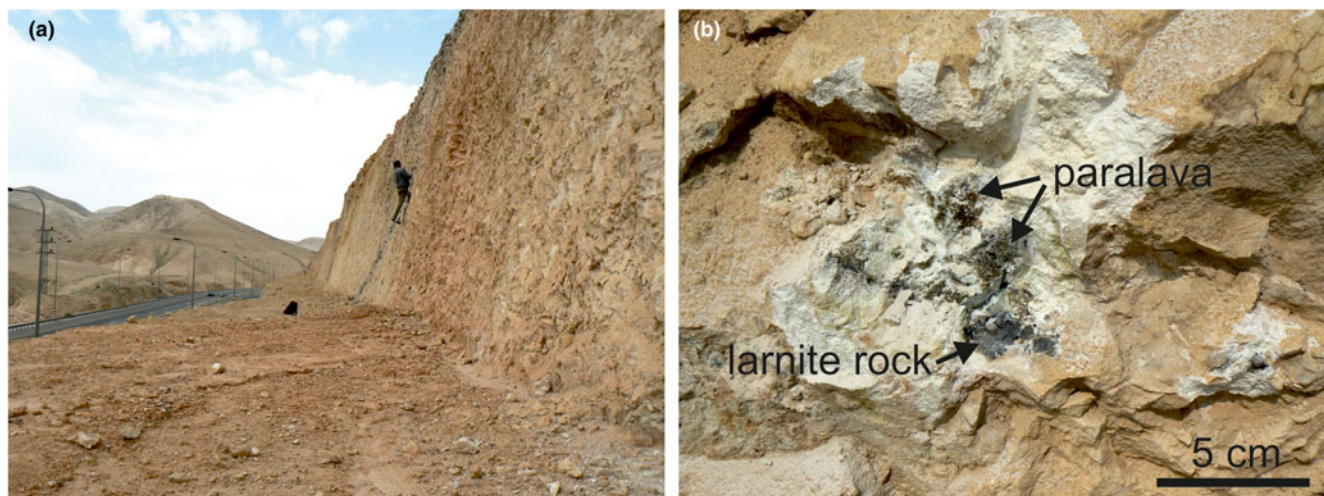


Figure 1. (a) Nabi Musa locality along the Jerusalem–Jericho highway truncation. (b) Gehlenite–rankinite–wollastonite paralava nest in altered hydrogrossular-bearing rock.

the Dead Sea Rift on the territories of Israel, Palestine and Jordan (Bentor *et al.*, 1963a, 1963b; Gross, 1977; Burg *et al.*, 1991, 1999; Novikov *et al.*, 2013; Khoury *et al.*, 2016). Paralavas of different composition occur within pyrometamorphic rocks of the Complex (Vapnik *et al.*, 2007), among them gehlenite–wollastonite–rankinite oxidised paralavas, in which qeltite was discovered and which contain only Fe^{3+} -bearing minerals (Galuskin *et al.*, 2022). Rarely, reduced phosphide-bearing gehlenite and diopside paralavas are encountered (Britvin *et al.*, 2015; Galuskin *et al.*, 2023). The genesis of the Hatrurim Complex rocks remains enigmatic and is considered an unsolved problem (Galuskina *et al.*, 2014). Two proposed hypotheses – the ‘classic’ hypothesis, assuming that pyrometamorphic transformation was driven by dispersed organic matter in a sedimentary protolith (Burg *et al.*, 1991, 1999), and the ‘mud volcanos’ hypothesis, proposing the participation of methane in the activation of the combustion processes (Sokol *et al.*, 2010; Novikov *et al.*, 2013) – cannot explain a number of geological particularities of the Complex, such as thick almost homogeneous beds of pyrometamorphic rocks extending across a dozen square kilometres. Pyrometamorphic rocks of the Hatrurim Complex are characterised by an extraordinary variety of minerals caused by the reactions of combustion by-products (gases, fluids and melts) with earlier minerals of the clinker association and altered country rocks (Galuskin *et al.*, 2016).

The qeltite-type locality ‘Nabi Musa’, near the Palestinian village Nabi Musa, lies close to a historical place with the same name (probably the Tomb of Moses), situated in the Judean Desert, West Bank, Palestine (31°48'N, 35°25'E) (Fig. 1). Nabi Musa is one of several localities of the Hatrurim Complex located in the Judean Desert in the vicinity of the Jerusalem–Jericho highway, and most of the outcrops are at the road truncation (Fig. 1a). According to Sokol *et al.* (2010), the Nabi Musa locality is a huge crater-like structure. A massive, brecciated fragment of pyrometamorphic rocks, mainly larnite, gehlenite, spurrite, are embedded in altered rock represented by zeolitic and calcium silicate hydrated rocks. Small paralava bodies form veins and nests up to 0.15 m long (Fig. 1b). Paralava containing qeltite is composed of rankinite, gehlenite, rarer wollastonite, Ti-bearing andradite and kalsilite. Minerals of the khesinite–dorrite series,

barioferrite, minerals of magnesioferrite–magnetite–maghemite series, hematite, Si-bearing perovskite, Si–V-bearing fluorapatite, gurimite, hexacelsian and an unidentified Ca–U-silicate are accessory minerals (Fig. 2). Baryte, hydrated calcium silicates such as tobermorite, afwillite, tacharanite and a fabrièsite-like mineral are later, hydrothermal minerals.

Later, qeltite was detected in paralava at two localities in the Hatrurim Basin in the Negev Desert in Israel. The first locality is in the upper reaches of a tributary of the Halamish Wadi. Here, qeltite with composition $(\text{Ca}_{2.95}\text{Sr}_{0.02}\text{Ba}_{0.01}\text{Mn}_{0.01})_{\Sigma 2.99}\text{Ti}^{4+}(\text{Fe}_{1.55}\text{Si}_{0.57}\text{Al}_{0.46}\text{Ti}_{0.42}\text{Cr}_{0.01})_{\Sigma 3.01}\text{Si}_2\text{O}_{14}$ was found in gehlenite–wollastonite–Ti-bearing andradite paralava, which also contains a significant amount of fluorapatite–fluorellestadite-group minerals. Andradite and åkermanite are minor minerals, and khesinite, barioferrite, magnesioferrite, dorrite and perovskite are accessory minerals in this rock. Another locality with rankinite–gehlenite–Ti-bearing andradite paralava containing qeltite, $(\text{Ca}_{2.96}\text{Sr}_{0.03}\text{Ba}_{0.01})_{\Sigma 3}\text{Ti}^{4+}(\text{Fe}_{1.44}\text{Al}_{0.58}\text{Si}_{0.55}\text{Ti}_{0.44})_{\Sigma 3.01}\text{Si}_2\text{O}_{14}$, and its Ti-analogue, $\text{Ca}_3\text{Ti}^{4+}(\text{Fe}_{1.27}\text{Al}_{0.76}\text{Ti}_{0.55}\text{Si}_{0.43})_{\Sigma 3.01}\text{Si}_2\text{O}_{14}$, is located 700 m to the left of road no. 31 Arad–Dead Sea. Wollastonite, kalsilite and åkermanite are occasionally observed in this paralava. Barioferrite, magnesioferrite, perovskite, khesinite, fluorapatite, aradite, gurimite, Ba–U-perovskite are accessory minerals.

Qeltite generally forms aggregates of flattened crystals up to 40–50 μm in length and less than 5 μm in thickness. These aggregates occur in small enclaves 100–200 μm in size in rankinite (Fig. 2a–c). Rarely, tabular qeltite crystals with inclusions of fluorapatite (Fig. 2d) and hematite (Fig. 2e) more than 100 μm in length and ~ 10 μm in thickness are noted. In optical images it is clear that qeltite exhibits a light–brown colour with a red hue (Fig. 3b). It has a yellowish–white streak and a vitreous to subadamantine lustre. Its microhardness VHN_{25} is 708(17) kg/mm^2 ; average of 22 measurements; range 683–738 kg/mm^2 . It has a hardness of ~ 6 on the Mohs scale. Cleavage and parting are not observed. The mineral is brittle. It displays an uneven and conchoidal fracture. It is not magnetic. Qeltite is uniaxial (+), its refractive indexes are $\omega \approx 1.85$, $\epsilon \approx 1.90$, $\Delta \approx 0.05$ and its mean calculated refractive index is 1.871, $\epsilon = C$ ($\lambda = 589$ nm). It exhibits pleochroism, as it is light coloured, pink along Z and intensively coloured, red–brown along X/Y (Fig. 3b,c). The

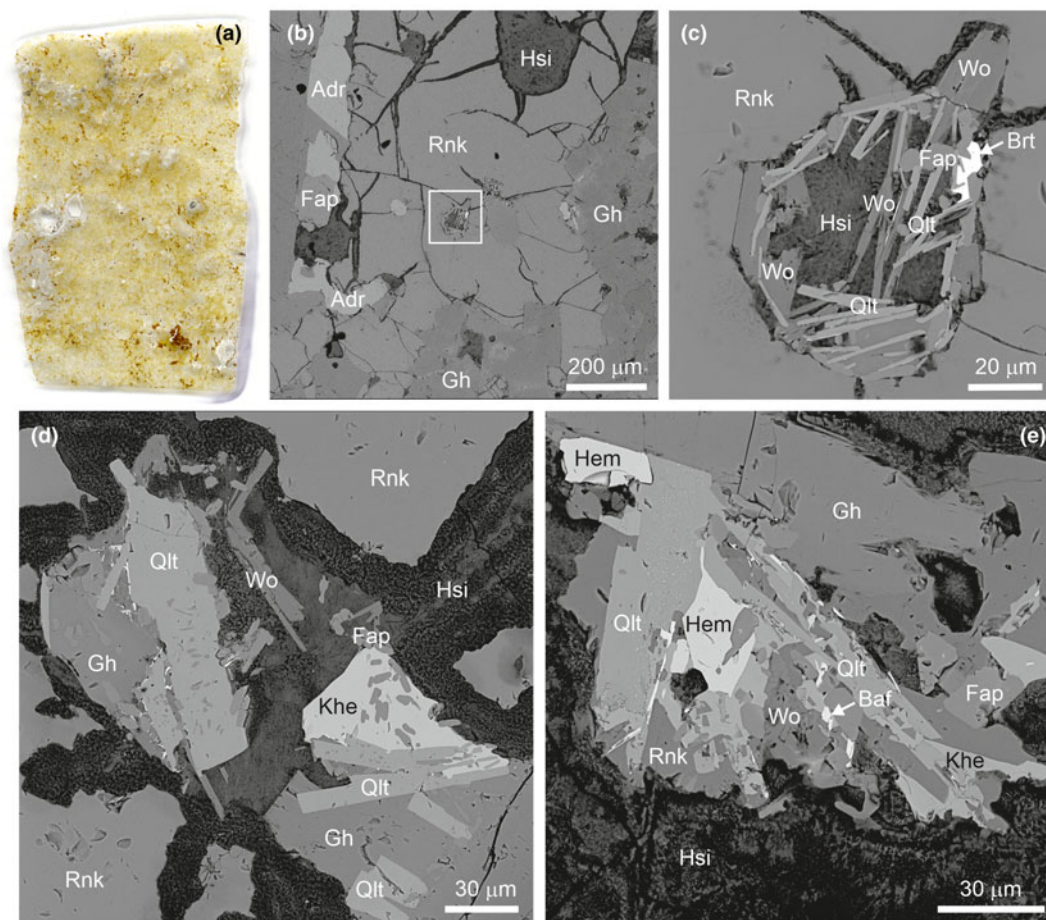


Figure 2. (a) Thin section made from paralava of the type specimen (5695/1) containing qeltite; yellow – gehlenite, brown – Ti-bearing andradite, and white and transparent – rankinite, wollastonite and hydrated calcium silicates. (b) Qeltite is in small enclaves inside rankinite grains; the fragment magnified in Fig. 2c is shown in the frame. (c) Flattened qeltite crystals. (d, e) Typical mineral association containing qeltite crystals. Qeltite often contains fluorapatite inclusions (d) and very small inclusions of hematite (e). (b–e) Back-scattered electron spectroscopy (BSE) images. Key: Adr – Ti-bearing andradite; Baf – barioferrite; Brt – baryte; Hem – hematite; Hsi – calcium hydrated silicate; Fap – fluorapatite; Gh – gehlenite; Khe – khesinite; Qlt – qeltite; Rnk – rankinite; Wo – wollastonite. The abbreviations are after Warr (2021).

density of qeltite was not measured because of the small size of its crystals. Its calculated density is $3.48 \text{ g}\cdot\text{cm}^{-3}$ based on the empirical formula and unit cell volume refined from the SCXRD data.

The Gladstone–Dale compatibility index is $1 - (K_p/K_c) = 0.030$ (excellent) (Mandarino, 1989).

The results of the electron microprobe analyses of qeltite are given in Table 1.

The qeltite studied is characterised by significant Ti and Al content (Table 1). The empirical formulas of qeltite, $(\text{Ca}_{2.96}\text{Sr}_{0.02}\text{Mn}_{0.01})_{\Sigma 2.99}(\text{Ti}_{0.99}\text{Cr}_{0.01})_{\Sigma 1.00}(\text{Fe}^{3+}\text{Si}_{1.59}\text{Si}_{0.60}\text{Al}_{0.43}\text{Ti}_{0.39})_{\Sigma 3.01}(\text{Si}_{1.99}\text{P}_{0.01})_{\Sigma 2.00}\text{O}_{14}$ (grain used for SCXRD) and $(\text{Ca}_{2.96}\text{Sr}_{0.02}\text{Ba}_{0.01}\text{Mn}_{0.01})_{\Sigma 3.00}(\text{Ti}_{0.96}\text{Cr}_{0.03}\text{Zr}_{0.01})_{\Sigma 1.00}(\text{Fe}^{3+}\text{Si}_{1.53}\text{Si}_{0.63}\text{Al}_{0.46}\text{Ti}_{0.38})_{\Sigma 3.00}(\text{Si}_{1.98}\text{P}_{0.02})_{\Sigma 2.00}\text{O}_{14}$ (Table 1, taking into account the dominant valence rule and possibility of double occupation at one structural site, can be simplified to $\text{Ca}_3\text{Ti}(\text{Fe}_2^3\text{Si})\text{Si}_2\text{O}_{14}$. The content of the paqueite end-member, $\text{Ca}_3\text{Ti}(\text{Al}_2\text{Ti})\text{Si}_2\text{O}_{14}$, in qeltite varies in the range 21–23%.

Raman spectroscopy

The features of the Raman spectra of qeltite depend on the crystal orientation (Fig. 4). The Raman spectrum of qeltite differs from the spectra of typical nesosilicates (for example, minerals of the garnet and schorlomite groups) by the fact that the strongest band in the qeltite spectrum at $611\text{--}613 \text{ cm}^{-1}$ is related to the symmetric stretching vibration of Ti–O in the ${}^B(\text{TiO}_6)^{8-}$

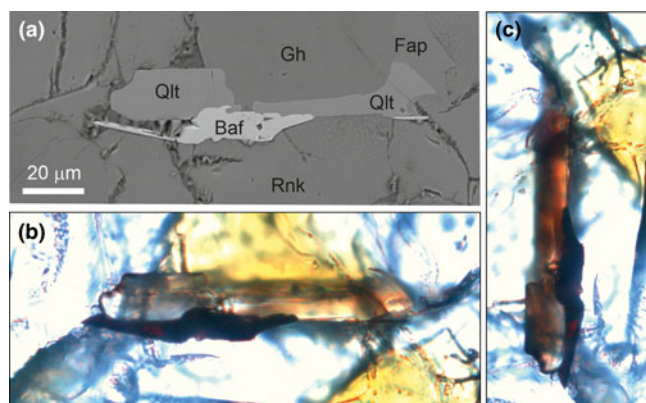


Figure 3. (a) BSE image of a qeltite crystal. (b–c) Optical images of the same qeltite crystal showing pleochroism changing from light brown ($\sim \parallel Z$) to dark brown with a red hue ($\sim \perp Z$). Key: Baf – barioferrite; Fap – fluorapatite; Gh – gehlenite; Qlt – qeltite; Rnk – rankinite. The abbreviations are after Warr (2021).

Table 1. Chemical data (in wt.%) for qeltite.

	Grain used for SCXRD			Other grains in this sample		
	Mean <i>n</i> = 9	Range	S.D.	Mean <i>n</i> = 16	Range	S.D.
MgO	n.d.			0.02	0–0.07	0.02
CaO	28.27	27.94–28.75	0.25	28.19	27.63–29.04	0.42
MnO	0.16	0.10–0.21	0.04	0.084	0.01–0.18	0.04
SrO	0.37	0.30–0.40	0.03	0.30	0.23–0.39	0.05
BaO	n.d.			0.15	0–0.34	0.11
Fe ₂ O ₃	21.62	21.08–22.12	0.30	20.71	19.14–21.80	0.79
Al ₂ O ₃	3.78	3.49–4.12	0.23	3.98	3.31–4.74	0.46
Cr ₂ O ₃	0.13	0.05–0.18	0.04	0.39	0.18–0.84	0.18
SiO ₂	26.45	25.73–27.84	0.70	26.48	23.10–29.79	2.25
TiO ₂	18.72	17.54–19.37	0.55	18.07	14.18–21.57	2.47
ZrO ₂	n.d.			0.24	0.05–0.36	0.09
P ₂ O ₅	0.11	0.05–0.17	0.04	0.22	0.13–0.50	0.10
Total	99.59			98.83		
Calculated on 140 per unit cell						
Ca	2.96			2.96		
Mn ²⁺	0.01			0.01		
Sr	0.02			0.02		
Ba				0.01		
A	2.99			3.00		
Ti ⁴⁺	0.99			0.96		
Cr ³⁺	0.01			0.03		
Zr				0.01		
B	1.00			1.00		
Si	1.99			1.98		
P ⁵⁺	0.01			0.02		
C	2.00			2.00		
Fe ³⁺	1.59			1.53		
Al	0.43			0.46		
Si	0.60			0.63		
Ti ⁴⁺	0.39			0.38		
D	3.01			3.00		

n.d. – not detected; S.D. – standard deviation.

octahedron (Frank *et al.*, 2012; Vásquez *et al.*, 2017; Su *et al.*, 2000; Heyns *et al.*, 2000). The bands of lower intensities are complex and are mainly connected with vibrations of Si–O, Fe³⁺–O, Al–O and Ti⁴⁺–O bonds at the tetrahedral sites C and D. The main bands in the qeltite Raman spectrum are as follows (Fig. 4, cm⁻¹, ~LZ/||Z): 166/172, 218/215 related to Ca–O vibrations and/or ν₂^B(TiO₆)⁸⁻; 244/252, 331/~353 related to the vibrations R(TO₄), ν₂^C(FeO₄)⁵⁻; 437/448 – ν₄^B(TiO₆)⁸⁻, ν₄^C(FeO₄)⁵⁻, ν₄^D(SiO₄)⁴⁻; 611/613 – ν₁^B(TiO₆)⁸⁻, ν^B(Ti–O^DTi); 713/718 – ν₁^D(FeO₄)⁵⁻; 766 – ν₁^C(TiO₄)⁴⁻, ν₁^C(AlO₄)⁵⁻; 855 – ν₁^D(SiO₄)⁴⁻; 978/986 – ν₃^D(SiO₄)⁴⁻, ν^C(Si–O^DSi). The interpretation of bands was on the basis of Raman data obtained by different authors for TiO₂ polymorphs, Ti-bearing garnets, titanite and other titanosilicates (Galuskina *et al.*, 2005; Frank *et al.*, 2012; Vásquez *et al.*, 2017; Su *et al.*, 2000; Heyns *et al.*, 2000).

Crystallography

Structural data were obtained for a 0.04 × 0.02 × 0.01 mm crystal at 295.5(4) K. Experimental data and the results of structure refinement are given in Tables 2–5. Bond valence sum (BVS) calculations are shown in Table 6.

Qeltite, Ca₃Ti(Fe₂³⁺Si)Si₂O₁₄ [P321, *a* = *b* = 8.0077(5), *c* = 4.9956(4) Å], belongs to the langasite structural type – a family of synthetic compounds with the general formula A₃BC₃D₂O₁₄ (Mill, 2009; Marty *et al.*, 2010; Lyubutin *et al.*, 2011; Markina *et al.*, 2019). Paqueite, Ca₃Ti(Al₂Ti)Si₂O₁₄ (there are only electron

back-scatter diffraction data; the structural model is the langasite-type synthetic phase Ca₃Ti(Al,Ti,Si)₃Si₂O₁₄: P321, *a* = *b* = 7.943, *c* = 4.930 Å; Scheuermann *et al.*, 2000), is known to exist in Nature, as it has been described in meteorites (Paque *et al.*, 1994; Ma and Beckett, 2016). Qeltite, Ca₃Ti(Fe₂³⁺Si)Si₂O₁₄, is an Fe³⁺-analogue of paqueite, at the D tetrahedra of which Si > Ti⁴⁺ (Table 5). The qeltite structure belongs to the trigonal non-centrosymmetric P321 space group. In qeltite, CaO₈ polyhedra and TiO₆ octahedra form a layer in which the central TiO₆ octahedron shares three edges with three CaO₈ polyhedra. These CaO₈ polyhedra are further connected to other CaO₈ polyhedra by corner sharing (Fig. 5, 6). The CaO₈ polyhedra are distorted, with bond lengths ranging from 2.358(5) to 2.868(4) Å. In fact, Ti at coordination 6 is at the centrum of a truncated trigonal prapzohedron with the distances Ti–O(3) = 1.954(5). In adjacent layers, SiO₄ tetrahedra share three corners (O1 atoms) with larger [(Fe³⁺,Al)₂(Si,Ti)]O₄ C tetrahedra. The base of the SiO₄ tetrahedron has three longer bond lengths of 1.638(4) Å to O1 atoms and one shorter bond length of 1.584(8) Å to O2, which connects the SiO₄ tetrahedra to three CaO₈ polyhedra from the next layer. These relatively weak Ca–O2 bonds of 2.645(3) Å contribute to the underbonding of O2 (Table 6). The limited degree of positional freedom (O2 lies on a three-fold axis, 2d Wyckoff position) prevents this underbonding from being relieved. Thus, the bonding deficiency is relieved by the remaining O atoms that show a little overbonding (Table 6). The bond valence sum for all anions per formula unit averages ideally to 2.00 valence units.

The [(Fe³⁺,Al)₂(Si,Ti)]O₄ tetrahedron has two shorter bonds of 1.791(5) to O3 atoms, connecting this tetrahedron to the TiO₆ octahedra, and two longer bonds of 1.883(4) to O1 atoms, connecting this tetrahedron to the CaO₈ polyhedra. We included two additional weak interactions of C-site cations to O3, with a distance of 2.564(6) Å, which contribute to O2 underbonding compensation. The obtained structural formula of qeltite Ca_{3.00}Ti(Fe_{1.75}Si_{1.25})Σ_{3.00}Si_{2.00}O₁₄, which is charge balanced due to the substitution of part of Fe³⁺ and Si by Ti⁴⁺ and Al at the C site, and the empirical formula, (Ca_{2.96}Sr_{0.02}Mn_{0.01})Σ_{2.99}(Ti_{0.99}Cr_{0.01})Σ_{1.00}(Fe_{1.59}Si_{0.60}Al_{0.43}Ti_{0.39})Σ_{3.01}(Si_{1.99}P_{0.01})Σ_{2.00}O₁₄, are well-matched. The number of electrons for the C tetrahedron in the structural formula is 20.96 and 21.30 electrons in the qeltite empirical formula calculated on the basis of microprobe analyses.

Discussion

In the last few years, a number of different mineral phases with the langasite-type structure and the general formula A₃BC₃D₂O₁₄, where A = Ca and Ba; B = Ti, Nb, Sb and Zr; C = Ti, Al, Fe and Si; and D = Si, have been detected in pyrometamorphic rocks of the Hatrurim Complex. Among them are minerals close in composition to Ti-rich garnets of the andradite–schorlomite series – for example, qeltite, Ca₃Ti⁴⁺(Fe₂³⁺Si)Si₂O₁₄, as described in this article – and minerals with exotic composition such as Ba₃Nb⁵⁺Fe₃³⁺Si₂O₁₄. We consider that the systematics and nomenclature of minerals with a langasite-type structure (dugganite supergroup) should be elaborated on after the full study of the minerals found in the Hatrurim Complex rocks (Galuskina *et al.*, 2023).

Following the discovery of qeltite in paralava of Nabi Musa locality, Palestine, it transpired that isostructural minerals with the common composition Ca₃Ti(Fe³⁺,Al,Si,Ti⁴⁺)₃Si₂O₁₄ are widely distributed in the paralavas of the Hatrurim Basin, Israel and often associate with garnets of the andradite–schorlomite

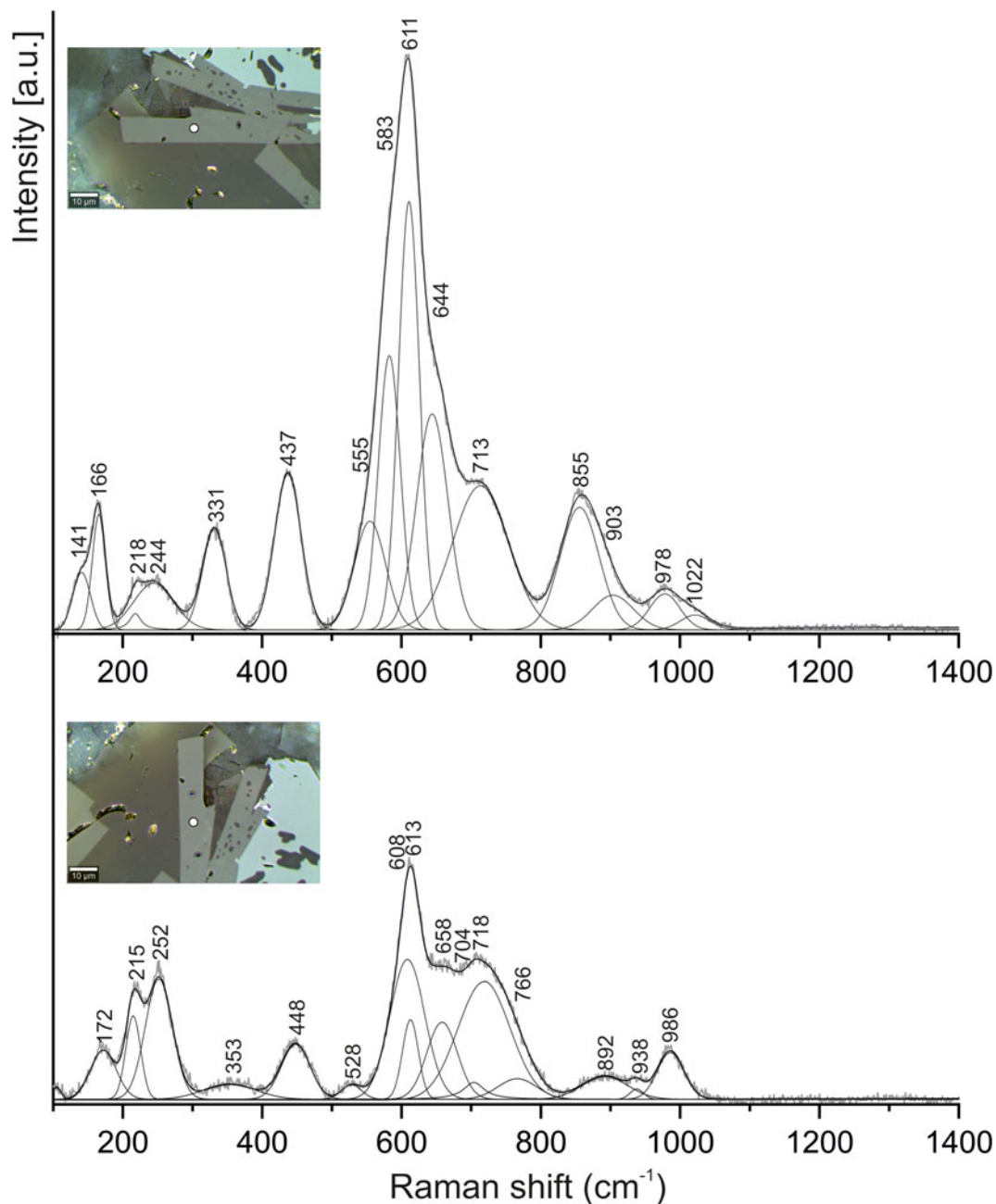


Figure 4. Raman spectra of qeltite on different orientations of a crystal.

series, which are similar by composition. In Ti-bearing garnets, $\text{Ca}_3(\text{Fe}^{3+}, \text{Al}^{3+}, \text{Ti}^{4+})_2(\text{Si}, \text{Fe}^{3+}, \text{Al})_3\text{O}_{12}$ an entry of Ti^{4+} at the octahedral site is facilitated by the substitution of some Si by trivalent cations at the tetrahedral site: ${}^{\text{VI}}(\text{Fe}^{3+}, \text{Al}^{3+})^{\text{IV}}\text{Si} \rightarrow {}^{\text{VI}}(\text{Ti}^{4+})^{\text{IV}}(\text{Fe}^{3+}, \text{Al})$. In qeltite, $\text{Ca}_3\text{Ti}(\text{Fe}_2^{3+}\text{Si})\text{Si}_2\text{O}_{14}$, Ti^{4+} occupies the octahedral site and can enter the tetrahedral site, replacing Si. Increasing Fe^{3+} and Al content at the tetrahedral site to more than 2 atoms per formula unit can be related to the presence of Nb^{5+} or Sb^{5+} at the octahedral site according to the isomorphous scheme ${}^{\text{VI}}(\text{Ti}^{4+})^{\text{IV}}(\text{Si}, \text{Ti}^{4+}) \rightarrow {}^{\text{VI}}(\text{Nb}^{5+}, \text{Sb}^{5+})^{\text{IV}}(\text{Fe}^{3+}, \text{Al})$ (Galuskina *et al.*, 2023). The appearance of Ti^{4+} at the tetrahedral coordination is an exceedingly rare phenomenon, which has also been noted in Si, Al-deficient pyroxenes and amphiboles (Carbonin *et al.*, 1989; Oberti *et al.*, 1992). Titanium in qeltite shares a site

coordinated by $\text{O}1 \times 2$ ($M-\text{O} = 1.883 \text{ \AA}$) and $\text{O}3 \times 2$ ($M-\text{O} = 1.791 \text{ \AA}$) with Al, Si and Fe^{3+} , for which the tetrahedral coordination is usual. The C site can be considered 4+2 coordinated, as two O3 atoms are at 2.564 \AA from the centre of the tetrahedron (Table 5). The effect of these two additional oxygens on the cation at the C site is relatively insignificant in the case of Si and Al, but in the case of Fe^{3+} and Ti^{4+} the effect is noticeable (Table 6). A unique aspect of the qeltite structure (close to the composition of isostructural minerals) is the wide isomorphism of cations at the C tetrahedral site, including Ti^{4+} , for which this coordination is atypical. We consider that the entry of Ti^{4+} (and other large cations) at the C site is simplified by a change of its coordination to 4+2 (octahedral). It is likely that qeltite has a domain structure due to the significant differences among the cation sizes of the C site.

Table 2. The crystal information and details of X-ray diffraction data collection and refinement for qeltite.

Crystal data	
Structural formula	$\text{Ca}_{3.00}\text{Ti}_{1.00}\text{Fe}_{1.75}\text{Si}^{*}_{3.25}\text{O}_{14}$
Crystal dimensions (mm)	$0.04 \times 0.02 \times 0.01$
Crystal system, space group	Trigonal, $P321$
Temperature (K)	295.5(4)
a (Å)	8.0077(5)
b (Å)	8.0077(5)
c (Å)	4.9956(4)
$\alpha \beta \gamma$ (°)	90, 90, 120
V (Å ³)	277.42(4)
Z	1
Calculated density (g cm ⁻³)	3.479
μ (mm ⁻¹)	2.433
Data collection	
Instrument	4-circle Supernova, CCD EOS (Agilent)
Radiation type, wavelength (Å)	$\text{AgK}\alpha$, 0.56087
Number of frames	748
θ range (°)	2.3176, 22.1203
Absorption correction	Multi-scan (Rigaku Oxford Diffraction, 2019)
T_{\min} , T_{\max}	0.83838, 0.83643
No. of measured and independent reflections	3825, 460
R_{int}	0.0561
Data completeness to $19.69^\circ\theta$	100%
Indices range of hkl	$-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $-6 \leq l \leq 6$
Refinement details	
Refinement	Full-matrix least squares on F^2
Number of reflections, parameters, restraints	460/38/0
R_1 [$I > 2\sigma(I)$], R_1 (all)	0.0342, 0.0622
wR_2 [$I > 2\sigma(I)$], wR_2 (all)	0.0382, 0.0631
GoF	1.235
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e ⁻ Å ⁻³)	0.55, -0.70
Flack parameter	-0.07(5)
Determined using 153 quotients [$(I+)$ - $(I-)$]/ $[(I+)+(I-)]$ (Flack, 1983; Parson et al., 2013)	

* - including Al.

Table 3. Site occupation factor (s.o.f.), atomic coordinates and isotropic displacement parameters (Å²) for qeltite.

Site	Atom	s.o.f.	x/a	y/b	z/c	U_{eq}
CaA	Ca	1	0.5745(2)	0	0	0.0159(5)
TiB	Ti	1	1	0	0	0.0125(6)
FeC	Fe	0.584(12)	0	0.23812(19)	0.5	0.0121(5)
SiC	Si	0.416(12)	0	0.23812(19)	0.5	0.0121(5)
SiD	Si	1	0.3333	0.6667	0.4550(6)	0.0103(6)
O1	O	1	0.1549(6)	0.4729(6)	0.3206(8)	0.0149(10)
O2	O	1	0.3333	0.6667	0.7721(15)	0.0171(16)
O3	O	1	0.8560(8)	0.0735(8)	0.2421(10)	0.0315(14)

Table 4. Anisotropic displacement parameters (Å²).

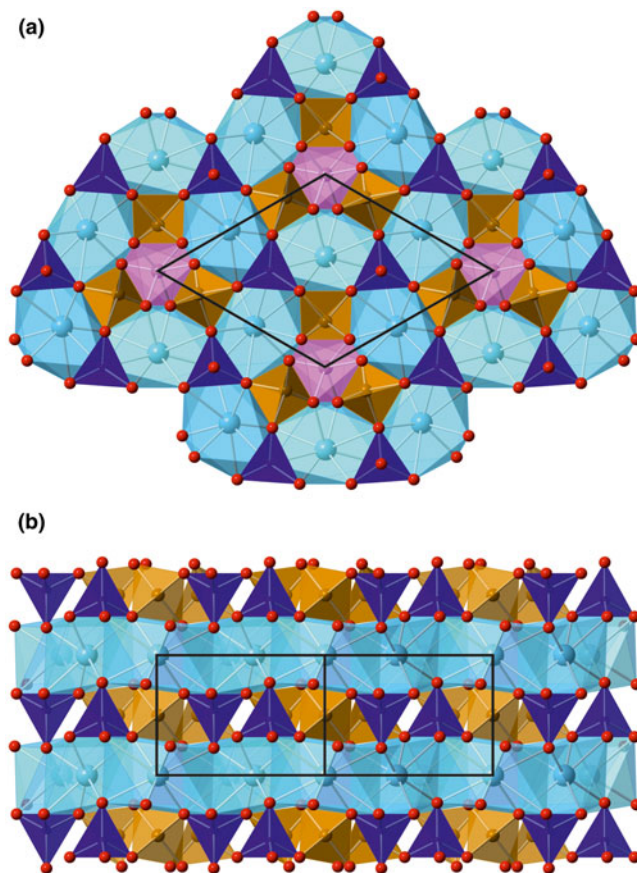
Site	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
CaA	0.0150(7)	0.0218(12)	0.0133(9)	0.0109(6)	0.0014(4)	0.0028(8)
TiB	0.0138(9)	0.0138(9)	0.0099(14)	0.0069(4)	0	0
FeC	0.0123(9)	0.0128(7)	0.0111(8)	0.0062(4)	-0.0035(6)	-0.0018(3)
SiC	0.0123(9)	0.0128(7)	0.0111(8)	0.0062(4)	-0.0035(6)	-0.0018(3)
SiD	0.0105(9)	0.0105(9)	0.0100(14)	0.0052(4)	0	0
O1	0.016(2)	0.011(2)	0.012(2)	0.0024(19)	-0.0044(17)	0.0012(18)
O2	0.020(3)	0.020(3)	0.011(4)	0.0100(13)	0	0
O3	0.018(3)	0.041(3)	0.037(3)	0.017(3)	-0.003(2)	-0.020(2)

Table 5. Selected interatomic distances (Å) for qeltite.

^A Ca-O1	2.403(4) × 2	^C Fe-O1	1.883(4) × 2
^A Ca-O1	2.868(4) × 2	^C Fe-O3	1.791(5) × 2
^A Ca-O2	2.645(3) × 2	Mean	1.837
^A Ca-O3	2.358(5) × 2	^C Fe-O3	2.564(6) × 2
Mean	2.569	Mean	2.079
^B Ti-O3	1.954(5) × 6	^D Si-O1	1.638(4) × 3
		^D Si-O2	1.584(8)
		Mean	1.62

Table 6. Bond valence calculations for qeltite (valence units). Bond valence parameters were taken from (Gagné and Hawthorne, 2015).

	O1	O2	O3	Sum
^A Ca	0.2974 ^{2→1} 0.0954 ^{2→1}	0.1646 ^{2→31}	0.3320 ^{2→1}	1.78
^B Ti			0.6739 ^{6→1}	4.04
^C (Fe _{0.53} Si _{0.20} Al _{0.15} Ti _{0.13})	0.7225 ^{2→1}		0.9329 ^{2→1} 0.1090 ^{2→1}	3.29
^D Si	0.9647 ^{3→1}	1.1083		4.00
Sum	2.08	1.60	2.05	

**Figure 5.** Structure of qeltite. (a) projection on (001), (b) projection on (100). The unit cell is shown by a black line. Key: Ca polyhedra - blue; Ti octahedra - pink; Si tetrahedra - navy blue; Fe tetrahedra - light brown. Drawn using *CrystalMaker*® software for Windows 2.7.

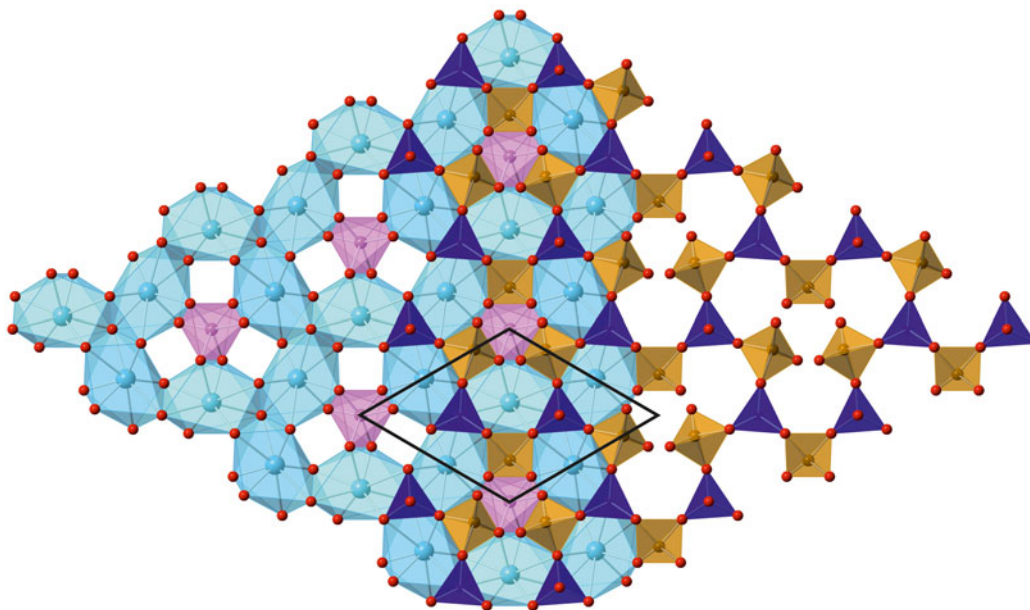


Figure 6. Projection of qeltite structure on (001). Two layers – polyhedral ($z=0$) and tetrahedral ($z=1/2$) in the qeltite structure are shown. Unit cell is shown by the black line. Key: Ca polyhedra – blue; Ti octahedra – pink; Si tetrahedra – navy blue; Fe tetrahedra – light brown. Drawn using *CrystalMaker*[®] software for Windows 2.7.

The Ti^{4+} site coordinated by six oxygens is usually called the octahedral site. However, a more accurate description would be a trigonal trapezohedron truncated by a pinacoid, which has left and right forms. Comparison of the structures of paqueite and qeltite shows that they are right and left forms of the archetypal langasite structure (Galuskina *et al.*, 2023). It is interesting that the qeltite space group $P321$ does not have screw axes, which are a necessary condition for the appearance of enantiomorphic forms (Fecher *et al.*, 2022). Chirality in phases with the langasite-type structure is related to the effects of specific structural disordering in the distribution of electron density, which leads to the formation of a pseudoscrew axis with the period $3c$ (Dudka and Mill, 2014).

Qeltite in paralava is usually confined to small oval aggregates of fine-grained minerals against a coarse-grained background of rock-forming minerals (Fig. 2b,c). As a rule, these aggregates are enriched in elements that are incompatible with rock-forming minerals, such as Ti, Fe, Ba, U, V and Nb (Galuskina *et al.*, 2017a). In similar aggregates, a series of new minerals and varieties characterised by unusual composition and structure, such as hexacelsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$, zadovite, $\text{BaCa}_6[(\text{SiO}_4)(\text{PO}_4)](\text{PO}_4)_2\text{F}$, aradite, $\text{BaCa}_6[(\text{SiO}_4)(\text{VO}_4)](\text{VO}_4)_2\text{F}$, gurimite, $\text{Ba}_3(\text{VO}_4)_2$, mazorite, $\text{Ba}_3(\text{PO}_4)_2$, benneshierite, $\text{Ba}_2\text{Fe}^{2+}[\text{Si}_2\text{O}_7]$, uranium-bearing cuspidine, $\text{Ca}_8(\text{Si}_2\text{O}_7)_2\text{F}_4$, vorlanite, $\text{Ca}(\text{U}^{6+})\text{O}_4$, and khesinite, $\text{Ca}_4\text{Mg}_2\text{Fe}_{10}^{3+}\text{O}_4[(\text{Fe}_{10}^{3+}\text{Si}_2)\text{O}_{36}]$, has been described. Previously, we interpreted similar aggregates as a crystallisation of minerals from residual melt (liquid) enriched with incompatible elements, which remained between crystals of pre-existing rock-forming minerals. The paralavas have no flow structures and are completely crystallised, and the size of rock-forming minerals reaches more than 1 cm. These aggregates rather resemble pegmatites and veins, in which minerals crystallise in a particular direction from the walls of a cavity. We also cannot exclude the possibility that the enrichment of small fragments of paralava is conditional on the inhomogeneity of protholith and weakly homogenised melt. If such an assumption is valid, the aggregates with Ba, U, Fe–Ti and V mineralisation should be

interpreted as refractory inclusions, like those which occur in meteorites. The Ti–Al-analogue of qeltite – paqueite, $\text{Ca}_3\text{Ti}(\text{Al}_2\text{Ti})\text{Si}_2\text{O}_{14}$ – has been described in such inclusions (Ma *et al.*, 2022). Khesinite, a mineral analogue of the SFCA phase (silico-ferrite of calcium and aluminium), which appears in products of the calcination of iron ore at temperatures above 1200°C (Galuskina *et al.*, 2017b), occurs in association with qeltite. The temperature of crystallisation of paqueite in association with iron phosphides, osbornite and pseudowollastonite from explosive breccia of the Hatrurim Complex in Israel was higher than 1250°C (Galuskin *et al.*, 2022). Similarly, the temperature of qeltite crystallisation in paralava was $\sim 1200^\circ\text{C}$. High-temperature and near-surface conditions of qeltite genesis probably defines its absence in terrestrial magmatic and metamorphic rocks, which contain widely distributed Ti-rich garnets close to it in composition. Nevertheless, intimate intergrowths of qeltite with Ti-garnets in paralavas of the Hatrurim Complex indicate that the conditions for its crystallisation can be realised in high-temperature magmatic systems of defined composition.

Acknowledgements. The authors thank Peter Leverett, Sergey Britvin and the anonymous Reviewer for their careful revision and useful comments that improved an early version of the manuscript. Investigations were supported by the National Science Center of Poland [grant number 2021/41/B/ST10/00130 (E.G., I.G.) and grant number 2019/33/B/ST10/02671 (K.W.)].

Supplementary material. The supplementary material for this article can be found at <https://doi.org/10.1180/mgm.2024.38>.

Competing interests. The authors declare none.

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