

CAYSICHITE-(Y) $\text{Ca}_4(\text{Y,REE})_4(\text{Si}_8\text{O}_{20})(\text{CO}_3)_6 \cdot 8\text{H}_2\text{O}$: ENDMEMBER COMPOSITION AND STRUCTURE ESTABLISHED FROM NEW OCCURRENCES ACROSS DIFFERENT GEOLOGIC SETTINGS

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ABSTRACT

The heavy rare earth element silicate-carbonate mineral caysichite-(Y) $[\text{Ca}_4(\text{Y,REE})_4(\text{Si}_8\text{O}_{20})(\text{CO}_3)_6 \cdot 8\text{H}_2\text{O}]$ was discovered in the alkaline granite of the Golden Horn Batholith, near Washington Pass, Okanogan County, Washington, USA, as sub-millimeter euhedral orthorhombic pale white crystals in a single miarolitic cavity in biotite granite. Based on comparative electron microprobe, single-crystal X-ray diffraction, and Raman analyses of caysichite-(Y) from both the Golden Horn and Mount Malosa (Malawi) localities, the ideal endmember composition and space group *Pnmm* with orthorhombic unit cell parameters $a = 13.2577(5) \text{ \AA}$, $b = 13.9816(5) \text{ \AA}$, and $c = 9.7440(4) \text{ \AA}$ was determined. This structure and range of composition is distinct from caysichite-(Y) from the type locality Evans-Lou (Canada), where re-investigation confirms the space

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group $Ccm2_1$, with high REE Σ_{REE} (0.7–1.0) *apfu* and Al^{3+} (0.02–0.23) *apfu* in agreement with the original work of Mellini & Merlino (1978) and Hogarth *et al.* (1974), respectively. In contrast, Golden Horn and Mount Malosa caysichite-(Y), with an absence of Al^{3+} and Σ_{REE} (0.5–0.8) *apfu*, exhibit a euhedral crystal habit with distinct Ca-Y site ordering, establishing the ideal endmember composition of $Ca_4(Y,REE)_4(Si_8O_{20})(CO_3)_6 \cdot 8H_2O$. The Evans-Lou composition, close to $(Ca,REE)_3(Y,REE)_5(Si_8O_{20})(CO_3)_6(OH) \cdot 7H_2O$, derives from the two coupled substitutions $Ca^{2+} + H_2O \leftrightarrow REE^{3+} + OH^-$ and $Si^{4+} + Ca^{2+} \leftrightarrow REE^{3+} + Al^{3+}$. The substitutions together with the Ca-Y site disorder suggest rapid crystallization from a secondary hydrothermal solution as fine grained acicular crusts, whereas the well-defined Golden Horn and Mount Malosa caysichite-(Y) crystals appear to have derived from late-stage primary fluids.

Keywords: caysichite-(Y), Golden Horn Batholith, Evans-Lou Mine, Mount Malosa, crystal structure, endmember, coupled substitution.

INTRODUCTION

Caysichite-(Y) (abbreviation Cay-Y) was first identified from the pegmatite of the Evans-Lou feldspar mine (Quebec, Canada) by Hogarth *et al.* (1974). The mineral occurs as intergrown microscopic needles forming a thin crust, lining cavities in a rare earth element (REE)-rich granite pegmatite (Brown 1982). It is named after its composition of calcium (Ca), yttrium (Y), silicon (Si), carbon (C), and hydrogen (H) as Ca-Y-Si-C-H-ite. Hogarth *et al.* (1974) reported the unit cell of Evans-Lou caysichite-(Y) as orthorhombic with $a = 13.30 \text{ \AA}$, $b = 13.95 \text{ \AA}$, and $c = 9.74 \text{ \AA}$, with possible space groups $Ccmm$ or $Ccm2_1$. The crystal structure of this material was subsequently solved and reported as $Ccm2_1$ by Mellini & Merlino (1978).

Caysichite-(Y) has since been reported from a number of primarily granitic localities worldwide. Most significantly, it has qualitatively been identified from the alkaline granites of Mount Malosa, Zomba, Malawi (Massanek 1999), occurring locally as up to ~1 cm large euhedral rhombohedral crystals, which suggests possible differences in crystal chemistry and structure compared to Evans-Lou. Recently, up to millimeter-sized euhedral caysichite-(Y) of similar habit was discovered (Becker 2018, *pers. commun.*) from a new locality in the alkali granite of the Golden Horn Batholith at Washington Pass, Okanogan County, Washington State, USA, in small cavities in a REE-mineral rich pegmatite.

The chemical composition by Hogarth *et al.* (1974) with low Y, high REE, and significant Al, suggests an unusual composition because of the secondary alteration origin of caysichite-(Y) at the Evans-Lou locality. Moreover, the original space group and structure refinement is uncertain because of the low number of diffraction peaks analyzed (Mellini & Merlino 1978). With the increasing economic and scientific importance of heavy rare earth element (HREE) minerals and related synthetic materials, a better understanding of composition, structure, and geological setting of caysichite-(Y), and similar HREE silicate-carbonate minerals, is highly desirable.

We performed electron probe microanalysis (EPMA), single-crystal X-ray diffraction (XRD) and micro-Raman spectroscopy to reinvestigate and compare caysichite-(Y) from the Evans-Lou locality with caysichite-(Y) from the Golden Horn and Mount Malosa. We observe distinct differences in morphology, space groups, Ca-Y site ordering, and composition and establish substitution vectors and endmember relationships.

Caysichite-(Y)

Initial work by Miles *et al.* (1971) at the Evans-Lou pegmatites recognized a yet unknown mineral species by preliminary XRD. The mineral occurs as thin crusts of acicular crystals of long prismatic habit with the prism $\{hk0\}$ in combination with a dipyrmaid $\{hkl\}$, with some crystals also showing a pinacoid $\{100\}$ or $\{010\}$ and a prism $\{0kl\}$ or $\{h0l\}$. The cross section appears pseudotetragonal. This unknown mineral was subsequently identified as caysichite-(Y) by Hogarth *et al.* (1974) and Mellini & Merlino (1978) based on electron microprobe and XRD analyses. Caysichite-(Y) was described as having Mohs hardness of $4\frac{1}{2}$, having a density of 3.03 g/cm^3 , and being optically biaxial (–), with suggested ideal endmember formula $Ca_2Y_2Si_4O_{10}(CO_3)_3 \cdot 4H_2O$ (Hogarth *et al.* 1974).

Caysichite-(Y) was subsequently reported from similar geological settings from Rio Stogia (Liguria, Italy), Ploskaya Mountain (Murmansk Oblast, Russia) (Krivovichev *et al.* 2025), Rovgora Mountain (Russia) (Pekov *et al.* 2009), Lindvikskollen-Kalstadgangen pegmatite (Kragersø, Vestfold og Telemark, Norway), Röhrnbach (Freyung-Grafenau District, Bavaria, Germany), Verkhnee Espe Deposit (Kazakhstan) (Dolgoplova *et al.* 2017), Paratoo Copper Mine (Flinders Range, South Australia) (Wallwork *et al.* 2002), and the Suishouyama Pegmatite (Fukushima Prefecture, Japan) (Kristiansen 1993, 2010), all as small grains or crusts.

In 1999 large specimens from Mount Malosa (Malawi) in the collection of the Bergakademie Freiberg that were originally misidentified as natrolite were recognized as caysichite-(Y) (Massanek 1999). In

contrast to the sub-millimeter crystals from other localities, Mount Malosa caysichite-(Y) stands out with pale to light pink, elongated, well-defined prismatic crystals occasionally exceeding 1 cm in length. The crystals appear to be zoned, with a clear core and a white opaque rim. Most recently, we discovered caysichite-(Y) of similar habit, yet of smaller (<2 mm) size, in the Golden Horn Batholith of the North Cascades (Washington State, USA).

GEOLOGICAL SETTINGS

Golden Horn Batholith

The Golden Horn Batholith is a shallow peralkaline granitic intrusion of Eocene age (50–47 Ma) in the crystalline core of the North Cascade Mountains in Washington State, USA (Misch 1966, Stull 1969, Boggs 1984, Eddy *et al.* 2016). There are four phases of granitic intrusions in the batholith. These phases range from a peralkaline arfvedsonite granite, a less alkaline transitional “border granite”, and two different types of biotite granites (Boggs 1984). The granites are unusually rich in otherwise rare, Zr-bearing silicate minerals. These include the Zr-bearing milarite-group mineral sogdianite $\text{KZr}_2\text{Li}_3\text{Si}_{12}\text{O}_{30}$ (Dusmatov *et al.* 1968, Cooper *et al.* 1999, Sokolova *et al.* 2000), the related tihualite-group mineral zektzerite $\text{LiNa}(\text{Zr,Ti,Hf})[\text{Si}_6\text{O}_{15}]$ (type locality, Dunn *et al.* 1977; Boggs 1984), and their intergrowth. Both minerals are in part rock forming but also occur locally abundantly in miarolitic cavities as euhedral crystals up to several centimeters in size. In addition, the Golden Horn Batholith is the type locality of the hilairite group mineral calciohilairite $\text{CaZrSi}_3\text{O}_9(\text{H}_2\text{O})_3$ (Boggs 1988) and of okanoganite-(Y) $(\text{Y,REE,Ca,Na,Th})_{16}(\text{Fe}^{3+},\text{Ti})(\text{Si,B,P})_{10}(\text{O,OH})_{38}\text{F}_{10}$ (Boggs 1980). A wide range of other rare REE minerals have been noted in small miarolitic cavities in the Golden Horn Batholith, including REE-carbonates (bastnäsite and synchysite), allanite-(Ce), clinofergusonite-(Y), chevkinite-(Ce), euxenite-(Y), gadolinite, gagarinite, kainosite-(Y), and pyrochlore group minerals (Becker 1991, Boggs 1980, 1984, 1988). Following these early works, the unusual mineral assemblage of the Golden Horn Batholith has again attracted recent interest with the discovery and description of the milarite-group mineral brannockite $\text{KLi}_3\text{Sn}_2\text{Si}_{12}\text{O}_{30}$ as only the second known occurrence (Raschke *et al.* 2016) and of the rare HREE silicate thalénite-(Y) (Raschke *et al.* 2018).

Golden Horn caysichite-(Y)

The Golden Horn caysichite-(Y) was found in a single pegmatite body in arfvedsonite granite (Becker 1978).

The “Sogdianite Pegmatite,” as it is called by local collectors due to the abundant sogdianite and zektzerite which occur as both rock-forming minerals as well as etched crystals in cavities together with caysichite-(Y), originally had approximate dimensions of $120 \times 60 \times 20$ cm and was exposed only on one side in a talus slope below State Highway 20 near milepost 164.5. The pegmatite, now partially removed, consisted of massive coarse-grained dark smoky quartz, pale greenish white microcline, and pink to purple masses and crystal sections of intergrown sogdianite and zektzerite (Boggs 1984). The exposed core of the pegmatite contained abundant miarolitic cavities up to 5 cm in diameter, decreasing in number and size toward the margin of the pegmatite. Caysichite-(Y) was typically found as up to 1 mm long, opaque, white crystals of square cross section, with either no or crude terminations, but sometimes with a clear core. Many crystals are partially or completely altered to a white clay. Associated with caysichite-(Y) are well-formed crystals of smoky quartz, microcline, aegirine, titanite, polyolithionite, bastnäsite-synchysite, as well as etched sogdianite, zektzerite, and kainosite-(Y) (Boggs 1984), all of which are frequently covered in brown iron oxides.

Mount Malosa caysichite-(Y)

The pear-shaped Zomba plateau north of the town of Zomba is separated into the Zomba mountains in the south and Mount Malosa in the north. It is part of the Cretaceous Chilwa alkaline province, which hosts several granite, syenite, and nepheline-syenite plutons (Eby *et al.* 1995, Cairncross 2002, Guastoni *et al.* 2007). The Zomba-Malosa pluton is composed of a central syenite core and a peralkaline granite margin (Bloomfield 1965 and references therein, Eby *et al.* 1995). The miarolitic alkaline pegmatites crystallized at shallow depth occur primarily on Mount Malosa itself and the flanks of the Zomba-Malosa massif. The pegmatites are sub-horizontal with large meter-size cavities containing albite, aegirine, arfvedsonite, microcline, niobophyllite, pyrochlore, different Nb-Ta-Y oxides, Be-Na-Y-Zr-Ba-silicates (notably epididymite and berylite), quartz, synchysite, bastnäsite-(Ce), parisite, kainosite-(Y), xenotime-(Y), zircon, and minor other REE and rare element minerals.

Caysichite-(Y) occurs as well-formed euhedral centimeter-sized white crystals in the REE-rich granite pegmatites, isolated or as aggregates, often associated with or growing on aegirine and associated with quartz and orthoclase.

Evans-Lou caysichite-(Y)

The Evans-Lou Mine is on a granitic pegmatite in the Grenville Province, near the town of Wakefield,

Quebec, located *ca.* 40 km north of Ottawa, Papineau Co., Quebec. The Evans-Lou pegmatite is one of several REE-mineral bearing pegmatites in the region. The pegmatite is characterized by asymmetric zoning, chiefly with an outer perthite-plagioclase-quartz zone, inner perthite-quartz zone with large vugs, and a quartz core, with REE mineralization concentrated at the contact between the core and the host quartz diorite-granodiorite, quartz monzonite, and calc-silicate rock (Miles *et al.* 1971). The rock types reflect the geodynamic development during the Grenville orogeny in which island arcs and backarc basins were subducted below Laurentia before its collision with two crustal blocks.

The pegmatite dike of the Evans-Lou Mine has a maximum width of 25 m and was intermittently mined for quartz and feldspar from 1932 to 1952 (Miles *et al.* 1971). The Evans-Lou pegmatite is mineralogically highly diverse, with more than 66 mineral species identified to date, with most of the REE mineralization near the contacts of the quartz core with the perthite-quartz zone (Sabina 1986). It contains large primary hellandite, fergusonite, allanite, and Y-bearing spessartine. Caysichite-(Y), kainosite-(Y), lokkaite-(Y), tengerite-(Y), and synchysite-(Y) as the main REE bearing carbonates are thought to have formed from alteration of hellandite-(Y) from carbonate containing slightly alkaline hydrothermal fluids percolating through the vuggy quartz. Besides caysichite-(Y), the Evans-Lou pegmatite is the type locality for wakefieldite-(Y) $\text{Y}(\text{VO}_4)$ (Miles *et al.* 1971) and moydite-(Y) $(\text{Y,REE})[\text{B}(\text{OH})_4](\text{CO}_3)$ (Grice *et al.* 1986, Grice & Ercit 1986).

As seen in Figure 1a, Caysichite-(Y) occurs at the Evans-Lou pegmatite as colorless to white or rarely yellow to green crystals, ranging from a powdery coating to radiating crystal aggregates, with individual acicular crystals up to ~ 0.5 mm in length, coating fractures and cavity walls in quartz, feldspar, and hellandite-(Y), often associated with fergusonite-(Y), kainosite-(Y), tengerite-(Y), and lokkaite-(Y).

MATERIAL AND ANALYTICAL METHODS

Single-crystal XRD of different samples was performed on two different instruments. XRD of the Golden Horn and Mount Malosa samples was performed at the University of Colorado (D8 Quest ECO diffractometer, Bruker) using $\text{MoK}\alpha$ X-ray radiation ($\lambda = 0.71073$ Å, source operating at 50 kV and 20 mA) with a CMOS area detector (PHOTON 50) to record diffraction patterns in a shutterless mode at controlled 300 K (Cryostream cryostat, Oxford Instruments). Three caysichite-(Y) crystal grains from the Golden Horn (WP108, WP108_S3, and WP108_11) and one from the Mount Malosa (CE_ML_12) locality were

selected and mounted in arbitrary orientation. For data collection parameters see Table 1. Unit cell parameters were refined from intensity position parameters of well-resolved peaks.

For XRD of Evans-Lou caysichite-(Y), crystal fragments were taken from sample KNR 36689 at the Natural History Museum, Oslo. XRD was performed at the Natural History Museum (Synergy-S diffractometer, Rigaku) at room temperature both with $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) and $\text{CuK}\alpha$ ($\lambda = 1.54184$ Å) radiation provided by microfocus sources operating at 50 kV and 1 mA (PhotonJet). A hybrid photon counting detector (HyPix-6000He) was used and data collection, subsequent data reduction, and absorption correction were carried out with the CrysAlisPro software.

Quantitative electron probe microanalysis and imaging was performed at the Center for Geosciences (GFZ) Potsdam (field-emission JEOL Hyperprobe JXA 8530F+). Individual crystals and crystal aggregates of caysichite-(Y) from the three localities were embedded into a 25 mm epoxy mount, polished, and carbon coated. The electron probe microanalysis was performed in wavelength-dispersive mode using an acceleration voltage of 20 kV, a beam current of 5 nA, and an electron beam size of 15 μm . The low current and de-focused beam ensured minimal beam damage to the sample. Counting times on the peaks varied between 10 and 40 s, and corresponding backgrounds were collected in half of the peak acquisition time. Matrix correction was performed using a $\phi(\rho Z)$ correction scheme (CITZAF; Armstrong 1995). Under these conditions, detection limits are ≤ 0.02 wt.% for Al, Mg, Ca; ≤ 0.03 wt.% for Lu, Yb, Eu, Fe; ≤ 0.04 wt.% for Ce, La, Si; ≤ 0.05 wt.% for Dy, Tb, Nd, Sm, Ho, Er, Gd, Pr, and *ca.* 0.07 wt.% for Y. Analytical errors are $< 1\%$ for elements with a concentration ≥ 10 wt.% and 10–20% at the 0.2–1 wt.% level. Details about the X-ray lines, the diffracting crystals, and the peak position as well as standard information and overlap corrections can be found in Table S1. Back-scattered electron (BSE) and secondary-electron (SE) images were also obtained. Element distribution maps were acquired at 20 kV, 4 nA, with 1 μm electron beam size and x-y measurement intervals of 1 μm , avoiding overlaps. Dwell time was set to 100 ms to avoid crystal damage.

Micro-Raman spectroscopy was performed on a custom micro-Raman microscope at the University of Colorado (Department of Physics), with 633 nm HeNe laser excitation at 1 mW, 100 $\times$ objective of NA = 0.8, using an imaging spectrograph (Princeton Instruments SP-2500 with ProEM 1600² thermoelectrically cooled) calibrated on multiple lines using a neon-argon lamp.

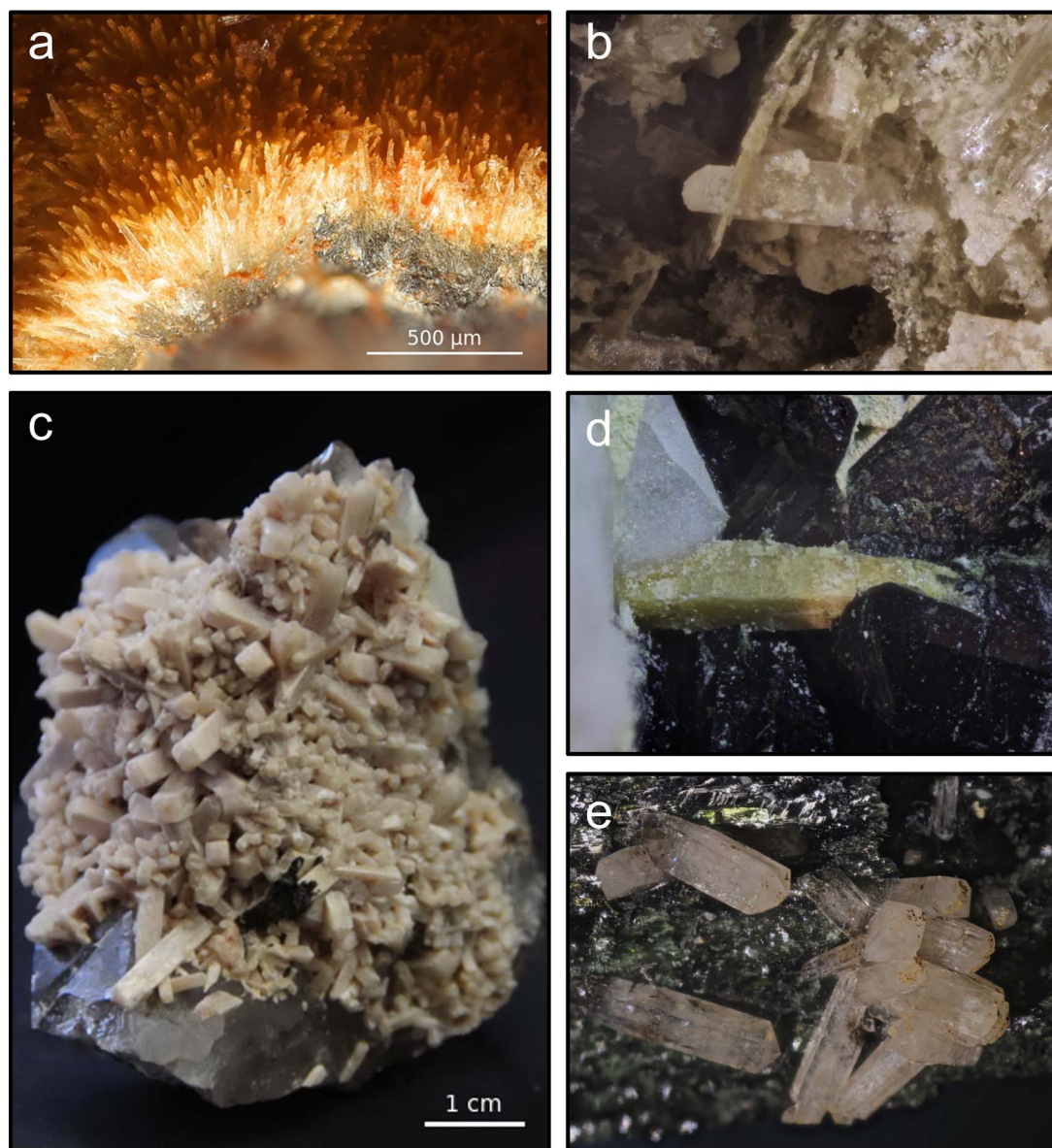


FIG. 1. (a) Caysichite-(Y) encrustation from Evans-Lou Mine, Quebec, Canada (Mindat Photo ID: 688154, photograph by Stephan Wolfsried, used with permission). (b) Caysichite-(Y) cluster on arfvedsonite matrix with annite from Washington Pass, Golden Horn Batholith, Washington, USA. The crystals are typically tan opaque; the crystal in the center is penetrating annite. (c) Larger pale caysichite-(Y) crystals up to 1 cm in length from Mount Malosa, Malawi (Mindat Photo ID: 493722, photograph by László Horváth). (d) Tan brown caysichite-(Y) embedded in a matrix of arfvedsonite and microcline. (e) Cluster of caysichite-(Y) on aegirine from Mount Malosa, Zomba, Malawi, as characteristic semi-transparent pink crystals (photograph by Michael Goble).

TABLE 1. UNIT CELL AND DATA COLLECTION PARAMETERS FOR CAYSICHITE-(Y)

	Golden Horn		Mt. Malosa		Evans-Lou	
	WP108	WP108-S3	WP108-11	CE-ML-12	EL-osme1	Mellini ^a
Crystal size	0.12 × 0.10 × 0.08 mm					0.05 × 0.03 × 0.18 mm
a (Å)	13.2577(5)	13.2604(5)	13.2439(3)	13.2545(4)	13.2753(3)	13.27(1)
b (Å)	13.9816(5)	13.9834(5)	13.9685(4)	13.9805(5)	13.9232(3)	13.91(1)
c (Å)	9.7440(4)	9.7453(4)	9.7351(2)	9.7337(3)	9.7362(2)	9.73(1)
V (Å ³)	1806.19(9)	1807.03(5)	1800.97(4)	1803.70(5)	1799.57(3)	
Space group	<i>Pnmm</i>	<i>Pnmm</i>	<i>Pnmm</i>	<i>Pnmm</i>	<i>Pnmm</i>	<i>Ccmm</i> or <i>Ccm2₁</i>
2θ max	72.94°	71.26°	80.76°	80.80°	72.57°	70°
Reflections measured	145,945	144,591	218,074	186,096	42,964	2169
Unique reflections	4567	4297	5872	5898	4273	959
R (σ)	0.0216	0.0245	0.0284	0.0337	0.0440	0.06
R _{int}	0.0829	0.1047	0.1103	0.1221	0.028	
R1	0.033	0.036	0.042	0.071	0.069	

^a Mellini & Merlino (1978).

RESULTS

Composition and substitution

Back-scattered electron imaging and elemental mapping of Al, Si, Dy, Y, Yb, and Er were performed to identify chemical zonation and variations between crystals, with selected images shown in Figure 2. Evans-Lou samples (Fig. 2a) show no zonation but some pronounced crystal-to-crystal compositional variation in the concentration of Al. The Mount Malosa samples (Fig. 2b–d) exhibit a mostly homogeneous crystal core, but variations in HREE concentration near the rim. This is also reflected in the cross section of a larger crystal fragment (Fig. 2e). In contrast, the Golden Horn samples (Fig. 2f–h) show no detectable zonation and only small crystal-to-crystal variations in REE concentration.

Table 2 shows representative analysis results and averages of analyses of similar composition reflecting the range and main compositional characteristics observed. The atomic proportions have been calculated assuming a total of 26.5 *apfu* oxygen equivalents and fixed values of 6 CO₃^{2–}.

The Golden Horn caysichite-(Y) is characterized by small chemical variations with high Ca²⁺ and Y+REE close to 4 *apfu*. Mount Malosa caysichite-(Y) shows a wider variation, compositionally overlapping with the Golden Horn, yet extending to lower Ca and higher Y+REE values, and Y locally exceeding 4 *apfu*. In contrast, the Evans-Lou caysichite-(Y) is compositionally distinct, with high Y (3.91–4.05 *apfu*), REE locally > 1 *apfu*, REE+Y (4.80–4.93 *apfu*), low Ca (2.91–3.06 *apfu*), and the presence of Al (0.02–0.23 *apfu*). The composition for Evans-Lou caysichite-(Y) is in very good agreement with the original analysis of Hogarth *et al.* (1974) from the Evans-Lou Mine, with only slightly larger medium REE yet smaller HREE content. The Ca deficit of 1.08 *apfu* with respect to the ideal value of 4 seems largely compensated by an excess of REE+Y by 0.80 *apfu* to which REE contribute with >0.8 *apfu*, implying charge balancing through Si⁴⁺ ↔ Al³⁺.

Figure 3 shows a plot of Ca²⁺ + Fe²⁺ versus REE³⁺ + Y³⁺ + Al³⁺ reflecting the above trends. The good agreement of the ideal slope of –1 (dashed line) with the linear fit (slope –0.883 with R² = 0.98) establishes the coupled substitution vectors Ca²⁺ + H₂O ↔ REE³⁺ + OH[–] and Si⁴⁺ + Ca²⁺ ↔ REE³⁺ + Al³⁺. Based on these substitutions the OH[–] content can be derived, ranging from 0.64 to as low as 0.16 *apfu* for Golden Horn and Mount Malosa, with higher values of 0.78–0.89 for Evans-Lou. These findings establish the ideal endmember compositions as Ca₄(Y,REE)₄(Si₈O₂₀)(CO₃)₆·8H₂O for the case of four Ca²⁺ and no OH[–] and as (Ca,REE)₃(Y,REE)₅(Si₈O₂₀)(CO₃)₆(OH)·7H₂O

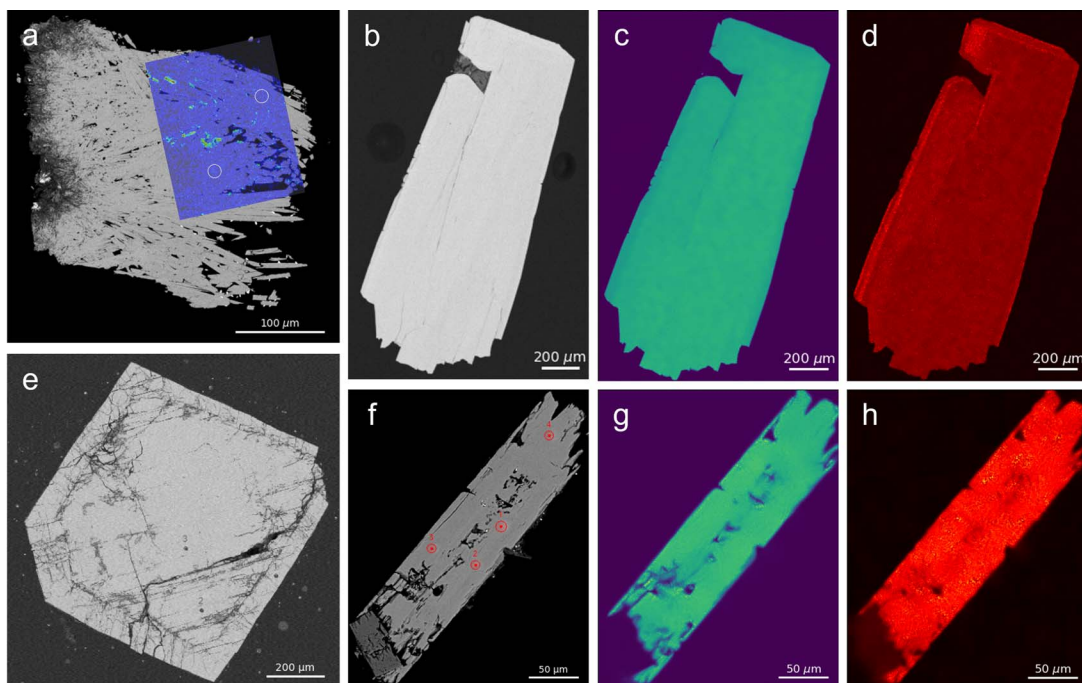


FIG. 2. BSE element maps of caysichite-(Y). (a) SEM image of Evans-Lou caysichite-(Y) with overlay of Al element map (blue) with homogeneous regions circled. (b) Mount Malosa caysichite-(Y) crystal, with element maps of (c) Y and (d) Er and (e) cross section. Golden Horn caysichite-(Y), with element maps of (g) Y and (h) Er. Element map images were processed with a non-local means denoising algorithm to improve clarity (with $h = 18$ and 22 for the Mount Malosa and Golden Horn images, respectively).

for the case of REE substitution on the Ca site with the introduction of OH^- to replace H_2O .

We thus infer representative chemical formulae as follows with charge neutrality achieved by the conversion of H_2O into OH^- based on the substitution vector above:

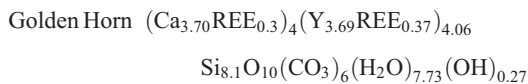
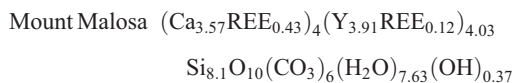
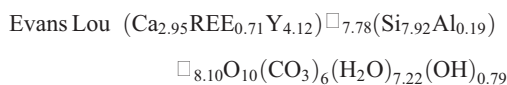


Figure 4 shows a comparison of the chondrite-normalized REE+Y pattern of the average values of the three localities and the original data from Hogarth *et al.* (1974). Distinct Eu anomalies are observed in the data for

all localities, yet not in the original analysis of Hogarth *et al.* (1974). The low REE content of Golden Horn caysichite-(Y) is evident, with Ce below detection limit, possibly due to the presence of monazite taking up the available Ce. The overall trend of an increase in HREE content is typical for a Y-bearing mineral and corresponding preferential HREE substitution at the respective lattice site.

What stands out are the different trends for the heaviest REE of Tm, Yb, and Lu with decreasing HREE content for Golden Horn and Mount Malosa, compared to a continuous increase or convergence for Evans-Lou caysichite-(Y) for the heaviest of the HREE. That same trend of the depletion of the heaviest HREE (Tm to Lu) was also previously observed in thalénite-(Y) from Golden Horn (Raschke *et al.* 2018). A characteristic M-type tetrad effect is seen and is most pronounced for Golden Horn and Mount Malosa.

Crystallography, structure, and similarities to kainosite

The intensity data collection parameters, as well as refined unit cell parameters, are summarized in Table 1.

TABLE 2A. REPRESENTATIVE AVERAGES OF EPMA FOR CAYSICHITE-(Y)

	Golden Horn		Mount Malosa			Evans-Lou			Mellini
	low REE	avg.	low REE	high REE	avg.	low Al	high Al	avg.	
wt.% oxide									
SiO ₂	30.12	29.72	30.07	29.41	29.74	28.14	28.91	29.08	28.84
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.02	0.07	0.72	0.66	0.58
Y ₂ O ₃	23.58	25.45	24.23	28.79	27.07	25.85	27.93	26.95	28.18
La ₂ O ₃	0.07	0.01	0.01	0.01	0.06	0.13	0.00	0.05	0.08
Ce ₂ O ₃	0.04	0.00	0.18	0.07	0.05	0.36	0.24	0.30	0.24
Pr ₂ O ₃	<0.06	0.04	0.09	0.00	0.08	0.07	0.07	0.06	0.09
Nd ₂ O ₃	0.00	0.16	0.22	0.11	0.05	0.55	0.45	0.47	0.30
Sm ₂ O ₃	0.41	0.11	0.30	0.01	0.06	0.56	0.42	0.43	0.20
Eu ₂ O ₃	0.00	0.00	0.02	0.00	0.02	0.05	0.09	0.05	0.09
Gd ₂ O ₃	1.22	0.69	1.14	0.55	0.69	1.38	1.61	1.45	0.51
Tb ₂ O ₃	0.54	0.22	0.45	0.28	0.28	0.27	0.43	0.38	0.16
Dy ₂ O ₃	3.49	2.57	3.08	2.48	2.48	2.60	2.15	2.18	1.16
Ho ₂ O ₃	0.79	0.56	0.55	0.64	0.55	0.75	0.58	0.58	0.66
Er ₂ O ₃	1.79	2.06	1.32	1.62	1.34	1.92	1.97	1.84	1.84
Tm ₂ O ₃	0.06	0.20	0.08	0.10	0.09	0.25	0.22	0.20	0.21
Yb ₂ O ₃	0.45	0.94	0.34	0.77	0.49	1.85	1.58	1.48	2.12
Lu ₂ O ₃	0.00	0.08	0.03	0.05	0.05	0.23	0.14	0.22	0.42
FeO	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01	0.00
CaO	12.96	12.66	13.11	11.43	12.26	10.06	9.96	9.90	10.04
CO ₂	16.15	16.12	16.16	16.23	16.19	15.58	16.19	16.06	16.01
H ₂ O (H ⁺)	0.92	0.804	0.94	0.40	0.70	0.12	0.18	0.24	0.24
H ₂ O	8.63	8.51	8.66	8.15	8.43	7.56	7.91	7.91	7.88
Total	101.2	100.9	101.0	101.1	100.7	98.35	101.8	100.5	99.9

^a Mellini (1978).

The crystal structure was solved using direct methods in space group *Pnnm* with $a = 9.7440(4)$ Å, $b = 13.2577(5)$ Å, and $c = 13.9816(5)$ Å for Golden Horn (WP108) as example. To maintain consistency with the previously determined structure (Mellini & Merlino 1978), we transposed the cell to space group *Pnmm* with $a = 13.2577(5)$ Å, $b = 13.9816(5)$ Å, and $c = 9.7440(4)$ Å.

The original structure was reported in space group *Ccmm* or *Ccm2₁* (Mellini & Merlino 1978). Because of the small number of reflections measured (2169) the authors may not have observed reflections in violation of C-centering. They recognized that the structure was inconsistent with the *Ccmm* space group and assumed that the structure belonged to the acentric subgroup *Ccm2₁*.

With our much larger data sets for Mount Malosa and Golden Horn samples, we observe reflections inconsistent with a C-space group, such as odd-indexed h reflections in the $(hk1)$ plane, violating the hkl symmetry rule of $h + k = 2n$ (Fig. 5). The data is instead consistent with a primitive *Pnmm* space group which we attribute to the high degree of site ordering between the Ca and Y sites. In contrast, and consistent with Mellini &

Merlino (1978), for our Evans-Lou samples the refinement still suggests the *Ccm2₁* space group as a viable alternative, with this higher symmetry consistent with the lack of site ordering of the Ca and Y sites.

Consequently, for comparison we carried out refinement in both space groups, with both the *Pnmm* and *Ccm2₁* space groups yielding good fits with low R1 values, making the possibility of twinning unlikely. As shown in Table 3, both refinements result in disorder between the Ca and Y sites, making refinement in the higher symmetry C-space group possible. Mellini & Merlino (1978) initially observed a distorted carbonate group when attempting the refinements in the *Ccmm* space group; similarly to Mellini & Merlino (1978), we find that refinement of the Evans-Lou sample in the lower symmetry space group of *Ccm2₁* does not cause distortions to the carbonate groups.

Refinements were conducted using SHELXL (Sheldrick 2015, Hübschle *et al.* 2011). Ionized atom scattering factors for cations (Cromer & Mann 1968) and O²⁻ (Azavant & Lichanot 1993) were used throughout. The scattering factor for Ca²⁺ was used for the Ca site and La³⁺ for the Y site to approximate its mixed Y-HREE

TABLE 2B. REPRESENTATIVE AVERAGES OF EPMA FOR CAYSICHITE-(Y)

	Golden Horn		Mount Malosa			Evans-Lou			Mellini	Ideal
	low REE	avg.	low REE	high REE	avg.	low Al	high Al	avg.		
<i>apfu</i> *										
Si ⁴⁺	8.082	8.010	8.058	7.957	8.006	7.989	7.884	7.983	7.943	8
Al ³⁺	0.000	0.000	0.000	0.000	0.006	0.024	0.231	0.213	0.188	
Y ³⁺	3.367	3.650	3.455	4.145	3.877	3.905	4.053	3.937	4.130	4
La	0.007	0.001	0.001	0.001	0.006	0.013	0.000	0.005	0.008	
Ce	0.004	0.000	0.018	0.007	0.005	0.037	0.024	0.031	0.024	
Pr	0.000	0.004	0.008	0.000	0.008	0.007	0.006	0.006	0.009	
Nd	0.000	0.015	0.021	0.011	0.004	0.056	0.044	0.046	0.030	
Sm	0.038	0.010	0.027	0.001	0.006	0.055	0.040	0.040	0.019	
Eu	0.000	0.000	0.002	0.000	0.002	0.005	0.008	0.004	0.008	
Gd	0.109	0.062	0.101	0.049	0.062	0.130	0.146	0.132	0.047	
Tb	0.047	0.019	0.040	0.025	0.024	0.025	0.039	0.034	0.014	
Dy	0.302	0.223	0.266	0.216	0.215	0.238	0.189	0.193	0.103	
Ho	0.068	0.048	0.047	0.055	0.047	0.067	0.050	0.051	0.058	
Er	0.151	0.175	0.111	0.138	0.114	0.171	0.169	0.158	0.159	
Tm	0.005	0.017	0.006	0.009	0.007	0.022	0.018	0.017	0.018	
Yb	0.037	0.077	0.028	0.063	0.040	0.160	0.131	0.123	0.178	
Lu	0.000	0.006	0.002	0.004	0.004	0.020	0.012	0.018	0.035	
Σ _{REE}	0.766	0.659	0.679	0.579	0.544	1.007	0.876	0.858	0.710	
Σ _{REE+Y}	4.133	4.310	4.134	4.724	4.421	4.912	4.929	4.795	4.824	
Fe ²⁺	0.000	0.000	0.000	0.008	0.000	0.000	0.000	0.002	0.000	
Ca ²⁺	3.725	3.655	3.763	3.312	3.535	3.060	2.910	2.912	2.963	4
Σ _{2+,3+}	7.858	7.964	7.898	8.043	7.962	7.996	8.070	7.922	7.991	
CO ₃ ²⁻ (fixed)	6	6	6	6	6	6	6	6	6	6
H ₂ O	7.824	7.723	7.840	7.361	7.624	7.114	7.164	7.217	7.216	8
OH ⁻	0.176	0.277	0.160	0.639	0.376	0.886	0.836	0.783	0.784	
O ²⁻ (fixed)	20	20	20	20	20	20	20	20	20	20
Total cation	15.94	15.97	15.96	16.00	15.97	15.99	15.95	15.90	15.93	16

* Atomic proportions calculated assuming a total of 26.5 oxygen equivalents and fixed values of 6 CO₃²⁻ ions. The water and OH⁻ ion content is calculated by using the ratios of REE³⁺:Ca²⁺ and Al³⁺:Si⁴⁺ to solve for the amount of OH⁻ needed to achieve charge balance assuming the coupled substitution reaction Ca²⁺ + H₂O ↔ REE³⁺ + OH⁻ and Si⁴⁺ + Ca²⁺ ↔ REE³⁺ + Al³⁺, and assuming ideal compositions of Ca₄(Y,REE)₄(Si₈O₂₀)(CO₃)₆·8H₂O and (Ca, REE)₃(Y,REE)₅(Si₈O₂₀)(CO₃)₆(OH)·7H₂O.

occupation. Occupancies were refined resulting in nominal values greater than one for Ca and less than one for the Y site. These fractional occupancies were converted to electrons in Table 4 and show site ordering, yet suggest minor Y and REE substitution at the Ca site and REE substitution at the Y site for Golden Horn and Mount Malosa. However, the nearly equal electrons per site for Y and Ca in the Evans-Lou samples suggests nearly complete site disorder. Occupancy of the water molecule sites (Ow) was refined initially with all occupancies free (Table S2) and then with occupancies fixed for OH1 and OH2, because of their near full occupancy, with only OW variable. The results show values slightly less than 8 for Golden Horn (7.25–7.55) and Mount Malosa (7.48) and 8.20 for Evans-Lou (compared to 7.86 determined by Hogarth *et al.* (1974) by the Penfield

method). Since we cannot distinguish between O²⁻, OH⁻, and H₂O from the structure refinement alone, we additionally calculated the bond valence sums for the oxygen sites as shown in Table 5. The valence sums for all sites are approximately 2, indicating fully bonded O²⁻ ions, except for OH1 and OH2, which have values of approximately 0.5, consistent with their assignment as OH⁻ or H₂O. Notably, the OH2 site is more strongly bonded in the Evans-Lou sample, indicating a substitution of OH⁻ for H₂O.

Selected bond distances are also shown in Table 6 (for atomic position coordinates and anisotropic displacement parameters see Table S3 in the supplementary data). Final atom positions are reported in the cif files. The bond distances are derived from refinements using neutral atom scattering factors. Bond distances

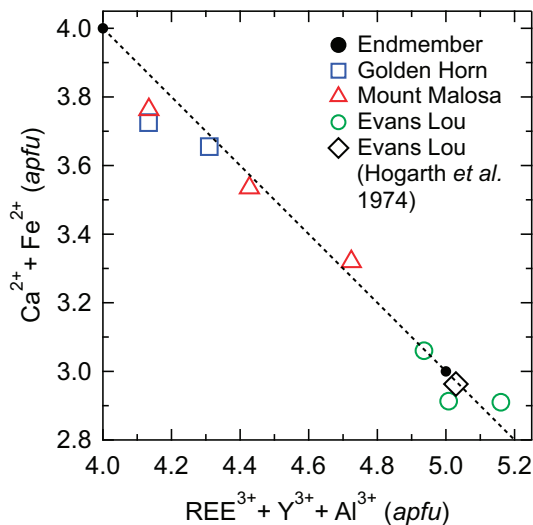


FIG. 3. Occupancy of Ca^{2+} and Fe^{2+} compared to REE^{3+} , Y^{3+} , and Al^{3+} for caysichite-(Y) from the three discussed localities. A linear fit to the measured *apfu* values with slope -0.883 ($R^2 = 0.98$) closely matches the expected anti-correlation for the coupled substitution exchange vector (dashed line) as discussed in the text.

generated using ionic scattering factors are similar and within the uncertainty of the values using atomic scattering factors.

The crystal structure shown in Figure 6 and illustrated in polyhedral form represents the actual relative atomic distances from the refinement. The structure consists of two large-radius sites for the Ca and the rare earth element Y sites, respectively.

There are two silicate tetrahedral sites, Si1 and Si2, that together form a double crankshaft chain parallel to *c*, similar to that in feldspar except that they are isolated and do not form a three-dimensional tetrahedral framework. In the silicate crankshaft chain there are five bridging oxygens, designated Ob1 to Ob5, that bond only to two Si atoms and two silicate oxygens that are bonded to one Si and two of the large-radius cations. The sizes of the tetrahedra are consistent with full occupancy of Si^{4+} cations.

There are two triangular carbonate groups with carbon atoms C1 and C2, one of which lies in a special position on a mirror plane. The two carbonate groups are nearly planar but are not parallel relative to each other as is the case for most pure carbonate minerals. In the carbonate groups, there are five oxygen atoms that are each bonded to one C atom as well as the large-radius cations. The mean C–O distances of both carbonate groups are consistent with pure CO_3^{2-} groups and thus show no indication of N or B substitution.

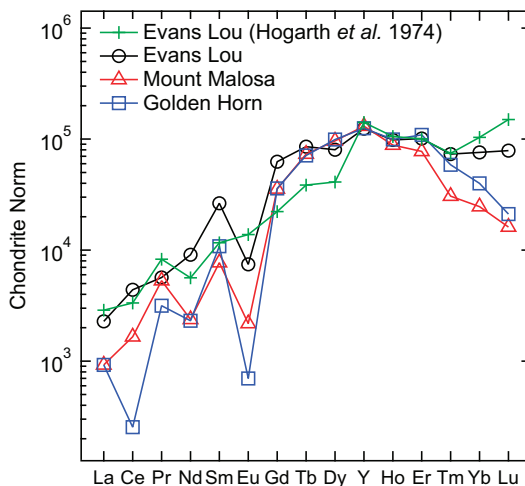


FIG. 4. Chondrite-normalized REE distribution for Golden Horn, Mount Malosa, and Evans-Lou caysichite-(Y) with a distinct pattern for HREE between Golden Horn and Mount Malosa versus Evans-Lou.

One of the water molecule sites (Ow) lies on the mirror plane and is only partially occupied. There are two hydroxyl oxygens that are bonded to one H as well as the large-radius cations. We observe positive electron residua in the difference map that we interpret as H positions on OH1 and OH2. Crystal structure refinement electron densities also showed positive residual positions corresponding to H positions on each of the OH anions. The hydroxyl groups are bonded only to the large-radius cations and not to the Si or C atoms.

For the structure refinements we first assume that the Ca and Y sites are fully occupied. Second, with the radii of the Ca and Y sites both consistent with heavy rather than light REE, we allow for substitution of REE or Y^{3+} on the Ca site following the coupled substitution vector $\text{Ca}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{REE}^{3+} + \text{OH}^-$ as proposed by Mellini & Merlino (1978). Further, they noted that when O(14) is occupied by H_2O both associated cations are expected to be Ca^{2+} . In contrast, if occupied by OH^- one of the linked cations is REE^{3+} . Conversely, on the Y site, we allow for HREE substitution $\text{Y}^{3+} \leftrightarrow \text{REE}^{3+}$.

The refined electron occupancies of the Y and Ca sites indicate electron over-occupancies on both, which we assume to be due to HREE substitution and distribution between both sites. Based on the EPMA results, we identify Dy^{3+} as the representative REE atomic species for the REE site occupancy calculation. We then model the scattering of the Y site with Y^{3+} and Dy^{3+} and the Ca site with Ca^{2+} and Dy^{3+} . We thereby obtained both the Y and Dy as well as the Ca and Dy occupancies for the Y and Ca sites, respectively, as shown in Table 3. The Y, Ca, and Dy *apfu* values, as well as the REE distribution

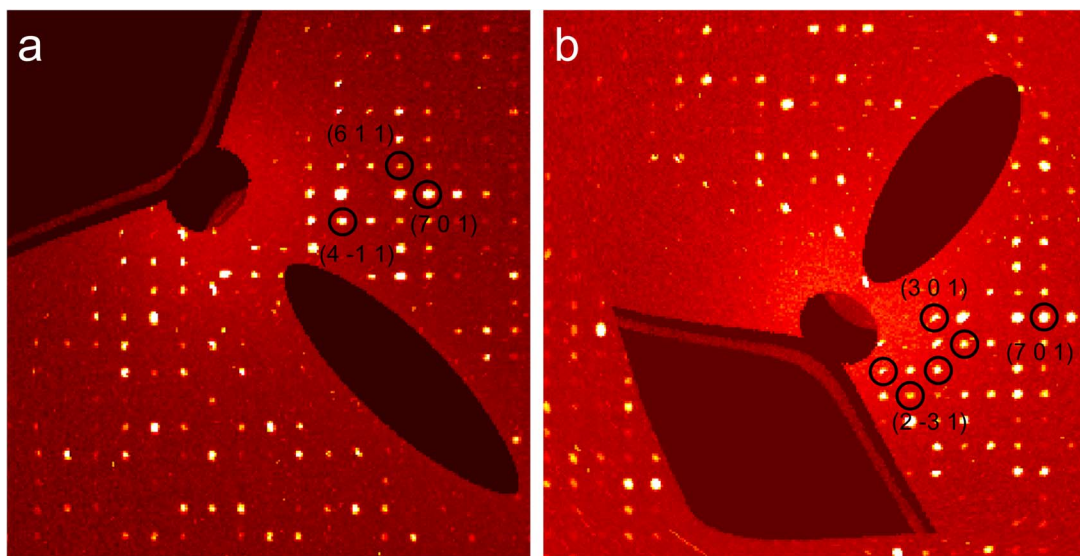


FIG. 5. Precession images of (a) Golden Horn sample WP108-11 and (b) Mount Malosa sample CE-ML-12 in the (hk1) plane. Selected reflections violating the $Ccm2_1$ reflection rules for the hkl family ($h + k = 2n$) are circled in black.

between the sites (with Dy as a stand-in for REE), are in good agreement with the total *apfu* values as derived from EPMA within the uncertainties of EPMA and $\pm 1 e^-$ for XRD *epfu* values. It should be noted, however, that likely some Y^{3+} also resides on the Ca site, compensated by variations in REE distribution. The distinct behavior of the Evans-Lou samples stands out again with its site disorder and higher REE values.

The structural and chemical similarity of caysichite-(Y) to kainosite [ideally $Ca_2(Y,Ce)_2Si_4O_{12}(CO_3) \cdot (H_2O)$] was noted by Mellini & Merlino (1978). Kainosite was identified by single-crystal XRD associated with caysichite-(Y) from Golden Horn as part of this study. It is orthorhombic (point group $2/m2/m2/m$).

Similar to caysichite-(Y), in kainosite-(Y) Ca^{2+} and Y^{3+} occupy crystallographically distinct eight-cornered oxygen polyhedra with 12 triangular faces (D-dodecahedra), with the Ca^{2+} polyhedra being larger and more distorted than the Y^{3+} (Rumanova 1967). The Ca^{2+} and Y^{3+} alternate, forming a checkerboard pattern linked by shared corners and CO_3^{2-} , creating channels holding, in this case, isolated four-membered $[Si_4O_{12}]^{8-}$ rings (metasilicate).

Analyses reporting $Ca_2(Y_{1.53}RE_{0.45}Fe_{0.02})_{\Sigma 2.00}Si_{3.87}O_{12}(CO_3) \cdot (H_2O)$ from the occurrence in Baveno (Italy) (Giuseppetti *et al.* 1989) and $Ca_{2.02}(Y_{1.50}RE_{0.50})_{\Sigma 2.00}(Si_{4.02}Al_{0.08})_{\Sigma 4.10}O_{12}(CO_3)_{0.70} \cdot (H_2O)_{1.93}$ from Bancroft (Canada) (Pouliot 1964) suggest simple substitution of

TABLE 3. SITE SCATTERING REFINEMENT WITH EPFU AND SITE POPULATION

	Site	e^- per site	Avg.	Site population from XRD (<i>apfu</i>)	Site population from EPMA (<i>apfu</i>)	Predicted*
Golden Horn	Y	39.12	29.83	$3.54 Y^{3+} + 0.46 Dy^{3+}$	$3.65 Y^{3+} + 3.66 Ca^{2+}$	29.84
	Ca	20.54		$3.77 Ca^{2+} + 0.23 Dy^{3+}$	$+ 0.66 REE = 7.96$	
Mt. Malosa	Y	36.65	29.19	$3.90 Y^{3+} + 0.10 Dy^{3+}$	$3.88 Y^{3+} + 3.54 Ca^{2+}$	29.69
	Ca	21.72		$3.67 Ca^{2+} + 0.33 Dy^{3+}$	$+ 0.54 REE = 7.96$	
Evans-Lou (<i>Pnmn</i>)	Y	32.62	32.82	$3.94 Y^{3+} + 3 (fix.)$	$3.94 Y^{3+} + 2.91 Ca^{2+}$	31.03
	Ca	33.02		$Ca^{2+} + 1.06 Dy^{3+}$	$+ 0.86 REE = 7.71$	
Evans-Lou (<i>Ccm2_1</i>)	Y	32.05	31.64	$4.29 Y^{3+} + 3 (fix.)$	$3.94 Y^{3+} + 2.91 Ca^{2+}$	31.03
	Ca	31.24		$Ca^{2+} + 0.71 Dy^{3+}$	$+ 0.86 REE = 7.71$	

* The predicted site scatterings values are derived based on the EPMA result. REE for site population modeled as Dy^{3+} based on the average molecular weight of REE from EPMA.

TABLE 4. OCCUPANCY REFINEMENTS FOR Ca, Y, AND Ow SITES IN CAYSICHITE-(Y)

	Ideal	Golden Horn			Mt. Malosa	Evans-Lou	
	(<i>apfu</i>)	WP108	WP108-S3	WP108-11	CE-ML-12	(Pn _{mn})	(Ccm2 ₁)
Y* (e ⁻)	1	39.12	38.88	38.63	36.65	32.62	32.05
Ca (e ⁻)	1	20.54	20.35	19.83	21.72	33.02	31.24
OW (¼pfu [†])	0.5	0.31	0.31	0.39	0.37	0.55	0.38
water+OH ⁻ (<i>pfu</i>)	8	7.25	7.25	7.55	7.48	8.20	7.53

* Based on ionic scattering factors with Y site modeled as La³⁺. Si1, Si2, OH1, and OH2 site occupancies were fixed to 1, 1, 1, and 0.5 for ¼ formula unit (as justified based on their near full occupancy, see Table S2).

† based on 6 e⁻

Y³⁺ ↔ REE³⁺. These results are generally consistent with Boggs (1984), yet suggest some excess Ca²⁺ resides on the Y/REE site: (Ca_{1.91}Na_{0.07}K_{0.02})Σ2.00(Y_{1.54}RE_{0.29}Ca_{0.14}Th_{0.01}U_{0.02})Σ2.00(Si_{3.94}Al_{0.08})Σ4.02O₁₂(CO₃)·(H₂O). As such, both minerals might be “pseudochemo-morphs”, responding with their growth to small scale and temporary changes for the availability of elements and physical conditions of their environment.

Raman spectroscopy

Figure 7 shows Raman spectra for both the Golden Horn and Mount Malosa caysichite-(Y). The prominent carbonate 1100 cm⁻¹ mode is split likely due to variations of the local structural environment of the carbonate group within the caysichite-(Y) structure. The presence of crystal water is confirmed with the peak at 3500 cm⁻¹ coming from the asymmetric and symmetric water stretch modes. The spectra are nearly identical in peak positions and line width with negligible background,

indicating high structural integrity of the crystals from both localities.

DISCUSSION

Analysis of EPMA from Boggs 1984

Boggs (1984) analyzed an unknown mineral described to occur as white square prismatic crystals up to 1 mm in size from the same sogdianite pegmatite, associated with sogdianite–zektzerite intergrowths, aegirine, bastnäsit–synchysite intergrowth, and microcline. Despite that contextual similarity with caysichite-(Y), the three quantitative EPMA analyses showed an FeO content of 4.3 to 5.4 wt.% and a total ranging from 83.7 to 85.9 wt.% (despite Tm, Yb, and Lu not being analyzed), inconsistent with caysichite-(Y).

Crystallization conditions and geodynamic context

The distinct habit of caysichite-(Y) between Evans-Lou on the one hand and Golden Horn and Mount

TABLE 5. BOND VALENCE SUMS FOR OXYGEN SITES

	Golden Horn			Mt. Malosa	Evans-Lou
	WP108	WP108-S3	WP108-11	CE-ML-12	EL-osme1
Ob1	2.008	2.014	2.017	2.030	2.035
Ob2	2.049	2.055	2.062	2.063	2.054
Ob3	1.974	1.979	1.985	1.977	1.964
Ob4	2.023	2.022	2.039	2.042	2.040
Ob5	1.997	1.998	2.006	2.005	1.981
O6	1.931	1.934	1.944	1.938	1.888
O7	1.938	1.940	1.949	1.932	1.899
Oc11	1.947	1.954	1.956	1.984	2.046
Oc12	2.040	2.039	2.057	2.042	2.026
Oc21	2.076	2.073	2.079	2.098	2.056
Oc22	1.967	1.965	1.965	1.969	1.967
Oc23	1.604	1.602	1.604	1.554	1.481
OH1	0.503	0.502	0.504	0.499	0.480
OH2	0.409	0.408	0.409	0.411	0.646

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) AND POLYHEDRAL VOLUMES

	Golden Horn			Mt. Malosa	Evans-Lou
	WP108	WP108-S3	WP108-11	CE-ML-12	EL-osme1
Y–O6	2.2802(17)	2.2802(19)	2.2799(19)	2.293(4)	2.326(5)
Y–O7	2.2223(18)	2.2263(20)	2.2189(18)	2.225(3)	2.261(6)
Y–OH1	2.5018(19)	2.5030(21)	2.5011(21)	2.506(4)	2.531(5)
Y–OC11	2.3983(4)	2.3985(3)	2.3965(3)	2.3953(6)	2.355(1)
Y–OC12	2.4021(17)	2.4026(20)	2.4005(20)	2.405(4)	2.412(5)
Y–OC21	2.3737(18)	2.3727(19)	2.3671(19)	2.365(4)	2.383(6)
Y–OC21	2.3313(18)	2.3336(19)	2.3280(19)	2.329(4)	2.353(6)
Y–OC23	2.5100(20)	2.5120(23)	2.5053(22)	2.524(5)	2.896(8)
Mean <Y–O>	2.3775	2.3786	2.3747	2.3803	2.4397
Y Poly. Vol. (Å ³)	23.001	23.037	22.934	23.089	24.363
Y Occupancy (e [−])	39.12(9)	38.88(10)	38.63(9)	36.65(15)	32.62(16)
Ca–O6	2.3371(18)	2.3411(20)	2.3386(18)	2.336(4)	2.269(5)
Ca–O7	2.4243(18)	2.4239(20)	2.4265(20)	2.417(4)	2.334(5)
Ca–OH1	2.5134(19)	2.5139(22)	2.5136(21)	2.515(4)	2.520(3)
Ca–OH2	2.5557(12)	2.5570(14)	2.5562(15)	2.554(3)	2.370(4)
Ca–OC12	2.3701(18)	2.3707(20)	2.3696(20)	2.375(4)	2.3741(4)
Ca–OC22	2.3896(18)	2.3906(20)	2.3857(20)	2.373(4)	2.358(6)
Ca–OC22	2.4360(18)	2.4337(20)	2.4308(21)	2.432(4)	2.388(6)
Mean <Ca–O>	2.4323	2.4330	2.4316	2.4288	2.373
Ca Poly. Vol. (Å ³)	20.6807	20.6925	20.6673	20.5852	24.213
Ca Occupancy (e [−])	20.54(7)	20.35(7)	19.82(6)	21.72(12)	33.01(16)
Si1–Ob1	1.6249(17)	1.6240(19)	1.6222(20)	1.622(4)	1.622(6)
Si1–Ob4	1.6192(10)	1.6198(11)	1.6165(11)	1.616(2)	1.616(3)
Si1–Ob5	1.6251(10)	1.6243(11)	1.6220(11)	1.614(4)	1.628(3)
Si1–O7	1.5849(18)	1.5820(20)	1.5818(19)	1.587(4)	1.606(5)
Mean <Si1–O>	1.6135	1.6125	1.6108	1.6119	1.6179
TQE	1.0033	1.0033	1.0033	1.0028	1.0017
Poly. Vol.	2.1455	2.1415	2.1347	2.1406	2.1679
Si2–Ob1	1.6207(17)	1.6189(19)	1.6196(20)	1.614(4)	1.613(6)
Si2–Ob2	1.6145(8)	1.6134(8)	1.6122(08)	1.612(2)	1.614(3)
Si2–Ob3	1.6298(11)	1.6282(12)	1.6270(12)	1.629(2)	1.631(3)
Si2–O6	1.5851(18)	1.5827(20)	1.5799(19)	1.578(4)	1.605(5)
Mean <Si2–O>	1.6125	1.6108	1.6097	1.6081	1.6155
TQE	1.0019	1.0018	1.0019	1.0017	1.0018
Poly. Vol.	2.1459	2.1393	2.1346	2.1291	2.1583
C1–Oc11	1.308(4)	1.311(5)	1.312(5)	1.304(9)	1.307(13)
C1–Oc12	1.274(3)	1.274(3)	1.270(3)	1.271(5)	1.276(8)
C1–Oc12	1.274(3)	1.274(3)	1.270(3)	1.271(5)	1.276(8)
<C1–O>	1.2857	1.286	1.2836	1.2822	1.2861
C2–Oc21	1.301(3)	1.300(3)	1.302(3)	1.297(6)	1.297(9)
C2–Oc22	1.267(3)	1.269(3)	1.270(3)	1.272(6)	1.285(10)
C2–Oc23	1.284(3)	1.284(3)	1.284(3)	1.296(6)	1.271(8)
<C2–O>	1.284	1.284	1.286	1.288	1.284

Malosa on the other indicates similar formation conditions for Golden Horn and Mount Malosa, where crystallization progressed slowly, resulting in euhedral crystals and well-defined site ordering. Conversely, at Evans-Lou caysichite-(Y) formed at a very

late stage and the fine fibrous nature of the mineral indicates rapid precipitation as the main driving force behind the high degree of site disorder between Ca and REE compared to Golden Horn and Mount Malosa.

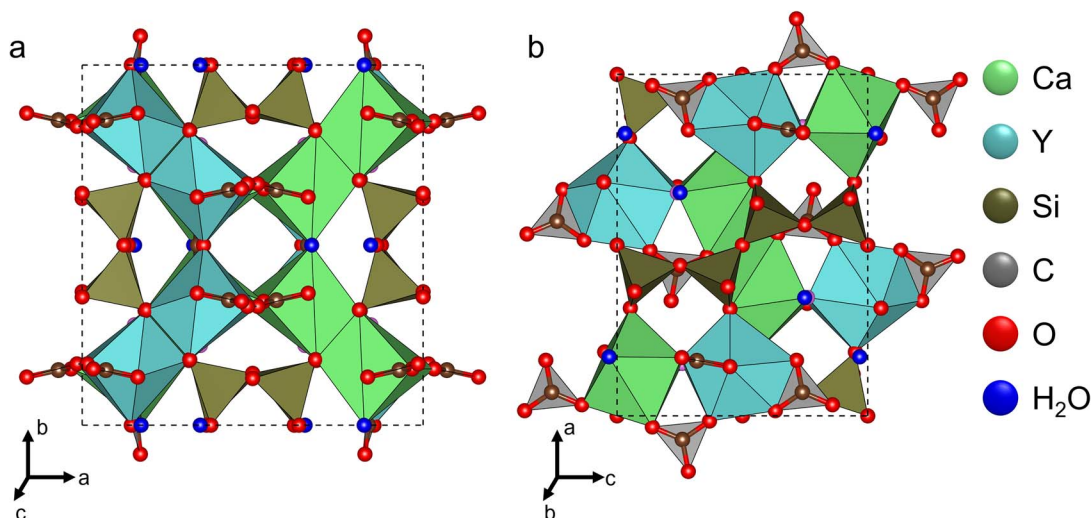


FIG. 6. Solved crystal structure of caysichite-(Y) in space group $Pnmn$ viewed along the (a) c -axis and (b) b -axis. Atoms are color coded as follows: red – O, silver – C, blue – water, brown – Si, green – Ca, teal – Y.

A significant factor influencing these differences is the geodynamic history of the host regions. The Evans-Lou pegmatite formed during the late-stage extensional tectonic magmatism of the Grenville orogeny (*ca.* 1.3–

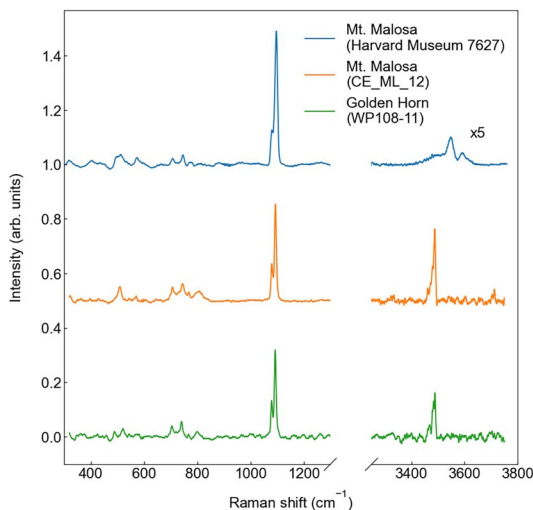


FIG. 7. Micro-Raman spectra of Mount Malosa (Harvard Museum 7627 and Collector's Edge CE_ML_12) and Golden Horn (WP108) caysichite-(Y) samples. Peaks at 710 and 1090 cm^{-1} are assigned to $(\text{CO}_3)^{2-}$ with the splitting of the 1090 cm^{-1} peak due to local variations in the chemical environment of $(\text{CO}_3)^{2-}$. The peak at 3500 cm^{-1} is assigned to water, with peak asymmetry due to the symmetric stretch mode redshifted from the asymmetric stretch mode.

0.98 Ga), a complex orogenic event resulting from the accretion of island arcs and backarc basins onto the Laurentian margin, followed by collisions with additional crustal fragments (Fowler & Doig 1983). This orogeny was characterized by alternating phases of compression and extension, leading to the emplacement of anorthosite-mangerite-charnockite-granite (AMCG) suites during extensional intervals (*e.g.*, Fowler & Doig 1983, Indares 2024 and references therein). The AMCG magmatism of the Grenville Province is typically metaluminous and enriched in Fe, Mg, and Mn, but lacks significant concentrations of incompatible elements such as REE and Zr (Seifert *et al.* 2010). Consequently, the availability of CO_2 and H_2O , essential components for caysichite-(Y) formation, was limited and the mineral likely precipitated from late-stage fluids with variable compositions, including CO_2 -rich fluids associated with charnockitic magmas and H_2O -rich fluids from granitic intrusions.

In contrast, the Golden Horn Batholith and Mount Malosa massif are younger, formed during the Eocene and Cretaceous periods, respectively, in tectonic settings conducive to the generation of peralkaline magmas rich in REE and other incompatible elements. These magmas provided a more favorable environment for the slow crystallization of caysichite-(Y), resulting in well-developed crystal habits.

The contrasting crystallization habits of caysichite-(Y) across these localities underscore the possible influence of tectonomagmatic settings on mineral formation. The complex tectonic evolution and associated magmatism of the Grenville orogeny led to rapid, late-stage mineralization under fluctuating fluid conditions, while the more stable,

REE-enriched magmatic systems of Golden Horn and Mount Malosa facilitated the development of primary magmatic well-formed euhedral caysichite-(Y) crystals.

OUTLOOK AND PERSPECTIVE

With the continuous discovery of new minerals in terms of species and variants from both the Golden Horn Batholith and Mount Malosa, yet comparatively limited mineralogical studies and limited attention paid to the suite of micro-minerals from Mount Malosa, both localities may still have potential for mineralogically new discoveries.

ACKNOWLEDGMENTS

We thank Bryan Lees from Collectors Edge for providing caysichite-(Y) from Mount Malosa for this study. We further thank Philip Persson for valuable discussions about this locality. We thank Russ Boggs for inspiring discussions and sharing additional sample material collected by his father Bob Boggs. We further wish to acknowledge Sebastian Müller and the Mineralogisches Museum of the Phillips-Universität Marburg for lending a caysichite-(Y) bearing specimen from the Evans-Lou locality. We acknowledge miscellaneous technical assistance by Evan Anderson, Roland Wilcken, and Sam Turner. Finally, we thank the reviewers and editors Stephen Prevec and Mackenzie Parker who evaluated the manuscript.

SUPPLEMENTARY DATA

Supplementary data is available alongside this article in the “Supplements” tab.

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Received July 18, 2025. Revised manuscript accepted February 18, 2026.