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CAYSICHITE, A NEW SILICO-CARBONATE OF YTTRIUM AND CALCIUM

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ABSTRACT

Caysichite, $(Y,Ca)_4Si_4O_{10}(CO_3)_3 \cdot 4H_2O$, occurs in granite pegmatite at the abandoned Evans-Lou feldspar mine, 22 miles north of Ottawa. The mineral is normally present as a coating on fractures or as incrustations up to 2 mm thick with a divergent columnar structure. Terminated crystals are rare. Caysichite is colourless to white, more rarely yellow or green. $H = 4\frac{1}{2}$, $D(\text{obs}) = 3.03$ and $D(\text{calc}) = 3.029$ g/cm^3. For the colourless variety, $\alpha = 1.586$, $\beta = 1.614$, $\gamma = 1.621$, $2V_x = 53°$, $X = b$, $Y = a$, $Z = c$, with positive elongation; yellow crystals have somewhat higher refractive indices and larger optic angle. The mineral is orthorhombic: $Ccm2_1$ or $Ccmm$ with $a = 13.282$, $b = 13.925$, $c = 9.727$Å (crystal elongation); $Z = 4$. Strongest lines (Cu$K\alpha$) are 6.93 (020,111) (100), 4.38 (130) (60), 4.22 (310) (60), 3.48 (040) (60), 3.32 (400) (90). IR absorptions occur at 3700-2600 cm^{-1} (H_2O), 1700-1240 cm^{-1} (CO_3) and 1200-900 cm^{-1} (SiO_4). On heating, dehydration is followed by two distinct stages of decarbonation. The DTA product (1120°C) has an apatite structure. Caysichite may have been derived from hellandite through low temperature solution and precipitation.

INTRODUCTION

Yttrium and lanthanide minerals are ubiquitous, though minor, constituents of Precambrian granite pegmatites that were once worked for feldspar and quartz in eastern Ontario and western Quebec. The minerals were generally looked upon as a nuisance by the operators and were discarded on the dumps, where they are turned up periodically by collectors. One such rare earth pegmatite is the Evans-Lou feldspar mine, some 22 miles north of Ottawa. This mine was quarried for feldspar and quartz from 1932 to 1956 and collections from the dumps have since yielded several interesting mineral species (Hogarth 1972) including a new yttrium calcium silico-carbonate, described in this paper. The mineral was first observed on the mine dump in May, 1969, as a white powder, coating perthite, and as it could not be identified by *x*-ray diffraction methods, the mineral was designated UN-11 of the unidentified Evans-Lou minerals. In August of the same year yellowish microcrystals from cavities in quartz specimens from the dump were *x*-rayed and designated UN-16 (Miles *et al.* 1971). Later, the *x*-ray patterns of UN-16 and UN-11 were found to be similar, differing only in intensities.

In the summer of 1970, the quarry was partly drained of water to permit the examination and collection of samples *in situ*. After the draining, UN-16 was observed as faintly yellowish crusts on quartz along a 2-foot length in the hanging (west) wall of the pegmatite and as white radiating crystals, within a 3-foot radius, at the north end of the quarry. These locations are 15 to 20 feet below the normal water level of the flooded quarry.

UN-16 has been named caysichite for its principal cations: Ca, Y, Si, C, H. The mineral and the name, syllabized cay-si-chite and pronounced KĀ.SICHAIT, have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The type material has been deposited with the Systematic Reference Series (No. 10402) of the National Mineral Collection, Geological Survey of Canada, Ottawa.

OCCURRENCE

At the Evans-Lou mine, caysichite occurs in granite pegmatite. It is especially common in quartz-rich areas of the giant perthite zone which surrounds the quartz core (Miles *et al.* 1971) but has not been found in the core itself. The mineral coats fractures and encrusts or completely fills cavities in quartz, perthite and hellandite, and is apparently of supergene origin. It is most closely associated with hellandite but is also found with the other rare earth-bearing minerals fergusonite, kainosite (cenosite), tengerite, lokkaite and yttrian thorogummite; less commonly with yttrian spessartine, xenotime, wakefieldite and synchisite-(Y). Further details of its association are given by Hogarth (1972).

Most commonly, caysichite lines cavities as a dull white pulverulent coating or as a cream stain. More rarely it is found as thin, brittle incrustations with a parallel to slightly divergent columnar structure and with a reniform surface somewhat resembling prehnite (Fig. 1). In this form it is coherent, though easily separable into 'splinters' up to 2 mm long. Additionally, the mineral occurs as radiating groups and terminated crystals, and, at one locality, as stalactites up to one cm in length.

PHYSICAL AND MORPHOLOGICAL PROPERTIES

Colourless, crystalline crusts of caysichite on samples from the hanging wall of the pegmatite (location EL-344, Hogarth 1972) were the most amenable to clean separation, and splinters, hand-picked from these samples under the binocular microscope, provided the material for most studies. The hardness is 4½ and the VHN is 551. The density, as determined by heavy liquids, is 3.03 g/cm^3. Specimens are non-fluorescent in long and short wave ultraviolet radiation but show a faint green cathodoluminescence under electron bombardment. In hand specimen the mineral is colourless, white to pale yellow, and rarely greenish. It has a vitreous lustre and white streak, and effervesces slowly in cold, dilute HCl. The rarely-observed caysichite crystals are prismatic, elongated parallel to *c* and terminated by {001} (Fig. 2). A prism and a dome

FIG. 1. Caysichite incrustations on quartz, Evans-Lou mine, Quebec.

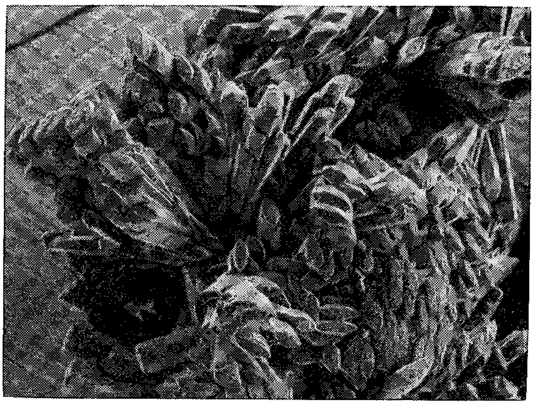

FIG. 2. Scanning electron photomicrograph of crystals of caysichite showing their prismatic habit and {001} termination, and also a poorly developed dome on some crystals. Width of crystal is 0.05 mm.

can be observed under high magnification but their Miller indices could not be determined because of poor signals on the optical goniometer.

The optical data (Table 1) were obtained at room temperature on the spindle stage using a sodium vapour lamp illuminator. All Cargille immersion liquids used were checked by an Abbe refractometer. The mineral is biaxial negative with parallel extinction and positive elongation. No dispersion was noted in any of the grains examined. In conventional immersion mounts, caysichite fragments give nearly centered acute bisectrix figures suggesting {010} cleavage.

TABLE 1. OPTICAL DATA FOR CAYSICHITE

Colourless crystal	Yellowish crystal
α = 1.586 ±0.004	α = 1.589 ±0.004
β = 1.614 ±0.001	β = 1.616 ±0.001
γ = 1.621 ±0.001	γ = 1.626 ±0.001
$2V_x$ = 53°(meas.); 54°30'(calc.)	$2V_x$ = 72°45'(calc.)
$X = b$, $Y = a$, $Z = c$	non-pleochroic

X-RAY CRYSTALLOGRAPHY

Crystals suitable for Weissenberg and precession studies were obtained only with considerable difficulty because of the sub-parallel growth of many individuals. The best single-crystal photographs, obtained from what is presumably a minute cleavage fragment, indicate that caysichite is orthorhombic with a = 13.30, b = 13.95, and c = 9.74Å. The observed systematic extinctions are consistent with those required by space groups $Ccm2_1$ and $Ccmm$.

X-ray powder diffraction data for the colourless caysichite are given in Table 2. With the single-crystal photographs as a guide, the powder pattern is readily indexed on the basis of the orthorhombic cell. The cell parameters derived from the single crystal studies were then refined by a least-squares method using the indexed powder data. The refined values are a = 13.282(3), b = 13.925(3) and c = 9.724(4)Å.

The powder pattern of the yellow variety is identical to that of the colourless crystals except for very minor differences in d-values and for the relative intensities of a few lines.

TABLE 2. X-RAY POWDER DIFFRACTION PATTERN OF CAYSICHITE (COLOURLESS)

hkl	I/I_o	d_{obs}	d_{calc}
001 110	5	9.62	9.727 9.661
020 111	100	6.93	6.962 6.838
002	40	4.87	4.864
130	60	4.38	4.382
310	60	4.22	4.219
022	10	3.985	3.987
311	10	3.866	3.871
040	60	3.481	3.481
400	90	3.321	3.320
132	5	3.257	3.255
330	30	3.201	3.204
401	10	3.146	3.142
240 113	30	3.077	3.083 3.072
420	<5	2.997	2.997
241	30	2.939	2.939
042	<5	2.829	2.831
402 150	30	2.733	2.742 2.726
332	30	2.677	2.675
133	30	2.608	2.606
313	10	2.574	2.571
511	5	2.517	2.520
004	5	2.434	2.432
440	<5	2.405	2.403
152	5	2.376	2.378
060	40	2.323	2.321
530	5	2.305	2.306
204	5	2.286	2.284
531 243	5	2.240	2.243 2.234
600	30	2.213	2.214
601 442	10	2.156	2.158 2.154
134	10	2.125	2.126
352	10	2.120	2.121
620 314	20	2.108	2.110 2.107
153	20	2.085	2.086
621	5	2.061	2.062
513	5	2.033	2.033
602	5	2.016	2.015
044	<5	1.994	1.994
404	5	1.965	1.962
234 622	10	1.937	1.937 1.935
550	5	1.920	1.922
460	10	1.904	1.902
710 533	30	1.879	1.880 1.879
263 370	10	1.814	1.815 1.814
514	10	1.778	1.779
462 623	10	1.771	1.772 1.768
730 712	30	1.754	1.756 1.754
372	<5	1.701	1.700
064	<5	1.680	1.679
553 732	20	1.653	1.654 1.652
082 604	5	1.637	1.639 1.637
660	10	1.600	1.602
155 661	5	1.582	1.580 1.584
802	5	1.573	1.571
190	10	1.538	1.537
662	10	1.520	1.521
752	5	1.491	1.492
390	5	1.461	1.461

plus other lines

114.6 mm camera, Cu$K\alpha$ radiation (λ=1.5418Å), Si standard, visual intensities

CHEMICAL COMPOSITION

Compositional data for caysichite are presented in Table 3. Water was determined on carefully hand-picked samples by a modified Penfield method, and carbon dioxide by both titrimetry and by total weight loss minus water (loss on ignition minus H_2O). All other quantitative data were obtained by electron probe analysis on ten optically clear splinters of colourless caysichite, less than 1 mm long and 0.2-0.3 mm

TABLE 3. CHEMICAL COMPOSITION OF CAYSICHITE

		Atoms per 19 Oxygens			
	Wt %		actual		ideal
CaO	10.04	Ca	1.473	3.878	4.000
Y_2O_3	28.18	Y	2.054		
La_2O_3	0.08	La	0.004		
CeO_2	0.24	Ce	0.011		
Pr_2O_3	0.09	Pr	0.004		
Nd_2O_3	0.30	Nd	0.015		
Sm_2O_3	0.20	Sm	0.009		
Eu_2O_3	0.09	Eu	0.004		
Gd_2O_3	0.51	Gd	0.023		
Tb_2O_3	0.16	Tb	0.007		
Dy_2O_3	1.16	Dy	0.051		
Ho_2O_3	0.66	Ho	0.029		
Er_2O_3	1.84	Er	0.079		
Tm_2O_3	0.21	Tm	0.009		
Yb_2O_3	2.12	Yb	0.089		
Lu_2O_3	0.42	Lu	0.017		
SiO_2	28.84	Si	3.950	4.044	4.000
Al_2O_3	0.58	Al	0.094		
CO_2	15.7*	C	2.937		3.000
H_2O	8.6**	H_2O	3.932		4.000
Total	100.02				

*total wt. loss on ignition of 17 mg of sample, less H_2O; 14.1% by titrimetry on 25 mg.

**modified Penfield method.

Additional minor elements by mass spectroscopy(wt. %): B 0.05, F 0.04, P 0.01, Mg 0.02, K 0.02, Sc 0.01, Cr 0.01, Mn 0.01, Ni 0.03, Cu 0.01, Sr 0.02, Sn 0.01, Ba 0.01, Pb 0.02.

wide. Energy dispersive analysis spectra of the splinters showed Ca, Y and Si to be the principal elements and lanthanides to be present in minor amounts. Quantitative determinations for these elements were carried out by conventional methods with a Materials Analysis Company electron microprobe using synthetic yttrium-iron garnet, kainosite (cenosite of Pouliot *et al.* 1964) and synthetic rare earth element glasses (Drake & Weill 1972) as standards. To avoid sample decomposition a beam diameter of 10 microns was employed, with a specimen current of 0.03 microamperes. The data were processed by using a revised and updated version of the computer program by Rucklidge (1967). The data in Table 3 are the average of at least 10 spot analyses for each element. The compositional range of 50 points in 5 grains for Y and Ca was: Y_2O_3 27.4-28.8% and CaO 10.3 - 9.8%, with the elements varying antipathetically. The elements Mg, Ba, Ti, Sr, Na, K, S, P, Cl and F were sought by electron microprobe analysis, and each found to be less than 0.05%. Fe, as high as 0.2%, was detected at a few points in some grains. Minor elements detected by mass spectrometry are noted at the bottom of the table.

The analysis, recalculated on the basis of 19 oxygen atoms, gives the following formula: $Y_{2.05}Ca_{1.47}RE_{.35}Si_{3.95}Al_{.09}O_{10.18}(CO_3)_{2.94} \cdot 3.93H_2O$, or ideally: $(Y,Ca)_4Si_4O_{10}(CO_3)_3 \cdot 4H_2O$. Assuming four formula units per cell the calculated density is 3.029 g/cm^3, which is in excellent agreement with the measured value.

Following identification of the yellowish variety of caysichite by optical and *x*-ray methods, a pale greenish yellow, cone-shaped grain, 1.2 x 1.1 mm and tapering to 0.3 mm, was mounted for analysis. In polished section, the greater part of the grain consists of interpenetrating acicular crystals of normal caysichite, which take a good polish, and which have rhomb-shaped cross-sections. Locally, the grain is rimmed by a veneer, up to 50 microns thick, of a calcium- and yttrium-rich mineral that is probably synchisite-(Y). Towards the margin of the grain, interstitial areas between the well-crystallized caysichite are filled with very finely crystalline material which has a poorer polish. This material is chemically similar to normal caysichite, except for a higher ratio of Y to Ca, with 32% Y_2O_3 and 7% CaO, and a small increase to 0.5% for Fe. The variations noted in the optical and *x*-ray data for the colourless and yellowish caysichite may therefore be due directly to variations in the Y/Ca ratios of the mineral.

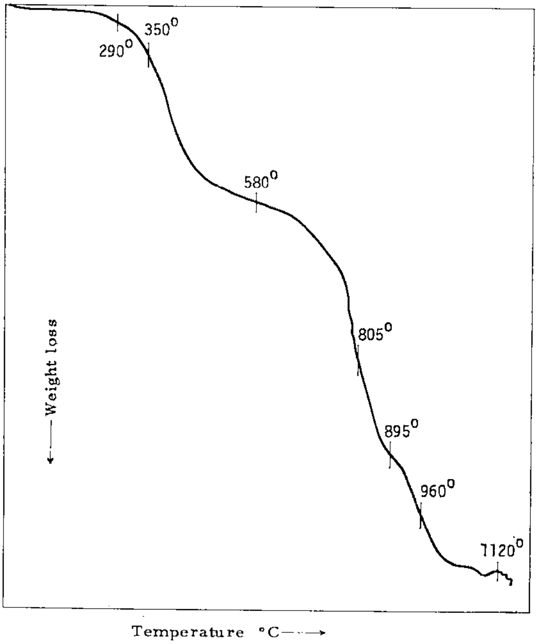

FIG. 3. Thermogravimetric curve of caysichite (heating rate = 12°C/min, in air).

THERMAL STUDIES

Thermal studies were carried out on four different hand-picked samples. Thermogravimetric analysis in air (Fig. 3) shows three stages of weight loss: (1) 290 - 580°C (8.3%) probably representing dehydration, (2) 580 - 895°C (10.6%), thought to represent a first stage decarbonation, (3) 895 - 1120° (5.3%) thought to represent a second stage decarbonation. The total weight loss was 24.3% and the end product gave an *x*-ray diffraction pattern of an apatite structure. The specimen had intumesced but not melted at the end-temperature (1120°C). These data can be correlated with the differential thermal analysis curve (Fig. 4) which shows two prominent endotherms at 431°C and 801°C and minor peaks from 935 - 1100°C.

In static heating studies, a sample heated in air for 15 minutes at 350°C showed a weight loss of 2.84%; for 15 minutes at 550°C, a loss of 9.37% (cumulative); and for 50 minutes at 1100°C, a loss of 24.85% (cumulative).

INFRARED STUDIES

The infrared spectra of caysichite are presented in Figure 5. The strong, broad band in the region 3700-2600 cm^{-1} is attributable to hydrogen-bonded water. This is consistent with the TGA and DTA observations that caysichite de-

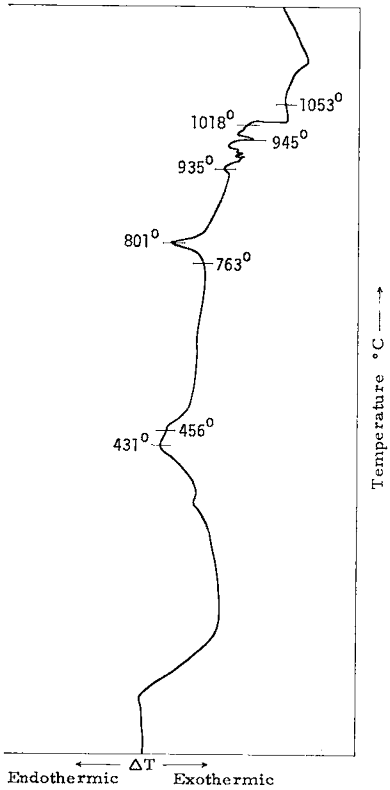

FIG. 4. Differential thermal analysis curve of caysichite, (heating rate = 10°C/min, in CO_2).

hydrates at a relatively high temperature (431-435°C). The strong bands in the region 1700-1240 cm^{-1} are due to the vibrations of the CO_3 group. The multiplicity and poor resolution of bands in this region may be due to the presence of two distinct CO_3 groups in the structure, as suggested by the two-stage decarbonation observed in the TGA study. The strong bands in the region 1200-900 cm^{-1} are attributed to Si-O stretching. The assignments of the minor bands in the spectra are: 3020-2800 cm^{-1} (overtone of ν_3 of CO_3); 1720 cm^{-1} (adsorbed water); 830 cm^{-1} (ν_2 of CO_3); 790 and 740 cm^{-1} (Si-Si stretching); 690, 630 and 620 cm^{-1} (ν_4 of CO_3).

ORIGIN

The close spatial relationship of caysichite and hellandite suggests that caysichite is secondary after hellandite. However, the distribution of lanthanides in Evans-Lou hellandite, caysichite and fergusonite (Fig. 6) shows a closer chemical relationship between caysichite and fergusonite. The absence of a gadolinium peak in caysichite may be ascribed to crystal-chemical control, the structure of caysichite being more selective than that of hellandite for the smaller and therefore the heavier members of the lanthanide group.

The crustiform, reniform and stalactitic nature of caysichite, as a partial or complete filling of cavities or open fractures, strongly suggests that it was formed at low or moderate temperatures. Solution and transportation may have taken place in mildly acidic carbonated groundwaters, with precipitation occurring when the pH was increased to a value approaching neutrality.

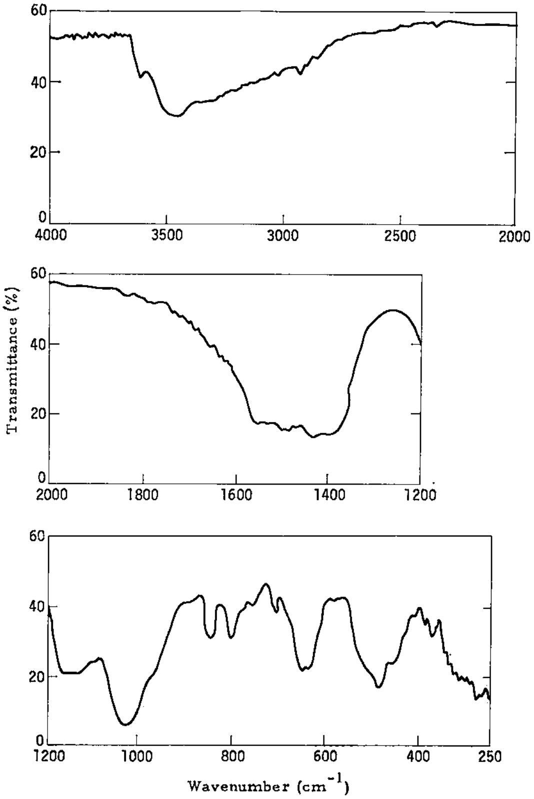

FIG. 5. Infrared spectra of caysichite.

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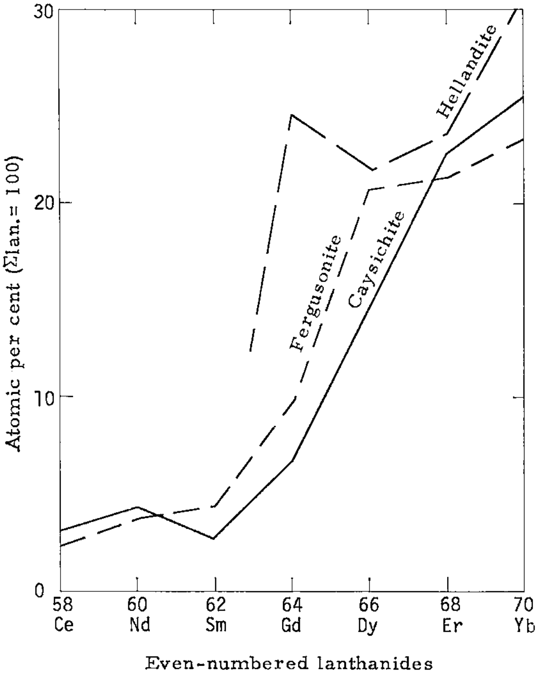

FIG. 6. Distribution of lanthanides in caysichite, hellandite and fergusonite, Evans-Lou mine, Quebec.

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REFERENCES

DRAKE, M. J. & WEILL, D. F. (1972): New rare earth element standards for electron microprobe analysis. *Chem. Geol.* **10**, 179-181.

HOGARTH, D. D. (1972): The Evans-Lou pegmatite, Quebec: a unique yttrium-niobium-bismuth-vanadium assemblage. *Mineral. Record* **3**, 69-77.

MILES, N. M., HOGARTH, D. D. & RUSSELL, D. S. (1971): Wakefieldite, yttrium vanadate, a new mineral from Quebec. *Amer. Mineral.* **56**, 395-410.

POULIOT, G., MAXWELL, J. A. & ROBINSON, S. C. (1964): Cenosite from Bancroft, Ontario. *Can. Mineral.* **8**, 1-10.

RUCKLIDGE, J. C. (1967): A computer program for processing microprobe data. *J. Geol.* **75**, 126.

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