CENOSITE FROM BANCROFT, ONTARIO[1]

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ABSTRACT

The second Canadian occurrence of cenosite Ca_2 (Y, Dy, Er, etc.)$_2$ $Si_4O_{12}CO_3.H_2O$ was found in a vug in uraniferous pegmatitic granite ore of the Bicroft mine, near Bancroft, Ontario. Associated minerals include chamosite, pyrite, quartz, calcite, sphalerite, biotite, molybdenite, fluorite, uraninite and zircon. Cenosite crystals are orthorhombic; space group *Pmnb*; with a 13.05Å, b 14.33, c 6.77; $Z = 4$. Physical properties are: good prismatic cleavage; S.G.:3.52; H:5; $\alpha = 1.665$, $\beta = 1.685$, $\gamma = 1.689$; $2V$ (−) 40°. A complete chemical analysis is given together with the indexed x-ray powder pattern and the infrared spectrum of the mineral. A characteristic feature of cenosite crystals from Bicroft is a core of granular cenosite deficient in CO_2.

INTRODUCTION

Cenosite (kainosite) from the Bicroft mine, near Bancroft, Ontario is the second recorded occurrence of this rare mineral in Canada. It was found by the late Mr. W. R. Montgomery, staff geologist at the mine, and referred to one of the authors (S. C. R.) for identification. Subsequently, additional material was generously made available by the company through Mr. E. E. G. Heaslip, Chief Geologist. Type specimens have been deposited in the Systematic Reference Series of the National Mineral Collection.

The first Canadian occurrence of cenosite, from North Burgess township, Ontario, was described by Graham & Ellsworth (1930) and a preliminary x-ray study of it was done by Berry & Thornton (1950). Rumanova & Volodina (1961) also studied the North Burgess mineral; their work was followed by a structure investigation by Volodina *et al.* (1963). In describing cenosite from Cotopaxi, Colorado, Heinrich *et al.* (1962) reviewed references to the mineral and listed additional European occurrences.

This paper records structural parameters and other crystallographic data of the Bicroft cenosite (G. Pouliot), complete chemical analysis (J. A. Maxwell) and a brief description of its occurrence and geological environment (S. C. Robinson).

It is a pleasure to acknowledge the kindness of Miss F. E. Goodspeed of the Mines Branch, Ottawa, who made the infrared absorption spectra.

OCCURRENCE AND GEOLOGICAL ENVIRONMENT

The Bicroft cenosite was found in an irregular vug measuring about 3 feet in diameter and 5 feet in length, in stope 4-J-11 of the mine. According to the present Chief Geologist, Mr. Cyril Holland, this vug was the largest of several found in a tubular mud seam that extended up dip a distance of roughly 100 feet. Cenosite was restricted to this one vug.

Geology of the area has been described by Hewitt (1959) and the uranium deposits were described by Satterly (1957), Robinson & Hewitt (1958) and Robinson (1960). At the Bicroft Mine a series of pegmatitic granite dykes and irregular branching lenses are distributed *en echelon* horizontally and vertically in metamorphosed, partly limy sediments near the eastern margin of the Cardiff plutonic complex. Ore shoots are restricted to the dykes, usually on their foot or hanging walls.

Primary ore minerals are uraninite and uranothorite with minor allanite and betafite and traces of fergusonite and polycrase. The dykes are composed of soda plagioclase, microcline and quartz with minor pyroxene, amphibole and/or magnetite and locally, biotite, calcite, chlorite, fluorite and muscovite. Of the accessory minerals, zircon and titanite are abundant and tourmaline, apatite, hematite, garnet, molybdenite and pyrrhotite are less common.

Vugs and late fractures in the dykes commonly contain calcite, quartz, green fluorite, hematite, pyrite, and/or marcasite and less commonly one or more of celestite, gypsum, talc, chamosite, kaolinite, uranophane and kasolite.

In the cenosite vug, the principal minerals, in order of abundance are: chamosite, pyrite, quartz, calcite, cenosite, sphalerite and fluorite with minor zircon, biotite, titanite, chlorite and gypsum and traces of jarosite, uraninite, and molybdenite. The walls of the vug were coated with massive chamosite containing anhedral pyrite and quartz, and subhedral titanite, zircon, uraninite, and molybdenite. Cellular crusts of pyrite are found in the chamosite and mantling its inner surfaces. Euhedral crystals of calcite, sphalerite, quartz and cenosite, variably interpenetrating, form an open lattice-work on the chamosite. These crystals in turn are coated by smaller crystals of quartz, green fluorite and pyrite. Sparse films of gypsum and jarosite are found locally on other minerals.

Composition of the vug differs significantly from that of the dykes: in the presence of sphalerite and cenosite; in the abundance of chamosite; in the presence of green rather than purple fluorite; in the prevalence of pyrite instead of pyrrhotite; and in the absence of major constituents of the ore dykes other than quartz. Obviously the vug was filled subsequently to formation of the dykes; under markedly different conditions, and in part at least, from a different source.

DESCRIPTION OF CENOSITE

Cenosite commonly occurs as a network of individual crystals whose length is parallel to the walls of the vug. Less commonly it occurs in sub-parallel sheaves. Crystals range in length from 0.5 mm. to 350 mm. and in width from 0.1 mm. to 3 mm.: dimensions of the average prism are 0.5×3 mm.

A characteristic feature of cenosite from Bicroft is the presence in most crystals of a central core of granular, white to honey-coloured material (Fig. 1). This core is parallel to the length, (c axis), is round to irregular

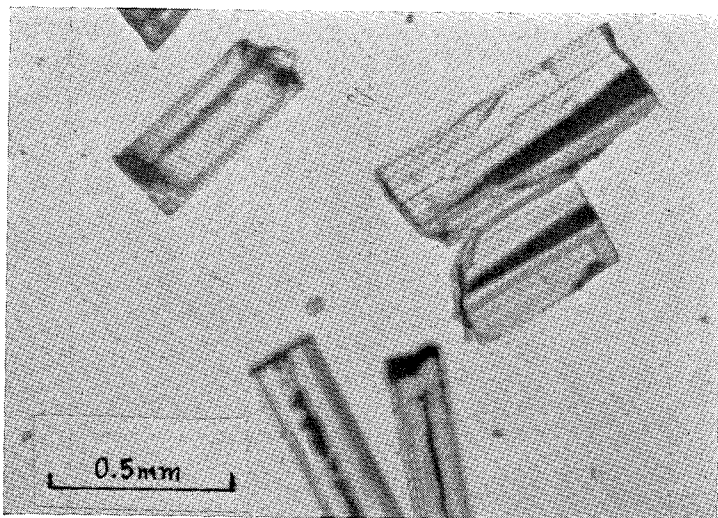FIG. 1. Cenosite crystals from Bicroft. Plain light $\times 50$. The central part of the crystals is occupied by a core of granular cenosite deficient in CO_2.

in cross-section and widens toward the terminal faces of the crystals. Terminal faces are typically composed of this material. Less commonly, this core has a euhedral cross-section that parallels the outline of the unit prism, and in turn, contains an inner zone of clear cenosite.

The granular material yields an x-ray powder pattern identical to that of clear cenosite and is hereafter referred to as "granular cenosite." It is apparently identical in composition with clear cenosite except for a deficiency in CO_2. The sample of cenosite used for analysis (Table 3) contained about 20 per cent of granular cenosite and was found to contain 4.60 per cent CO_2 as compared with 6.58 per cent required by stoichiometry. Subsequent analysis of 34 mg. of selected cenosite free from granular material gave 7 per cent CO_2.

Minute grains of pyrite are so intimately associated in and on crystals of cenosite, particularly on the terminal faces, that it was impossible to obtain a sample of cenosite completely free from suphide. A correction for pyrite had to be made therefore, in the analysis shown in Table 3.

Physical properties

Physical properties of Bicroft cenosite are as follows: Cleavage {110} (?) good. Fracture sub-conchoidal. Brittle. H 5. S.G. 3.52 measured, 3.542 calculated. Lustre vitreous to resinous. Colour chestnut brown through straw yellow to colourless. Transparent to translucent.

The mineral effervesces only very slowly in cold dilute HCl. Tests for radioactivity and fluorescence under ultraviolet were negative.

Optical properties are as follows: non-pleochroic. Parallel extinction, length fast with $\alpha = c$, $\beta = b$, $\gamma = a$. In Na light; $\alpha = 1.665$, $\beta = 1.685$, $\gamma = 1.689$ all $\pm$ 0.001. $2V$ (−), calc. 49.5°, measured 40°. Dispersion indistinct.

Macro-crystallography

Crystals are slender, prismatic and a minority of them exhibit terminal faces. Forms of the prism zone are so numerous on some crystals that, as reported by Graham & Ellsworth (1930, p. 211) for the North Burgess cenosite, signals on the goniometer are so closely spaced as to be somewhat blurred. In extreme cases, the crystals are virtually circular in section. Terminal domes are too rough for measurement on the goniometer.

The forms and axial ratio of the prism zone for the Bicroft and North Burgess cenosites are compared in Table 1, using Graham & Ellsworth's orientation $(Z = c)$.

TABLE 1. PRISM ZONE OF THE BICROFT AND NORTH BURGESS CENOSITE

	Bicroft	North Burgess[1]
Forms	{100}, {010}, {120}, {110} {320}, {590}, {230}, {430} {410}.	{100}, {010}, {120}, {340}, {450}, {110}, {320}, {490}, {590}, {230}, {670}, {780}, {890}, {11.12.0}, {650}, {430}.
	{100} ∧ {110}: 42°23′	41°13′
	range (42°20′ − 42°26′)	40°13′ − 42°13′
	a:b 0.9126	0.8759
	a:b (x-ray) 0.9106	0.9117[2] 0.9042[3]

[1]Graham & Ellsworth (1930)
[2]Berry & Thornton (1950)
[3]Rumanova & Volodina (1962)

The terminal faces on the Bicroft cenosite are probably the same as reported for the North Burgess crystals, {101} and {011}. The basal pinacoid was not observed. The unit prism is the dominant form followed by the front and side pinacoids.

Evidence of twinning was not observed under either the binocular or petrographic microscopes.

X-RAY DIFFRACTION DATA

Precession photographs about a, b, and c and Weissenberg photographs about b and c were obtained for small colourless crystals using Cu$K\alpha$ radiation. These indicate an orthorhombic cell having a 13.05 Å, b 14.33, c 6.77 (all ± .01 Å) and a diffraction symbol *mmm Pnb* (space-groups *Pmnb* or *P2$_1$nb*). These results agree with those of Berry & Thornton (1950) who quote for the North Burgess cenosite; a 13.01 Å, b 14.27, c 6.75 and those of Rumanova & Volodina (1961) who determined for North Burgess mineral: a 12.93 Å, b 14.33, c 6.73 (all ± .03 Å). Based on the absence of piezoelectric effect and the goniometric measurements of Graham & Ellsworth (1930), Rumanova & Volodina concluded that the space-group is *Pmnb*. This was subsequently verified by structure analysis of the North Burgess cenosite by Volodina *et al.* (1963). In view of the similar crystallography of the Bicroft and North Burgess cenosites, it is assumed that they have same space-group. The only irregularity is

TABLE 2. *X*-RAY POWDER DATA FOR CENOSITE

I_v	d (meas.)	d (calc.)	hkl	Cotopaxi Colorado d^1	Hittero Norway d^1	Burgess twp. Ontario d^1	Bancroft Ontario d^1
				9.00* Å			
40	7.19 Å	7.165 Å	020	7.1	7.1 Å	7.1 Å	7.1 Å
100	6.52	6.525	200	6.50	6.6	6.50	6.56
2	6.29	6.280	120				
15	5.55	5.542	111	5.5		5.54	5.5
50	4.83	4.824	220	4.80	4.8	4.80	
7	4.60	4.604	121				4.6
<1	4.46	4.464	211				
20	3.66	3.660	301				3.65
30	3.54	3.546	311	3.55	3.55		3.54
70	3.45	3.455	140	3.44	3.46	3.45	3.45
80	3.29	3.294	012	3.28	3.29	3.29	3.29
5	3.26	3.262	400				
75	3.19	3.194	112	3.19	3.20	3.19	3.20
30	3.14	3.140	240	3.12		3.15	3.13
40(d)	3.06	{3.061 / 3.077	{022 / 141	3.03	3.05		3.04
5	2.97	{2.969 / 2.980	{420 / 122				
10	2.94	2.941	212				
20	2.906	2.905	331				
20	2.876	2.879	411				
20	2.844	2.849	241				
100	2.764	{2.765 / 2.771	{340 / 222	2.75	2.77	2.76	2.76
2	2.705	2.702	132				

TABLE 2 (*Concluded*)

I_v	d (meas.)	d (calc.)	hkl	Cotopaxi Colorado d^1	Hittero Norway d^1	Burgess twp. Ontario d^1	Bancroft Ontario d^1
5	2.629	2.626	312	2.62			
40	2.557	2.560	341	2.55	2.56	2.55	2.55
5	2.543	2.543	232				
10	2.502	2.503	431				
30(d)	2.438	{2.435 / 2.447}	{501 / 251}				2.44
40(d)	2.397	{2.401 / 2.388}	{511 / 060}	2.39–2.44			2.39
<1	2.352	2.349	402				
<1	2.305	2.306	521				
2	2.251	2.252	061				
5	2.224	2.229	013				
70	2.170	{2.175 / 2.170}	{600 / 531}	2.16	2.17	2.17	2.17
50	2.107	{2.109 / 2.109}	{540 / 213}	2.10	2.12	2.10	2.12
<1	2.074	2.074	252				
<1	2.045	2.044	223				
5	2.014	2.014	541				
<1	1.983	1.984	313		1.98		
40	1.957	1.959	071	1.95		1.95	1.96
60	1.929	1.930	162	1.92	1.93	1.93	1.92
<1	1.876	1.877	271	1.88*			
2	1.847	1.847	333				
5	1.815	{1.817 / 1.815}	{452 / 612}				
10	1.792(d)	{1.791 / 1.793}	{080 / 641}				
10	1.780(d)	{1.780 / 1.783}	{362 / 711}	1.778			
40	1.732	1.732	081	1.72		1.73	1.73
10	1.708	1.709	632	1.70			
5	1.696	1.692	004				
40	1.676	1.676	552	1.67			1.67
10	1.659	{1.661 / 1.656}	{523 / 380}				
5	1.640	1.640	063				
5	1.624	1.625	372	1.58–1.66 5 lines			
5	1.608	1.607	533				
5(d)	1.591	{1.590 / 1.595}	{820 / 034}				
<1	1.574	1.576	811				
2	1.433	{1.435 / 1.433}	{643 / 0100}	1.45			
2	1.418	{1.419 / 1.418}	{752 / 901}				
10(d)	1.403	{1.403 / 1.405}	{083 / 832}				
5	1.261	1.261	592	1.255			1.26

[1]Heinrich *et al.* (1962, p. 333)
*Line due to doverite
(d) Diffuse and/or possibility of a doublet
Camera diameter (114.6 mm.). Cu$K\alpha$

the presence of a weak, slightly diffuse forbidden reflection at 300. Because small amounts of $FeK\alpha$ have been identified in the x-ray beam, it is possible that traces of Cr radiation are also present. Diffraction of Cr radiation by the (200) plane would explain this anomalous spot.

The indexed pattern with visually estimated intensities is compared in Table 2 with powder data given by Heinrich *et al.* (1962, p. 333) for cenosites from various localities. In Table 2, the Cotopaxi cenosite has lines at 9.0 Å and 1.88 Å which probably result from small amounts of doverite present in the specimen; the Cotopaxi mineral is known to alter to doverite (Heinrich *et al.* 1962, p. 332). The cell elements and measured specific gravity of 3.52 (suspension in thallous formate-malonate), yield

TABLE 3. CHEMICAL ANALYSIS AND CELL CONTENT OF CENOSITE[a]

Oxides	Wt. (%)	Mol. Ratios		Metal Atoms Per Cell	Oxygen Atoms Per Cell
CaO	16.78	0.2992			
Na$_2$O	0.04	0.0006	$\dfrac{0.2999}{2} = 0.1499$	8.07 (8)[e]	8.05 (8)[e]
K$_2$O	0.01	0.0001			
MgO	0.00	0.0000			
Ce$_2$O$_3$[b]	0.38	0.0012			
Nd$_2$O$_3$	0.19	0.0006			
Sm$_2$O$_3$	0.27	0.0008			
Y$_2$O$_3$	25.27	0.1119			
Gd$_2$O$_3$	2.44	0.0067	$\dfrac{0.1492}{1} = 0.1492$	8.01 (8)	12.02 (12)
Dy$_2$O$_3$	3.10	0.0083			
Er$_2$O$_3$	3.53	0.0092			
Yb$_2$O$_3$	2.71	0.0069			
Fe$_2$O$_3$[e]	0.57	0.0036			
Al$_2$O$_3$	1.20	0.0118			
SiO$_2$	35.24	0.5867	$\dfrac{0.5989}{4} = 0.1497$	16.39 (16)	32.47 (32)
TiO$_2$	0.02	0.0003			
ThO$_2$	0.03	0.0001			
CO$_2$	4.60	0.1045	$\dfrac{0.1045}{1} = 0.1045$	2.80 (4)	5.61 (8)
H$_2$O$^+$	2.59	0.1437	$\dfrac{0.1437}{1} = 0.1437$	7.71 (8)	3.85 (4)
H$_2$O$^-$	.06				
FeS$_2$	.98	No. of atoms in the cell including 4H$_2$ (108)			
Total	100.20				
Less O ≡ S	.19				
	100.01[d]				

[a]J. A. Maxwell, Analyst.

[b]Rare earths and thorium were determined by x-ray fluorescence analysis of the rare earth chemical concentrate, G. R. Lachance, Analyst.

[e]Total Fe in cenosite, as Fe$_2$O$_3$; FeO not determined. Total Fe in sample was 1.22%, total S 0.52%. The S was combined with an equivalent amount of Fe to form pyrite (FeS$_2$) and the remainder of the Fe was assigned to cenosite.

[d]Includes MnO 0.01%, SrO 0.01%.

[e]Theoretical cell content.

a unit cell content of 4 molecular weights per cell. The calculated specific gravity based on the chemical analysis and assuming CO_2 stoichiometry is 3.542. The chemical analysis, molecular ratios, and the atomic content of the cell are given in Table 3. The deficiency in CO_2 apparent in Table 3 is thought to result, as previously mentioned, from the presence of granular CO_2- deficient cenosite in the analyzed specimen.

CHEMICAL ANALYSIS

The chemical analysis was made on 1 gram of material using conventional methods. SiO_2, CaO, MgO, and total S were determined gravimetrically; Al_2O_3 was obtained by difference following the separation of the R_2O_3 group (and removal of the rare earths) and the potentiometric and colorimetric determination respectively of total Fe and TiO_2 on the solution of the pyrosulphate fusion of the ignited R_2O_3 precipitate; MnO was also determined colorimetrically (periodate) but Na_2O, K_2O and SrO were obtained by a flame photometric procedure; H_2O was determined by the modified Penfield method and the CO_2 gravimetrically, following absorption of the gas liberated when the sample was boiled with dilute HCl. The bulk of the rare earths (and thorium) was separated by precipitation with oxalic acid and a further small recovery was made with ammonium sebacate from the filtrates remaining after the separation on the main portion constituents. The combined and ignited rare earth oxides were analyzed by x-ray fluorescence spectroscopy.

INFRARED SPECTRUM OF CENOSITE

The two infrared absorption spectra of Figure 2 were obtained from specimens of clear, stoichiometric cenosite, run at different concentrations.
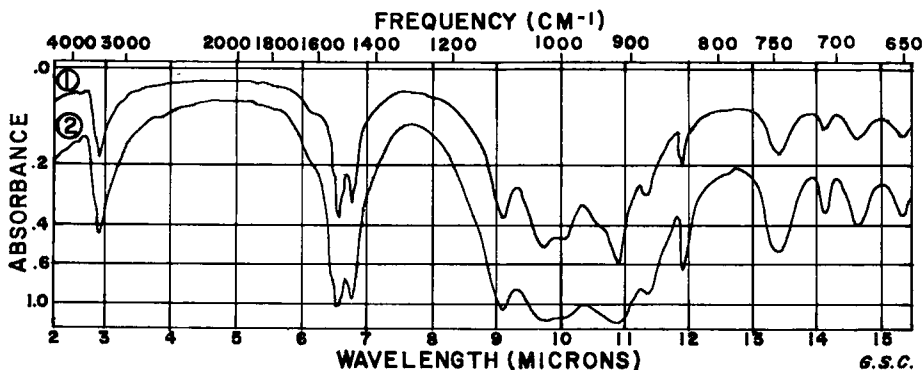

FIG. 2. Infrared absorption spectra of cenosite. KBr 1 mm. thick pellets (no. 1, 0.15% by weight, no. 2, 0.43% by weight) Perkin Elmer Model 21 instrument.

Both recordings yield virtually identical peak locations. Listed in order of increasing wavelength, Bicroft cenosite has absorption maxima located at (Fig. 2): 2.92, 6.15, (6.55, 6.77), (9.1, 9.72, 10.05, 10.60, 10.88, 11.34), 11.89, 13.42, 14.12, 14.64 and 15.34 microns.

From the limited data at hand it is only possible to work out a qualitative interpretation of the spectrum.

Absorption maxima in the 2.8–3.1 micron region of infrared spectra of minerals are characteristically associated with oxygen-hydrogen vibration frequencies (stretching, bending) of hydroxyl groups and/or water in the structure. Molecular water or adsorbed moisture generally yields additional absorption maxima in the 6 to 6.5 micron region. In the cenosite spectrum, the ill-defined peak at 6.15 microns is due to adsorbed moisture whereas the sharp maximum at 2.92 microns is attributed to O–H vibration frequencies in the cenosite structure.

Infrared spectra of carbonates are characterized by major absorption maxima in the 6.5–7.5 micron region and other bands of lesser intensity in the 11 to 14 micron region (Hunt *et al.* 1950). The major peak in the 6.55–6.77 micron region of the cenosite spectrum thus appears well accounted for by CO_3 vibration frequencies.

Silicates absorb strongly in the 9 to 11 micron region. Certain silicates, however, have additional maxima in the 13 to 15 micron region that may interfere with those due to CO_3 vibrations. The broad maximum covering the 9 to 11 micron region appears characteristic of the silicate bonding in the mineral. The identification of the remaining maxima, i.e. the 11 to 15 micron region is uncertain. By analogy to the infrared absorption spectra of the aragonite group of carbonates (Huang & Kerr, 1960: Adler & Kerr, 1962) the maxima at 14.12 and 14.64 microns are tentatively correlated with CO_3 vibrations. Their displacement to the long wavelength side of the location of the corresponding maxima in aragonite (11.63, 14.03, 14.30 microns), is attributable to the heavier atomic weight of the cations (Ca, Y, Er, etc.) in cenosite.

The infrared spectrum satisfactorily identifies the various ionic groups present in cenosite. Because very small quantities of material are needed to obtain a spectrum, the infrared technique can be a valuable guide for chemical analysis of complex minerals.

CONCLUSION

Cenosite at the Bicroft Uranium mine occurs in vugs. The different mineralogy of the vug compared to that of the dykes suggests that cenosite formed under different conditions, evidently later than the uraniferous ore mineralization associated with the dykes.

The mineral is similar in habit and morphology to the North Burgess cenosite. Except for a deficiency in CO_2 attributable to loss of CO_2 from zones of the crystals, Bicroft cenosite corresponds well with the formula $Ca_2(Y, Dy, Er, etc.)_2(Si_4O_{12})CO_3.H_2O$ calculated by Graham & Ellsworth (1930). The lack of a detailed rare earth analysis for the North Burgess mineral prevents the comparing of their chemistry. The rare earth content of the Cotopaxi and Bicroft cenosites, the only two minerals for which complete rare earth analyses are available, is compared below:

	Cotopaxi[1]	Bicroft
$(Ho, Tm, Tb)_2O_3$	0.5 (est. max)	not determined
$(La, Ce, Nd, Sm)_2O_3$	0.5 (est. max)	0.84
Gd_2O_3	0.5 (est. max)	2.44
Er_2O_3	2.3	3.53
Dy_2O_3	2.6	3.10
Yb_2O_3	2.3	2.71
Y_2O_3	29.0	25.27

[1]Heinrich *et al.* (1962, p. 334).

From this, the Bicroft cenosite is significantly lower in Y and richer in Yb, Dy, Er, Gd, than the Cotopaxi mineral. The higher content of heavier rare earths in the Bicroft mineral accounts for its higher specific gravity (3.52) than Cotopaxi cenosite (3.41).

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