

Calcian Ancylyte from Pennsylvania: NEW DATA

AUTHORS

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ABSTRACT

New data have been obtained on ancylite from Cornog, Pennsylvania. Ancylyte, an orthorhombic mineral of composition $(\text{Ce}, \text{La})_4(\text{Sr}, \text{Ca})_3(\text{CO}_3)_7(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ (thus a hydrated basic carbonate of strontium, calcium, and the cerium group of rare earths) occurs in minute, pale-pink crystals at the Keystone Trappe Rock quarry, Cornog, Chester County, Pennsylvania. Most crystals (the largest ones are 1-2 mm in length) possess but two forms: $\{111\}$ and $\{120\}$. Most of the observed crystal faces are curved. The refractive indices are: $\alpha = 1.654$, $\beta = 1.733$, $\gamma = 1.772$, birefringence 0.118, biaxial negative with $2V = 60$ -70 degrees, r/v barely perceptible. Ancylyte crystals from Cornog typically are perched on calcite or embedded in cellular calcite and quartz masses. X-ray photographs give unit cell dimensions of: $a = 4.97$, $b = 7.24$, and $c = 8.50$ Å. Color effects in the material can be explained on the basis of characteristic lanthanide absorption bands and variations in incident light.

Work on Cornog ancylite by the authors of this paper was distributed as follows: Montgomery, review of earlier work and literature, geology and occurrence of ancylite, and descriptive mineralogy; Keidel, crystal collecting, mineral separa-

tion and optical-absorption measurements; Wolfe, crystallographic data and x-ray analysis; Christian, x-ray fluorescence spectroscopic analysis.

Introduction

Ancylyte (ankylit) was first discovered by Gustav Flink in 1897 at Narsarsuk (Narssarsuk) near the southwesterly tip of Greenland. He described it four years later (Flink, 1901), including a chemical analysis by R. Mauzelius. The tiny, pale-yellow, octahedral-like orthorhombic crystals, associated with parisite, cordylite, and aegirine in pockets within a nepheline-syenite complex, show curved faces which gave rise to its name (for "curved" in Greek) and cause extreme inaccuracies in crystallographic measurement.

In 1923, S. G. Gordon collected extensively at Narsarsuk and obtained numerous specimens of ancylite. He determined the optical properties, incorrectly given in the first edition of the Larsen optical tables (Larsen, 1921). He reoriented the crystals with improved recognition of the forms and supplied new data on interfacial angles and crystallographic elements (Gordon, 1925). His crystallographic and optical data are those given for ancylite in *Dana's System of Mineralogy* (7th ed., vol. 2, 1951, pp. 291-293). The crystallographic data given here for superior crystals from Pennsylvania prove Gordon to have failed, as did Flink, in securing satisfactory data on interfacial angles and the derived crystallographic elements.

More than a dozen occurrences of ancylite have been described since Flink's original paper. Most

of the finds were made in Russia. Nearly all are found associated with carbonates and alkalic igneous rocks, chiefly syenitic pegmatites. Other Russian occurrences have been reported more recently, mostly in rocks from the Kola Peninsula but also from similar types of alkalic rocks elsewhere. Distinct crystals are generally absent but, where present, have formed very late.

Three occurrences have been described from localities in the United States and Canada. Ancylyte was found in the Bearpaw Mountains of Montana (Pecora and Kerr, 1953) in hydrothermal veins associated with mafic and felsic alkalic igneous rocks. It was later discovered in Ravalli County, Montana (Heinrich and Levinson, 1961) in carbonatic alkalic-type hydrothermal veins associated with marble and amphibolitic gneisses. Mandarino, Harris and Bradley (1965) recorded data for an ancylite-like mineral from St. Hilaire, Quebec, occurring in nepheline-syenite pegmatities in association with carbonates and alkalic-type minerals; certain of its properties, as its pinkish color and optical-absorption effects, are similar to those of the crystals from Cornog described in this paper and its x-ray powder pattern is almost identical with those of crystals from both Narsarsuk and Cornog.

Where separations of the fairly pure mineral have been made, chemical analyses typically show a ratio of roughly 2:1 for rare earths (chiefly Ce and La) compared to the sum of Sr and Ca, plus additional minor substituting cations. In most reported analyses Sr greatly exceeds Ca. The published analyses for Ca-

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*Publication approved by the Director, U.S. Geological Survey.

rich and Sr-lean (or Sr-free) ancylite (calcio-ancylite being defined in Dana's System, p. 293, as the end-member with $\text{Ca} > \text{Sr}$) refer in part to calcian ancylite from a nepheline-syenite pegmatite in the Kola Peninsula (Tschernik, 1923) and record but a single occurrence of "calcio-ancylite" from an uncertain locality in western Russia (Tschernik, 1904).

Geological Occurrence at Cornog

The original discovery of ancylite at the Keystone Trappe Rock quarry 1/2 mile east of Cornog, Chester County, Pa., 2 miles north of Lyndell and about 30 miles west of Philadelphia, was made in the nineteen-forties by S. G. Gordon. He had difficulty in identifying the mineral, and seems only to have mentioned the new find to others. This is why, by the early nineteen-sixties and long after Gordon's death, no more than vague rumors persisted about a possible occurrence of ancylite at the Keystone quarry.

In 1965 R. M. Eisenhauer picked up a loose fragment of amphibolite gneiss in the Keystone quarry showing several minute pale-pink crystals associated with well-crystallized calcite, pyrite, and actinolite. Eisenhauer at once suspected the crystals might be ancylite, recalling the similar habit shown in Gordon's crystal drawing in Dana (Fig. 3). A single crystal was determined to be ancylite by one of the authors (A.M.) by means of its optical properties and x-ray powder pattern. In 1967 Keidel found many more of the same crystals in small calcite-lined cavities of a large freshly-mined block of amphibolite lying near the entrance to the Keystone quarry. All of that material was studied at Lafayette College. It was not until 1968, with quarry operations abandoned, that Keidel and Montgomery were able to locate the source of the ancylite at the base of the quarry wall near its northwest corner (Fig. 1).

The Keystone quarry has an irregular shape, measuring roughly 700 feet northeast-southwest by 500 feet northwest-southeast, and is nearly 200 feet deep at its lower level. Quarrying has gone on inter-

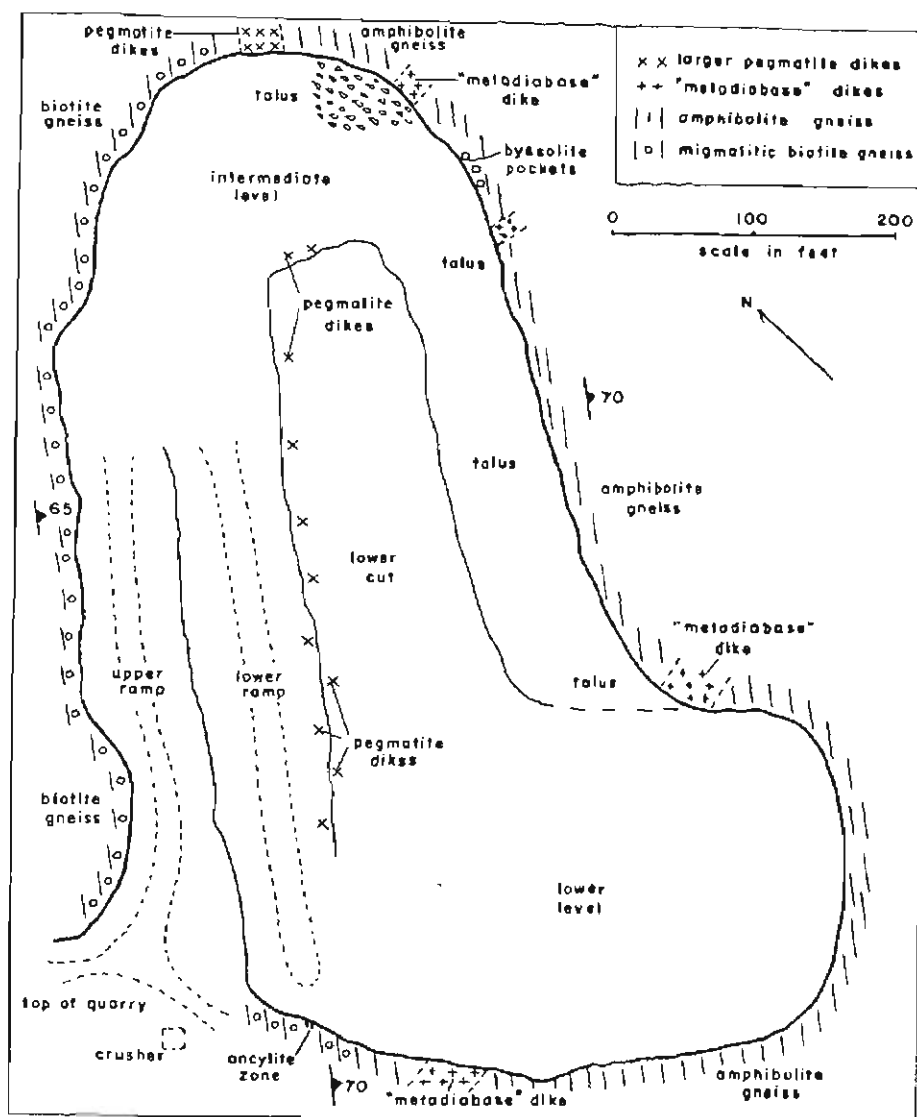


Fig. 1. Map of Keystone quarry, near Cornog, Pa., showing geology and location of the ancylite zone.

mittently from 1907 until 1968. The quarry was worked for crushed road-metal material and massive blocks for foundations and is now partly under water. During the nineteen-fifties and sixties the quarry became a highly productive mineral specimen locality, thanks to the generous cooperation of H. T. Galt, operator and owner until 1968. In the early sixties clinozoisite prisms of large size were found in fracture fillings of calcite and quartz in the amphibolite near the base of the southeast wall of the quarry. Blasting later exposed open pockets there (Fig. 1) in which were discovered excellent crystallized specimens of prehnite, actinolite, clinozoisite, axinite, titanite, apatite, adularia, albite and quartz. Coatings of hair-like actinolite (byssolite) occurred closely intergrown with those minerals. Montgomery (1964)

suggested that these pockets and their crystallized contents are similar to Alpine-cleft minerals, where the chemical constituents of the pocket crystals have been derived from the wall-rock and the newly-formed species chiefly represent regenerated minerals common in, or chemically related to, the adjoining rocks. The newly-formed crystals at Cornog were deposited in the cavities by hydrothermal solutions which first attacked and leached the wall-rock of some of its constituents. A complex paragenetic sequence of minerals and several periods of mineralization have been inferred for these occurrences (Montgomery, 1969). No trace of ancylite was ever found in that part of the quarry.

The rocks exposed in the Keystone quarry are mostly amphibolitic (hornblende-plagioclase) gneisses

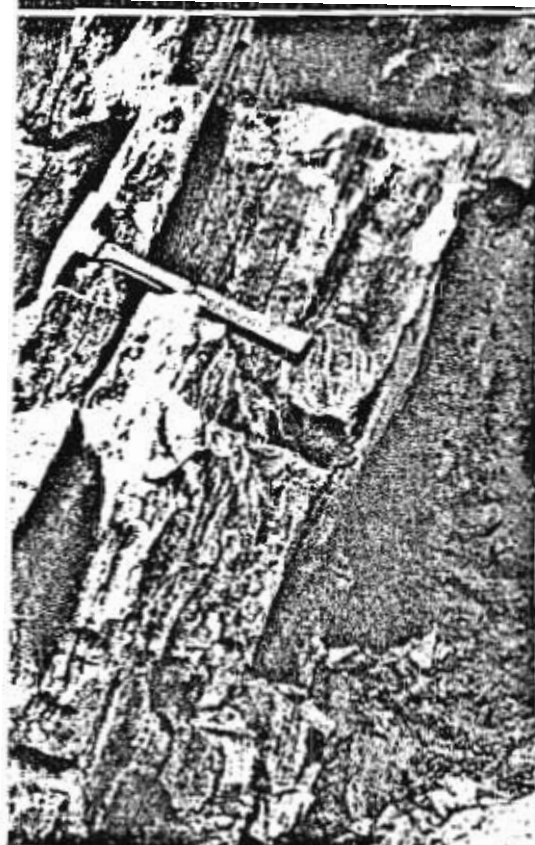


Fig. 2. Hammer crosses most of the 18-inch-wide ancylite zone exposed near base of northwest corner of Keystone quarry wall. Northwestern edge of zone is 5 inches to right of end of hammer. Note twisted gneissic banding (end of handle) and vuggy rock with calcite-lined cavities below hammer.

and migmatitic biotite gneisses. Also present are some dark bodies, very fine-grained and massive, and many smaller, whitish, layer-like dikes of coarse-grained granitic pegmatite spotted by abundant coarse, irregular or pod-shaped, grains of pale- to deep-bluish quartz. The latter two rock types display crosscutting relationships with respect to the foliated and well-banded amphibolites which Bascom and Stose (1938) incompletely mapped during early quarrying as "gabbroic gneiss" belonging to the Precambrian Pickering Gneiss. The dark, fine-grained bodies they regarded as "metadiabase" dikes of still later Precambrian age. The general area is one of very complex geology, with the Precambrian rocks here exposed forming part of the upfolded Honeybrook mass which grades westward into the Mine Ridge anticline.

The main part of the quarry is excavated in the greenish-

black, strongly-banded amphibolitic gneisses in which the whitish layers of intrusive pegmatite commonly occur, from thin bands intercalated with dark amphibolite bands up to sill-like layers 6 or 8 feet thick and extending for hundreds of feet parallel to the gneissic foliation. The dark fine-grained bodies, dark greenish-gray in color, are irregular obscurely-defined masses exposed in several places in the quarry walls where they appear to extend vertically from the floor to the lip of the quarry. They measure up to 20 feet across in horizontal dimension and at places distinctly cut across the gneissic banding of the surrounding amphibolite at a sharp angle. The dark- and white-banded, migmatitic biotite gneiss, in which thin, sheet-like, blackish biotite-rich layers stand out prominently, is almost entirely limited to the northwestern corner of the quarry, the northerly ramp-way areas below the north wall, and the 700-foot-long exposure of northerly quarry wall overlooking the ramp-ways. A major contact, although gradational, thus occurs along the area of the ramp-ways between amphibolite gneiss to the southeast and biotite gneiss to the northwest. A zone, up to 30 feet wide, primarily of large-scale pegmatite dikes parallel to the surrounding gneissic foliation lies along a good part of the northeasterly end of this contact. The strike of gneissic foliation and banding throughout the quarry ranges from N30E to N50E with a very steep, southeasterly dip averaging about 70 degrees.

The ancylite occurrence is limited to one narrow rock zone paralleling the layering of the biotite gneiss near the base of the northwesterly corner of the quarry wall. The gneiss here for some tens of feet both north and south of the ancylite zone consists mainly of a dark-and-light interlayering of gray-black, biotite-rich, granulitic bands, usually less than an inch thick and sometimes almost wholly biotite films and sheets, with whitish, pegmatitic layers. The latter appear to be of later origin than the biotite-rich bands, possibly injected into the host rock as thin sheets of granitic magma so as to become inter-layered with it in lit-par-lit fashion.

The resultant well-banded gneiss thus may be termed a migmatite. The thickness of individual layers of biotite gneiss and of pegmatite varies from less than an inch to more than 6 inches.

The almost vertical, layer-like, ancylite-bearing zone within the migmatitic biotite gneiss is about eighteen inches wide horizontally and extends from the quarry floor upward for about 20 feet in the wall above, where it pinches out or changes character so as to become indistinguishable from the surrounding gneiss. This zone is distinguished from the adjacent rocks by the: (1) irregular, deformed and twisted attitude of its gneissic layering; (2) presence of numerous irregular cavities, from narrow curving open fractures an inch or two long to lenticular pockets several inches wide and 8 or 10 inches in length, partly paralleling but also athwart the associated gneissic banding; (3) abundance of white calcite, much of it crystallized, with single crystals up to half-inch size, in and around the cavities which are almost all calcite-lined; (4) abundance of brassy-yellow pyrite both as a spotting of small cubes and as streaky films and masses through much of the rock, especially within and around the calcite-lined pockets; (5) presence throughout the zone of bright-greenish actinolite in felted mats of densely-aggregated, slender blade-like prisms of small size, as well as separate, clean-cut prisms intergrown with calcite crystals in and around the pockets. The rock comprising the zone, although distinguished by these features, nevertheless consists mostly of well-banded migmatitic biotite-actinolite gneiss not very different from, and in part gradational into, the surrounding rocks. Isolated masses of almost typical biotite gneiss, up to a foot in size, stand out here and there within the zone, but with the gneissic banding near their borders bent, disrupted and sheared off by sharp contact with crosscutting, streaky and vein-like rock. This latter rock contains "smeared-out" matings of grass-green actinolite blades and much granular whitish calcite; shows disrupted, partially broken-off and displaced bands of

pegmatite which have been also in part unmistakably etched and dissolved away; and is full of highly-irregular, curving, crystal-lined fractures and pockets.

Thin-section petrographic study of the migmatitic biotite gneiss surrounding the ancylite zone reveals these features: the thin dark layers consist of parallel trains of densely-aggregated biotite flakes of brownish to greenish-black pleochroism with interstitial grayish highly-sericitized and sausseritized feldspar; some biotite aggregates grade into mats and sprays of tiny slender greenish actinolite blades; streaks of minute dark granules, partly of epidote and iron-oxide, are strung out in and around the biotite trains, as are locally-abundant small lenticular grains of indistinct patchy perthite grains of medium size full of specks of kaolinite, calcite and sericitic material, except at the borders where clear rims of albite occur; small irregular grains of calcite are sparsely present in the feldspar or spotted along quartz-feldspar contacts in all sections studied; small cubes of pyrite occur in some sections; quartz grains of all sizes surround the feldspar, the larger showing undulatory extinction.

Migmatitic biotite gneiss from the pockety calcite-rich ancylite zone displays similar mineralogical and textural relations except for the following features: actinolite blades, of a brighter grass-green, are in clean-cut, isolated, as well as aggregated, crystals and abundant both in intergrowths with biotite and also strung out in parallel orientation through the feldspar and quartz; quartz is mostly in finely-granulated streaks and veinlets crossing rugged indistinct perthite grains; pyrite cubes ranging from 0.01 to 0.04mm in size are common, and sometimes abundant; calcite is common from small grains scattered through feldspar and against quartz up to grains of large size and irregular shape; in several sections scarce zircon grains, around 0.02mm in size and associated with biotite, occur as relic, fractured and broken-apart aggregates surrounded by wide dark borders possibly of iron-oxide; in two sections several round, fuzzy, partly-translucent, gray-brown grains, of average 0.01 to 0.02mm size and rimmed by wide black halos as well as by radially-aggregated clusters of transparent epidote prisms, may represent partly-altered crystals of allanite.

Origin

The rocks peculiar to the ancylite zone seem to be a locally highly-sheared and recrystallized version of the surrounding migmatitic biotite gneisses. The minerals of the ancylite pockets are general-

ly the same, except for ancylite, as those normal to the adjacent rocks, although they occur in larger and better crystals and more abundantly. Late-stage hydrothermal solutions, concentrated in their action along a narrow zone of intensely-deformed and fractured rock in which the more brittle pegmatite layers were broken apart and exposed to attack by the corrosive solutions, penetrated the fractures, partly dissolved the quartz, feldspar and other minerals of the wall-rock, and deposited new crystals of calcite, actinolite and pyrite in the cavities. Similar late-stage solutions probably formed the crystals in the prehnite-byssolite pockets elsewhere in the quarry, except that there the new minerals reflect the somewhat different chemistry and mineralogy of the associated amphibolite. Prehnite is missing from the ancylite pockets, possibly because calcium was used to make calcite instead of prehnite; while fibrous byssolite of the prehnite pockets finds its counterpart in the cleanly-crystallized actinolite of the ancylite cavities. Ancylite could have derived its rare-earth content from adjacent altered allanite grains, traces of which are observable in thin sections of the surrounding biotite gneisses and large crystals of which also occur in granitic-pegmatite dikes within 100 feet of the ancylite zone.

This paragenetic interpretation, based on thin-section study and the mineralogical and geological relationships observed throughout the Keystone quarry, suggests that ancylite could have formed elsewhere within the biotite gneiss. The only requirements would have been late localized shearing to create openings within the gneiss, and attendant hydrothermal solutions to leach the wall-rocks surrounding those openings so as to dissolve out some of their chemical constituents (including rare earths from breakdown of allanite) and deposit new crystals of late-stage minerals, including ancylite, inside the enlarged pockets.

It is the belief of one of the authors (A.M.) that the final transformed rock of the ancylite zone, rich in actinolite and calcite, owes

its actinolite to breakdown and recrystallization of relics of earlier hornblende once present in darker layers of the biotite gneiss, and owes its calcite, at least a part, to the albitization and freeing of calcium from breakdown and recrystallization of earlier calcium-sodium plagioclase, sausseritized relics of which are still evident in the dark bands of the biotite gneiss. The coarse-grained calcite commonly present in the pegmatite dikes exposed in the quarry, especially in portions of those close to contacts with amphibolite, is an example of such recrystallized calcite. The late hydrothermal solutions could have picked up most of their contained elements from the biotite gneiss which they penetrated and altered; they only would have needed to bring in, as new elements, an abundance of carbon-dioxide to make calcite and sulfur for pyrite.

Descriptive Mineralogy

The ancylite crystals vary in size from 0.2 to 2.0 mm but mostly fall into three categories: largest crystals, usually multiple units, 1-2 mm in length; medium-size ones near 0.5 mm in greatest dimension; and smallest individuals, of slender prismatic habit, averaging about 0.2 to 0.3 mm in length.

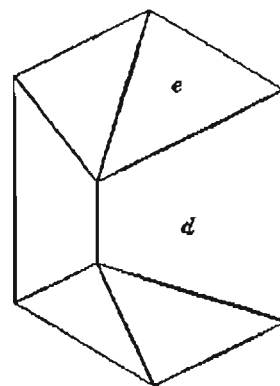


Fig. 3. Drawing of S. G. Gordon (1925, p. 2) of an ancylite crystal from Narsarsuk, Greenland, as given in **Dana's System of Mineralogy** (7th ed., vol. 2, 1951, p. 292).

A specific gravity determination of 3.95 was made by F. Cuttitta of the U.S. Geological Survey on a 7.9 mg. portion of the fine-grained crystal concentrate prepared for

x-ray fluorescence analysis. The determination was made with a micropycnometer according to the method described by May and Marinenko (1966).

Crystals of ancylite from Cornog are translucent and show a vitreous to distinctly greasy luster on fracture surfaces. The great majority exhibit a pale-pink color which shows up well in daylight or under non-fluorescent lamps, but disappears under ordinary household fluorescent-lamp illumination. In the latter case the crystals do not become completely colorless, but display a pale bluish-gray tinge. A few crystals fail to display pinkish color under any illumination, but remain whitish, grayish, or even brownish.

The optical properties of crushed fragments, which appear colorless in transmitted polarized light, are as follows: biaxial negative; refractive indices: $\alpha = 1.654$, $\beta = 1.733$, $\gamma = 1.772$ (± 0.003); birefringence = 0.118; $2V = 60-70$ degrees; $r < v$ barely perceptible.

The ancylite crystals occur typically perched on calcite crystals or on cellular masses of etched calcite or quartz. The distribution and abundance of crystals in the calcite-lined cavities are highly variable, and may be in part dependent on the size of the cavities. Perhaps fifty percent of the cavities studied

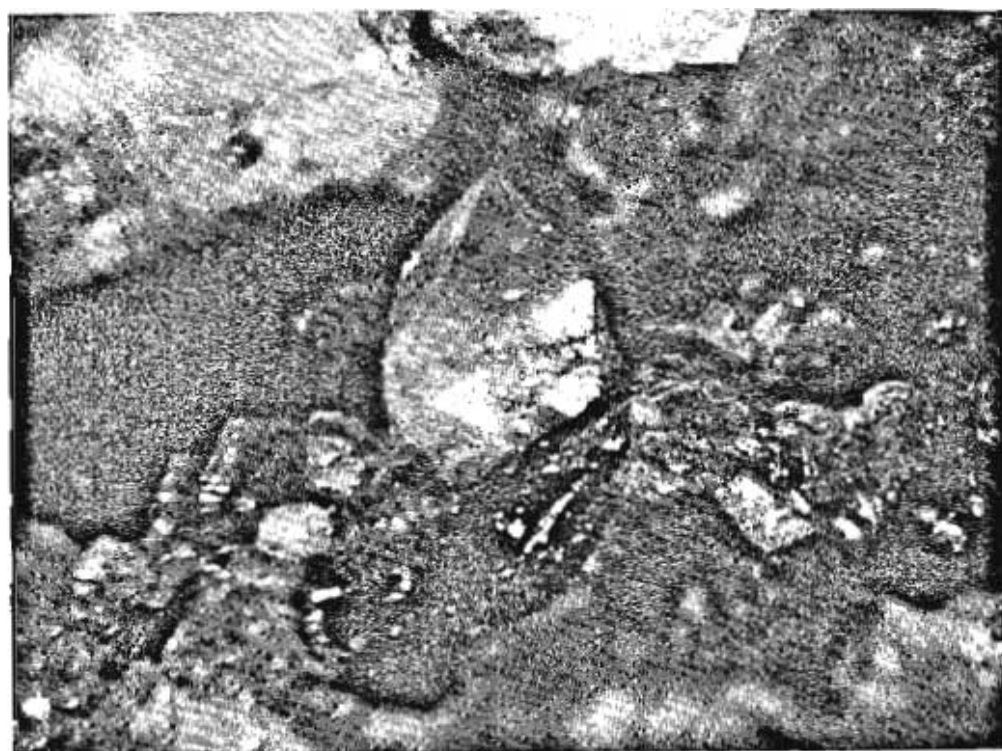


Fig. 4. Ancylite crystal (1 mm long) from Cornog, Pa., perched on calcite crystals and intergrown with actinolite blades. The vertical prism face (120) is illuminated. Photomicrograph by Louis Perloff.

contained a small number of crystals. Specimens collected from some pockets have contained numerous crystals, from up to a dozen of larger size to as many as fifty closely-associated individuals of the smallest category. The distribution appears to be entirely haphazard, both from cavity to cavity as well as within any one

pocket. Removal and breaking-up of a mass of rock within the ancylite zone, measuring more than 1x2x10 feet and weighing nearly a ton, have produced from the small open fractures and irregular pockets within it perhaps 2,000 crystals, most of them of smallest size.

Some crystals are intergrown with calcite crystals or masses; a

TABLE 1. Crystallographic measurements of ancylite

Form	No. Times	Av. Size	No. Crystals	Phi range	Rho range	Wgted phi	Wgted rho	Calc. phi	Calc. rho
{100}	2	line	1	88°53'-92°55'	90°00'	90°00'	90°00'	90°90'	90°00'
{010}	1	line	1	2 30	90 00	2 30	90 00	0 00	90 00
{120}	24	large	6	36 51 -37 37	90 00	36 55	90 00	36 55	90 00
{101}	4	line	3	90 15 -93 33	55 20 -57 48	90 00	56 34	90 00	58 55
{111}	24	medium	6	56 15 -59 26	58 29 -64 14	56 21	63 21	56 21	63 21

Angle table for ancylite — Orthorhombic; dipyrmidal 2/m 2/m 2/m

a:b:c=0.666:1:1.108; q:r:p=0.666:0.603:1; p:q:r=1.660:1.108:1 r:p:q=0.906:1.502:1							
Forms	Phi	Rho	Phi	Rho	Phi	Rho	
b {010}	0.00	90 00	90 00	90 00	-	0 00	
a {100}	90 00	90 00	-	0 00	0 00	90 00	
d {120}	36 55	90 00	90 00	53 05	0 00	36 55	
h {101}	90 00	58 55	0 00	31 05	58 55	90 00	
e {111}	56 21	63 21	47 39	41 56	31 05	60 19	

few appear intergrown with actinolite blades or with pyrite cubes around 0.5 to 1.0 mm in size. A good many crystals are also coated by, or intergrown with, in their outer portions, exceedingly minute pyrite cubes smaller than 0.05 mm in size. Rarely, whitish, etched and partly-dissolved, stubby-prismatic crystals of apophyllite, up to 5 mm in size, or blade-like crystals of whitish barite, up to 0.5 mm in length, are found closely associated with the ancylite. The relative positions of the crystals of all these minerals suggest very late-stage growth, similar to that of all the ancylite crystals observed, upon surfaces of earlier-crystallized calcite or etched masses of calcite or quartz.

Morphological and X-ray Crystallography

Morphology

No claim is made in this study for highly precise determination of the elements of ancylite, but the ones given undoubtedly have much higher validity than those obtained by Gordon (1925). Crystals are very small, less than 1 millimeter for the most part, and signals from faces of such crystals are poor even when the faces are completely planar. There was a slight curving to most of the measured faces and the quality of the signals was uniformly bad. In fact, the only signal which could be obtained was a blur of light in the field of the telescope. In the cases of the very small faces no signal was secured; but the faces could be well observed with the microscopic arrangement of the goniometer, and the position of brightest reflection from the face was set before making the angular readings.

Most of the crystals showed a well developed prism form and, to facilitate orientation of the crystal for measurement, this prism was set vertically. All of the crystals showed a well developed pyramidal form which was arbitrarily designated as $\{111\}$, even though such a designation required that the dominant prism be indexed as $\{120\}$ rather than $\{110\}$. X-ray determination of the unit-cell constants corroborated this choice.

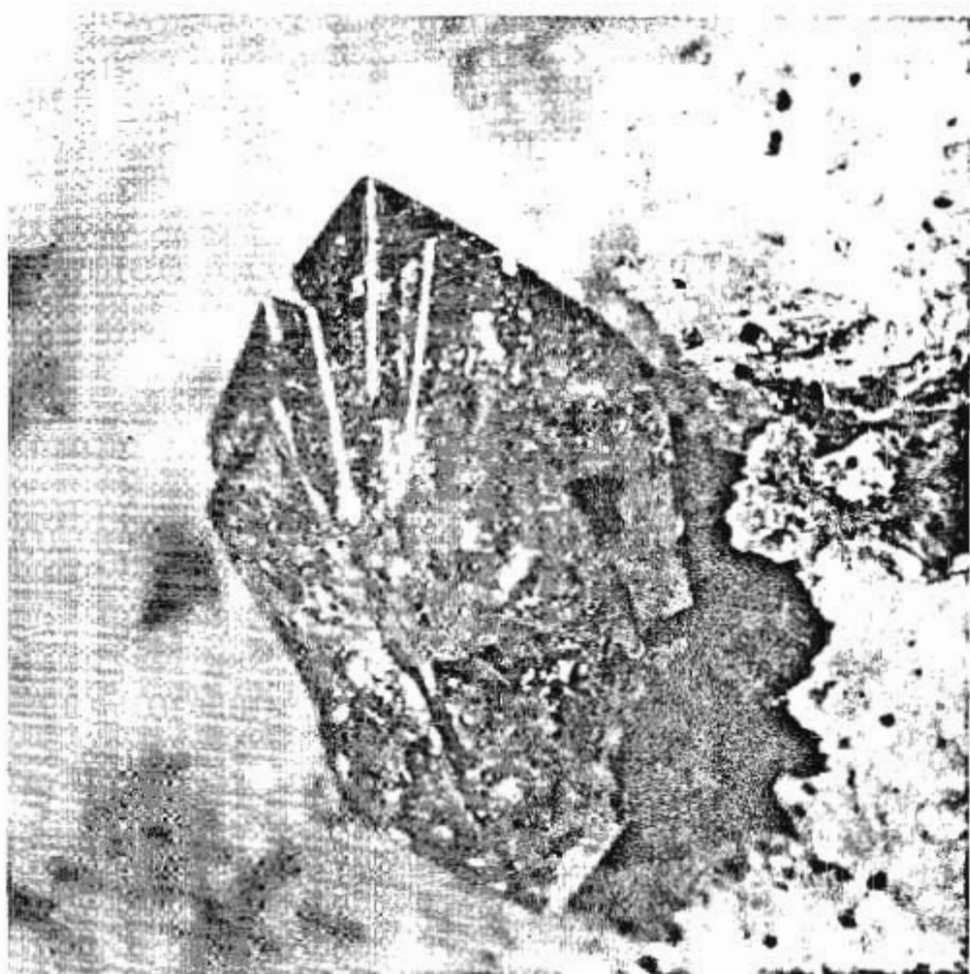
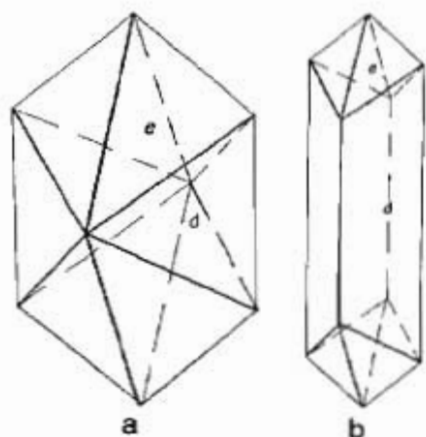


Fig. 5. Ancylite crystal (1 mm long) from Cornog, Pa., showing typical multiple unit made up of several subparallel individuals. The (101) line face is illuminated. Photomicrograph by Julius Weber.



Figs. 6a and 6b. Ancylite crystals from Keystone quarry, Cornog, Pa., showing dipyramidal habit (6a, left) common in larger individuals and slender prismatic habit (6b, right) typical of smallest crystals. The habit of dipyramidal crystals (6a) becomes pseudo-octahedral with the common rounding of the e faces (111) to make pairs of these appear as if single faces.

Two principal habits were observed. The most common is a pseudo-octahedral habit with a roughly equal development of the forms $\{111\}$ and $\{120\}$, as indicated in Fig. 6a. Other crystals are characterized by the larger development of the form $\{120\}$ and are stout prismatic to elongated prismatic in habit, as shown in Fig. 6b.

Six crystals proved suitable for goniometric measurement. The results are tabulated below. Although many of the crystals are doubly terminated, in no case were both ends of the crystal measured. There is no doubt, however, that the crystal class is orthorhombic, dipyramidal - $2/m \ 2/m \ 2/m$. The wide range of measurements listed for each form indicates the poor quality of the signals. Three crystals of the six measured were measured twice, and one three times, to ascertain the degree of precision with which the signals could be centered. As a result, it was con-

cluded that the angular positions of the signals could not be read with a greater precision than about 30 minutes. By implication, therefore, the original orientation of the crystals before measurement could not have had very great accuracy. The correlation between the goniometric elements and those obtained by X-ray measurements seems remarkable, and may be somewhat fortuitous:

	<i>a</i> to <i>b</i>	<i>b</i> to <i>c</i>
goniometric	0.666	1.108
X-ray	0.686	1.175

X-ray measurements

Rotation and zero- and first-layer Weissenberg photographs were taken about the *c* [001] and *b* [010] axes, with the following results: *a* = 4.97 Å, *b* = 7.24 Å, *c* = 8.50 Å (all ± 0.05 Å); *a*:*b*:*c* = 0.686:1:1.175.

Mandarino, Harris and Bradley (1965) reported cell dimensions of: *a* = 7.24, *b* = 8.49 and *c* = 5.02 Å based on x-ray measurements on crystals of their ancylite-like material from St. Hilaire, Quebec. Their data are in excellent agreement with those given above for ancylite from Cornog, except for the choice of axes. Their choice of axes follows the conventional orientation (*c* < *a* < *b*) for orthorhombic crystals; our x-ray measurements were made with the strongly developed {120} form set parallel to the *c*-axis, thus following the orientation adopted by Gordon (1925), and Flink (1901) before him, for ancylite crystals from Greenland. The space group of "ancylite" from St. Hilaire, as determined by Mandarino, Bradley and Harris, is *Pmmm*.

Optical-absorption Measurements

One of the most striking features of the ancylite from Cornog is its peculiar color behavior dependent on the type of illumination in which it is viewed. Although the crystals appear distinctly pink in daylight or under incandescent light, the color is pale bluish gray when ordinary fluorescent (cool white) illumination is used. Under the latter conditions, the small ancylite crystals are very difficult to recognize on matrix when surrounded

with calcite or quartz; there is too little difference in color. Crystals of the ancylite-like mineral from St. Hilaire, Quebec, behave in an identical manner.

This unusual behavior of Cornog ancylite prompted one of the authors (F.A.K.) to measure its absorption spectrum for visible light. Because of the small size of individual crystals and the availability of so very little material, it was necessary to employ a special microspectrophotometer, kindly made available in the Botany Department of Yale University, for these measurements. The sample chosen was a single crystal selected for clarity and freedom from included matter; it was about 0.5 x 0.2 mm in size. For convenience, it was mounted on a glass slide oriented in such a manner that a (120) face was parallel to the glass and perpendicular to the spectrophotometer light beam. The crystal thickness was 0.13 mm. The spectral transmission measurements were made relative to the clear glass slide and are in arbitrary units.

The results of the spectrum measurements are shown on the graph (Fig. 7) where the relative intensity of the transmitted light is plotted against wavelength in Angstrom units. Of particular interest are several unusually narrow absorption bands. Such bands are characteristic of members of the lanthanide (rare-earth) group of elements and attest to the presence of these elements in the ancylite. The reason for the sharpness of the bands is the fact that the electrons responsible for the energy absorption at these wavelengths are in inner orbits (the so-called 4f orbits) which are well shielded by additional outer electron shells against environmental disturbance. The shielding also results in the absorption spectrum being almost completely independent of the chemical or physical environment of the ions and is in contrast to the much broader and chemically dependent spectra of most other entities such as the transition element ions.

A comparison spectrum (Moeller and Brantley, 1950) of a solution of the compound NdCl₃ in water is also shown in the graph. This not

only indicates that a major cause of the observed absorption bands in ancylite is the element neodymium, but also illustrates the extent to which the bands are independent of the chemical environment, an aqueous solution being entirely distinct from a solid carbonate crystal. By careful comparison, a rough estimate of this element's concentration in ancylite, about 6-12 wgt. percent, was obtained. Most other lanthanides which may be present either have no strong absorption in the visible spectrum or else occur in relatively small amounts in the ancylite. Apart from neodymium, only praseodymium appears to contribute measurably to the spectrum. Incidentally, it is possible to observe the absorption spectrum visually under a microscope by substituting an appropriate hand spectrograph for the microscope eyepiece (W.M.D. Bryant, personal communication).

Returning to the question of color, it is now possible to understand how the absorption bands that are present affect the appearance. It will be noticed (Fig. 7) that two major absorbing regions show up in the green and yellow parts (5000-6000 Å) of the spectrum. When the ancylite is observed in incandescent light (or daylight) which contains a substantial fraction of orange and red (6000-7000 Å), the effect of the absorption of some of the green energy, but only a little of the red, is to make the material look pink relative to a white object such as a uniformly reflecting sheet of paper. With ordinary fluorescent light, however, there is very little orange and red (greater than 6000 Å) in the source present; thus the absorption of neighboring green and yellow under this illumination tends to cause the ancylite to appear more blue than does a white object. This behavior of ancylite is typical of materials containing neodymium which consequently exhibit narrow absorption bands near the center of the visible spectrum. A Corning Glass didymium (neodymium plus praseodymium) filter is an example of such a material. Its color behavior is almost identical to that of Cornog ancylite. If other spectrally diffuse coloring agents, how-

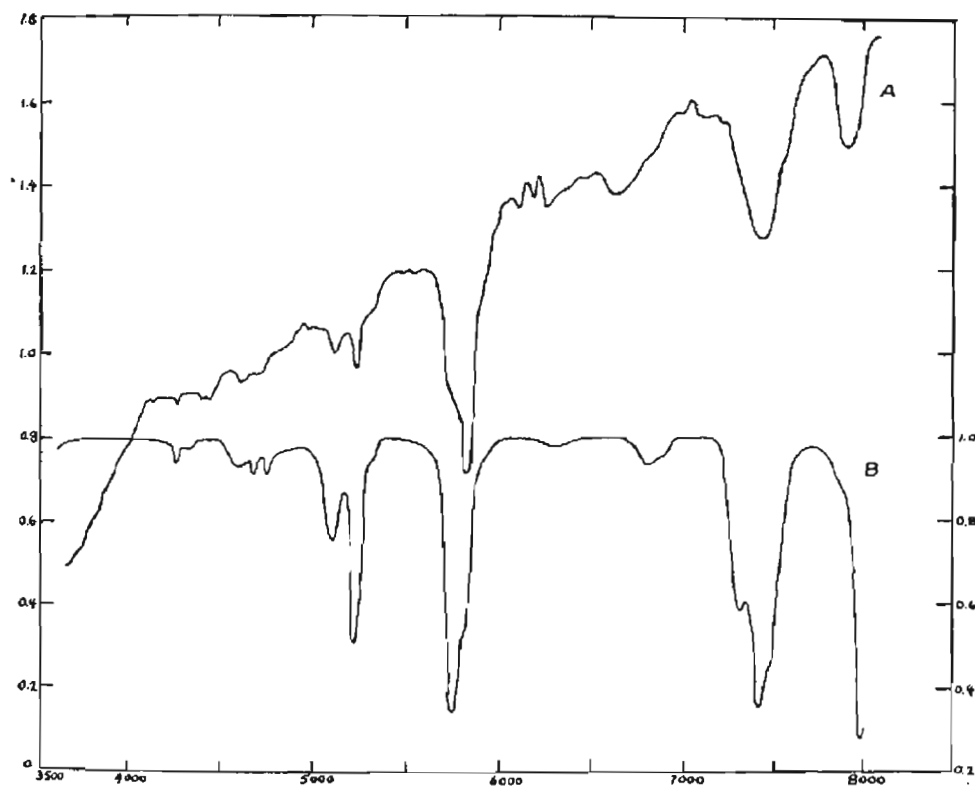


Fig. 7. Optical-transmission spectra: A—of ancylite, Cornog, Pa. (0.13 mm thick); B—of NdCl_3 in water recalculated for 10 g per 1.0 cm, from data of Moeller and Brantley (1950).

ever, such as iron (which is contained in Greenland ancylite) are also present in the sample, it is to be expected that the color effects caused by the neodymium will be largely masked.

Chemistry

A qualitative electron microprobe analysis of a single crystal of Cornog ancylite was made in 1967 in the Department of Geological Sciences at Harvard University through the courtesy of Dr. Clifford Frondel. Major constituents were found to be Ce, La and Ca. Minor constituents were reported to be Nd and Sr. The elements Ba, Fe, Mn and Y were not detected.

A sample of about 50 mg of separated ancylite crystals was prepared for the x-ray fluorescence spectroscopic analysis by one of the authors (F.A.K.). The crystals (at least 1000 of them, ranging in maximum dimension from about 0.2 mm to 1 mm) were selected on the basis of relative freedom from obvious inclusions. Calcite, actinolite, quartz, and other low-density fragments accidentally accumu-

lated in the concentrate were floated off with methylene iodide. The sample was then reexamined microscopically and non-ancylite grains, mostly pyrite and zircon, plus ancylite with inclusions or attachments, were manually removed. Special care was taken to remove all particles of calcite. It is estimated that considerably less than 2% of impurities, chiefly pyrite and actinolite, were left in the final sample.

A high-purity and a less pure fraction of the crystal-concentrate sample were analyzed by x-ray fluorescence spectroscopy. A preliminary qualitative x-ray scan of the sample had already indicated that only the rare-earth elements La, Ce, Pr, Nd and Sm were present in measurable amounts ($> 0.2\%$). Because of the small size of the two samples analyzed (less than 20 mg, for both) two other major constituents, CO_2 and H_2O (which amount to 25-30% or more in most ancylite analyses) were not determined. Remaining undetermined also were any minor cations such as Fe, Ba and Mn. The analyses are summarized in Table 2.

TABLE 2. X-ray fluorescence spectroscopic analyses of ancylite from Cornog, Pa.

Constituent	Ancylite (very pure)	Ancylite (not pure)
La_2O_3	14.6	13.5
Ce_2O_3	24.6	23.2
Pr_2O_3	2.55	2.35
Nd_2O_3	8.66	7.95
Sm_2O_3	0.34	0.32
Y_2O_3	0.00	0.00
CaO	8.35	9.20
SrO	3.07	3.27
TOTAL	62.17	59.79
milligrams used:	8.62	9.78

Analytical details

The rare earth samples and standards were prepared by a method similar to that described by Rose and Cuttitta (1968). The standards were prepared by dissolving weighed amounts of pure ignited oxides in dilute HNO_3 . Less than 10 mg. of the minerals were weighed and placed in 10 ml. beakers. Three ml. of 1:1 HNO_3 were added and the samples allowed to stand overnight. The samples were then heated and brought to dryness in a steambath. The evolution of CO_2 was very noticeable. Known amounts of each standard stock solution were added to 10 ml. beakers and allowed to dry on a steambath. To each beaker (both samples and standards) was added 0.8 ml. of 5:95 HNO_3 , and the solutions heated gently to dissolve the salts. Then 400 mg. of chromatographic cellulose powder was added to each beaker, along with a drop of methyl red indicator. All solutions were mixed thoroughly with a teflon rod, dried overnight at 90 C. and brought to a constant weight of 420 mg with the addition of cellulose powder. Each sample was then thoroughly mixed, ground and pressed at 40,000 psi into a 1-inch disc, on a backing of about 2 g of cellulose powder.

A single channel flat crystal x-ray spectrometer with a platinum target was used for this study. An operating voltage of 50 Kv with current of 40 ma was used in all measurements, along with a LiF

(continued on page 36)

particular relevance to the subject of the book. A case in point is the inclusion of numerous crystal structure diagrams which contribute nothing to a discussion of the origin and mineralogy of geodes.

The failure of the author to include an index greatly hampers the usefulness of the book.

As a picture book on geodes and geode minerals, Sinotte's work is unique in the literature. As a technical work on geode formation, the book is overburdened with material of little or no use to the average reader, and much of it not carefully presented. The book does include various arguments used in the past to explain the formation of geodes. However, a very critical reading of Sinotte's manuscript by scientists well-versed in thermodynamics, solution geochemistry and crystallography would have resulted in a much more useful and accurate text.

(continued on page 47)

ANCYLITE

(continued from page 25)

analyzing crystal (200 reflection), sealed proportional detector and pulse height analyzer set to a baseline of 4 volts. A helium atmosphere was used in the determination of all elements except Y and Sr, which were determined in air. The L α lines of La, Ce, Pr, Nd and Sm and the K α lines of Ca, Sr, and Y were the analytical lines used for measurement. Pr was corrected for interference by the L β_1 line of La, Nd was corrected for the Ce L β_1 line, and Sm was corrected for interference by the L β_2 line of Ce.

Conclusions

Noteworthy among the analytical results are the relatively high Nd content, among the rare earths, and the predominance of Ca over Sr. The latter finding suggests that this mineral from Cornog should be termed a calcian ancylite.

Acknowledgements

Grateful acknowledgement is made to the following: Dr. C. Frondel, Department of Geological Sciences, Harvard University, for a qualitative electron microprobe analysis of a Cornog ancylite crystal; Professors C. Sibley and D. Levin, Department of Botany,

Yale University, for cooperation in making available for optical-absorption measurements the microspectrophotometer at Yale; Dr. E. H. Watson, Department of Geology, Bryn Mawr College, for helpful advice on problems of regional Precambrian geology encountered at the Keystone quarry; Messrs. J. Weber and L. Perloff for photomicrographs of ancylite crystals from Cornog used in Figs. 4 and 5. Very special thanks go to Drs. Frank Cuttitta and Harry Rose, Jr., U.S. Geological Survey, for making possible the specific gravity determination (F.C.) and the x-ray fluorescence spectroscopic analysis of Cornog ancylite, and to Dr. Joel E. Arem, Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, for critical reading of the manuscript and improvement in its data and content.

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