

## Calcio-ancylite-(Nd), a new REE-carbonate from Baveno, Italy

PAOLO ORLANDI \*, MARCO PASERO\* and GIOVANNA VEZZALINI \*\*

\* Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italia

\*\* Istituto di Mineralogia e Petrologia, Università di Modena, Via S. Eufemia 19,  
I-41100 Modena, Italia

**Abstract :** Calcio-ancylite-(Nd), a new basic hydrated carbonate of calcium and REE, occurs as pink pine-cone-like crystals in miarolitic cavities of Baveno granite, Italy. Electron microprobe analysis yields the formula :  $(\text{Nd}_{0.90}\text{Ce}_{0.64}\text{Sm}_{0.33}\text{Gd}_{0.28}\text{Y}_{0.26}\text{Pr}_{0.15}\text{La}_{0.14}\text{Dy}_{0.07}\text{Tm}_{0.03})_{\Sigma=2.80}\text{Ca}_{1.20}(\text{CO}_3)_{3.98}(\text{OH})_{2.84} \cdot 1.01\text{H}_2\text{O}$  ( $Z = 1$ ). The mineral is monoclinic,  $Pm11$ , with  $a = 4.976(2)$ ,  $b = 8.468(2)$ ,  $c = 7.212(2)$  Å,  $\alpha = 90.04(3)^\circ$ ;  $d_{\text{meas}} > 4.02$  and  $d_{\text{calc}} = 4.08$  g/cm<sup>3</sup>; hardness (Mohs) 4-4.5; biaxial (-). The three strongest lines of the X-ray powder diffraction pattern are [ $d$  (Å), ( $hkl$ ),  $I$ ]: 4.26, (100), 100; 2.905, (102), 90; 2.048, (221), 80. The crystal structure refinement ( $R_w = 0.036$ ) confirms the main features of ancylite-(Ce), but provides evidence for a different distribution of alkaline earth and REE in the M sites. A re-examination of the discredited mineral "weibeyite" from Baveno shows that it is a calcio-ancylite-(Ce) with variable REE content.

**Key-words :** calcio-ancylite-(Nd), carbonate, crystal structure, Italy, "weibeyite".

### Introduction

According to the revised nomenclature for the REE-bearing minerals (Nickel & Mandarino, 1987), the basic hydrated carbonates of calcium, strontium and rare earths – formerly calcio-ancylite and ancylite on the basis of the dominant alkaline-earth element (calcium and strontium, respectively; Palache *et al.*, 1951) – have been renamed calcio-ancylite-(Ce) and ancylite-(Ce), taking into account the dominant rare-earth element.

Two occurrences of calcio-ancylite have so far been reported, one from an unstated locality in western Russia (see Chernik, *in* Palache *et al.*, 1951) and the other from Cornog, Pennsylvania, USA (Keidel *et al.*, 1971). In these two occurrences, the dominant REE is cerium, so the proper name for the mineral is calcio-ancylite-(Ce) (Nickel & Mandarino, 1987). The mineral referred as "calcio-ancylite" from the Kola peninsula, USSR (Fersman, 1922; Cher-

nik, 1923) is actually an ancylite with minor amount of Ca.

In this paper, a new basic hydrated carbonate of Ca and REE is characterized, in which the most abundant REE is neodymium. This new mineral has been called calcio-ancylite-(Nd). Both the mineral and its name were approved by the IMA Commission on New Minerals and Mineral Names before publication.

### Occurrence and paragenesis

Calcio-ancylite-(Nd) has been found in a miarolitic cavity within the granite (Montecatini quarry) at Baveno, Piedmont, Italy. The holotype is represented by a small pine-cone-like aggregate of crystals up to 1 mm long – characterized by a bipyramidal pseudorhombic habit (Fig. 1) – lying on a pinkish crystal of orthoclase which is associated with quartz and albite.

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Fig. 1. SEM photograph of calcio-ancylite-(Nd) from Baveno (scale bar : 50  $\mu\text{m}$ ).

Other REE-bearing carbonates found at Baveno are cenosite, parisite and "weibyeite". The last mineral was originally described by Brögger (1890) from Narsarsuk, Greenland. Its occurrence at Baveno has been reported by Artini (1915), who identified it on morphological grounds. Subsequently, the mineral was discredited by Saebø (1963), who showed that the "weibyeite" from Narsarsuk consists of bastnäsité pseudomorphs after ancylite as well as ancylite partly replaced by bastnäsité and bastnäsité-ancylite pseudomorphs after zircon.

The "weibyeite" from Baveno has been re-examined in the present study, together with calcio-ancylite-(Nd).

### Physical and chemical properties

Crystals of calcio-ancylite-(Nd) are transparent, not fluorescent, and present a pale pink colour, white streak, vitreous lustre, hardness 4-4.5 (Mohs). The mineral is brittle and shows an irregular fracture. The measured density is  $> 4.02 \text{ g/cm}^3$  (Clerici solution) and the calculated density is  $4.08 \text{ g/cm}^3$ .

Calcio-ancylite-(Nd) is optically biaxial (-),  $\alpha = 1.660(1)$ ,  $\beta = 1.725(1)$ ,  $\gamma = 1.765(1)$  in white light,  $2V_{\text{meas}} = 70^\circ$ ,  $2V_{\text{calc}} = 74^\circ$ , dispersion  $r < v$  weak, orientation  $c = \gamma$ , non pleochroic.

The powder diffraction pattern of calcio-ancylite-(Nd) is reported in Table 1. The unit-cell parameters refined from the powder data are : orthorhombic,  $a = 4.948(3)$ ,  $b = 8.469(6)$ ,  $c = 7.167(3) \text{ \AA}$ .

Table 1. Powder diffraction pattern of calcio-ancylite-(Nd) (Gandolfi camera, 114.6 mm diameter,  $\text{FeK}\alpha$  radiation).

i	$d_{\text{meas}}$	$d_{\text{calc}}$	hkl
60	5.49	5.47	011
100	4.26	4.27	110
70	3.67	3.67	111
10	3.55	3.58	002
30	3.298	3.300	012
90	2.905	2.902	102
40	2.625	2.626	031
40	2.474	2.474	200
20	2.396	2.394	122
70	2.320	2.320	131
10	2.287	2.299	013
10	2.155	2.135	220
10	2.112	2.117	040
80	2.048	2.047	221
10	2.027	2.027	041
70	1.979	1.979	212
30	1.918	1.918	123
10	1.873	1.878	141
10	1.791	1.792	004
10	1.713	1.711	133
10	1.682	1.685	104
		1.684	213
		1.652	114
10	1.651	1.650	232
		1.650	024
10	1.623	1.621	310

Chemical analyses were carried out with a wavelength dispersive ARL-SEM0 electron microprobe (operating conditions : accelerating voltage 20 kV, sample current 20 nA, beam size 15  $\mu\text{m}$ ). The standards REE-1, REE-2, REE-3 and REE-4 were used (Drake & Weill, 1972). The chemical analysis and calculated chemical for calcio-ancylite-(Nd) are reported in Table 2.

### Crystal structure analysis

Preliminary single crystal investigations, carried out on calcio-ancylite-(Nd) using precession and Weissenberg photographs, indicate an orthorhombic symmetry and systematic absences consistent with the space group  $Pm\bar{c}n$  (non-standard space group corresponding to  $Pnma$ ) given by Dal Negro *et al.* (1975) for an ancylite from Mont St. Hilaire, Quebec, Canada. However, a careful inspection of the intensity data reveals the presence of several

Table 2. Chemical data for calcio-ancylite-(Nd) and calcio-ancylite-(Ce) (formerly "weibeyite") from Baveno.

	1	2
La <sub>2</sub> O <sub>3</sub>	3.16	13.98
Ce <sub>2</sub> O <sub>3</sub>	14.18	25.12
Pr <sub>2</sub> O <sub>3</sub>	3.23	6.38
Nd <sub>2</sub> O <sub>3</sub>	20.23	11.76
Sm <sub>2</sub> O <sub>3</sub>	7.63	1.81
Eu <sub>2</sub> O <sub>3</sub>	n.o.	0.66
Gd <sub>2</sub> O <sub>3</sub>	6.68	3.29
Dy <sub>2</sub> O <sub>3</sub>	1.74	n.o.
Tm <sub>2</sub> O <sub>3</sub>	0.83	n.o.
Y <sub>2</sub> O <sub>3</sub>	3.93	n.o.
CaO	9.05	8.19
SrO	n.o.	n.o.
CO <sub>2</sub>	23.47 *	n.d.
H <sub>2</sub> O	5.87 **	n.d.
Σ	100.00	71.19
Chemical formulae based on 4 (REE+Ca):		
1). (Nd <sub>0.90</sub> Ce <sub>0.64</sub> Sm <sub>0.33</sub> Gd <sub>0.28</sub> Y <sub>0.26</sub> Pr <sub>0.15</sub> La <sub>0.14</sub> Dy <sub>0.07</sub> Tm <sub>0.03</sub> ) <sub>Σ=2.80</sub> Ca <sub>1.20</sub> (CO <sub>3</sub> ) <sub>3.98</sub> (OH) <sub>2.84</sub> · 1.01 H <sub>2</sub> O		
2). (Ce <sub>1.17</sub> La <sub>0.65</sub> Nd <sub>0.53</sub> Pr <sub>0.29</sub> Gd <sub>0.14</sub> Sm <sub>0.08</sub> Eu <sub>0.03</sub> ) <sub>Σ=2.89</sub> Ca <sub>1.11</sub>		
* By Carlo Erba 1104 elemental micro-analyzer on 0.47 mg.		
** By difference.		
n.o. = not observed      n.d. = not determined		
1. Calcio-ancylite-(Nd) from Baveno, Italy (average of 8 points).		
2. Calcio-ancylite-(Ce) (formerly "weibeyite") from Baveno, Italy (average of 7 points).		

forbidden, although weak, reflections ( $h0l$  with  $l = 2n + 1$  and  $hk0$  with  $h + k = 2n + 1$ ). A similar behaviour has been observed by Szymanski & Chao (1986), who refined the structure of ancylite in the monoclinic space group  $Pm$ . Therefore, we also carried out a structural refinement of calcio-ancylite-(Nd) in the monoclinic – but metrically nearly orthorhombic – space group  $Pm11$ . This was performed in a non-standard setting (*i.e.* with unique axis  $a$ ) to maintain the same orientation of ancylite (Dal Negro *et al.*, 1975) as well as of the other orthorhombic carbonates of the aragonite family (De Villiers, 1971; Dal Negro & Ungaretti, 1971). The following unit cell parameters

were obtained through least-squares fitting of  $2\theta$  values of 22 medium  $\theta$  reflections:  $a = 4.976(2)$ ,  $b = 8.468(2)$ ,  $c = 7.212(2)$  Å,  $\alpha = 90.04(3)^\circ$  (standard cell:  $a = 7.212$ ,  $b = 4.976$ ,  $c = 8.468$  Å,  $\beta = 90.04^\circ$ ). Details of the intensity data collection and the structural refinement are given in Table 3.

The scattering curves, which comprise contributions from the real and imaginary parts of the anomalous dispersion, were taken from the International Tables for X-ray Crystallography (1974); the scattering curve for Ce was used for all the REE (its atomic number (58) is close to the weighted average atomic number (58.27) derived from the chemical analysis).

Table 3. Experimental data for calcio-ancylite-(Nd).

Dimensions of the crystal	0.1x0.1x0.1 mm
Diffractometer	ITAL STRUCTURES
Radiation	MoK $\alpha$ ( $\lambda = 0.71069 \text{ \AA}$ )
Monochromator	Graphite crystal
Scan mode	$\omega$ -2 $\theta$
Scan width ( $\theta$ )	1.2°
Scan speed	0.033° sec <sup>-1</sup>
2 $\theta$ max	60°
Measured intensities	1863
Unique non-zero ( $I > 3\sigma$ ) reflections	1531
Absorption correction	DIFABS (Walker & Stuart, 1983)
Transmission factor range	0.79-1.41
R	0.044
R <sub>w</sub> [ $w = 1/\sigma^2(F_0)$ ]	0.036

Table 4. Site occupancies, fractional coordinates and  $U$  or  $U_{eq}$  (§) thermal parameters ( $\text{\AA}^2$ ) for calcio-ancylite-(Nd).

Site	x	y	z	U
M1	1/4	0.3399(*)	0.3524(*)	0.0132(8)§
M2	1/4	0.1677(5)	0.8517(6)	0.0149(10)§
M3	3/4	0.6609(2)	0.6448(2)	0.0102(7)§
M4	3/4	0.8440(3)	0.1445(4)	0.0082(5)§
C1	3/4	0.191(4)	0.177(4)	0.017(7)
C2	3/4	0.312(4)	0.699(4)	0.017(7)
C3	1/4	0.817(3)	0.805(4)	0.007(6)
C4	1/4	0.687(3)	0.314(4)	0.011(6)
O11	3/4	0.325(2)	0.272(3)	0.012(5)
O12	3/4	0.194(2)	0.790(2)	0.008(3)
O13	1/4	0.695(3)	0.705(3)	0.033(6)
O14	1/4	0.831(3)	0.241(3)	0.028(6)
O21	0.529(3)	0.125(2)	0.143(2)	0.015(4)
O22	0.520(3)	0.383(2)	0.649(3)	0.018(4)
O23	0.480(3)	0.885(2)	0.847(2)	0.023(4)
O24	0.473(3)	0.622(2)	0.353(2)	0.021(4)
O31	1/4	0.412(3)	0.036(3)	0.023(5)
O32	1/4	0.082(2)	0.526(3)	0.016(4)
O33	3/4	0.590(2)	0.981(3)	0.020(5)
O34	3/4	0.899(2)	0.463(2)	0.015(4)

(\*) held fixed to define the origin

Refined site occupancies:

M1: 70.0% REE - 30.0% Ca  
M2: 40.4% REE - 59.6% Ca  
M3: 63.3% REE - 36.7% Ca  
M4: 100.0% REE

Initial fractional coordinates are taken from Dal Negro *et al.* (1975), with the sign of the  $z$  coordinates taken as negative, because it corresponds to a better absolute configuration. For each atom given by Dal Negro *et al.* (1975), a total of four atoms were introduced

(*e.g.* C1, C2, C3 and C4 for C, O11, O12, O13 and O14 for O1, and so on), to take into account the lower multiplicity of the space group  $Pm$ . The percentages of REE and calcium in the four independent M sites were refined. Desymmetrization of the structure was achieved

and the refinement converged fairly well, notwithstanding the high pseudo-symmetry.

The final site occupancies, fractional coordinates and  $U$  ( $U_{eq}$  for the M cations only) thermal parameters are reported in Table 4, whereas bond distances are reported in Table 5. A list of observed and calculated structure factors may be obtained from the authors upon request.

A refinement was also attempted in the  $P2_1/m$  space group, the other possible monoclinic subgroup, although some forbidden  $h00$  reflections with  $h = 2n + 1$  were present. According to the Hamilton test (Hamilton, 1965) computed from  $RG$  values, the probability that the  $P2_1/m$  model describes the structure of calcio-ancylite-(Nd) better than the  $Pm$  model can be largely rejected at the 0.005 confidence level.

The main features of the crystal structure of calcio-ancylite-(Nd) are similar to those found by Dal Negro *et al.* (1975) for ancylite-(Ce). The M cations are ten-fold coordinated. Among the oxygen atoms involved in the M coordination polyhedra, the O1- and O2-type oxygen atoms are shared with regular triangular

$(CO_3)^{2-}$  groups; the O3-type oxygen atoms belong to hydroxyls or water molecules. The M-O distances range from 2.54 to 2.77 Å for O1- and O2-type oxygens, and from 2.35 to 2.52 Å for O3-type oxygens.

As regards cation occupancies within the M sites (Table 4), calcium is absent in the M4 site and is distributed among the other sites in variable amounts, ranging from 30 % to 60 %. By comparing our results with those obtained for the structure of ancylite-(Ce) – refined in the  $Pm$  space group by Szymanski & Chao (1986) – it is noteworthy that the percentages of the alkaline-earth elements (both Sr and Ca) are, in the latter case, 92, 9, 12 and 22 % for the four independent M sites. Therefore, in ancylite-(Ce), a M site exists which is specific for alkaline earth cations. This is probably due to an ionic radius for Sr which is greater than that for Ca and REE. In calcio-ancylite-(Nd) only Ca and REE – with similar ionic radii – are present; the M4 site is specialized to host “heavy” atoms only, and this is the main reason for the lowering of the symmetry from  $Pm$  to  $Pm$  in this case.

Table 5. Bond distances (Å) in calcio-ancylite-(Nd).

M1 - 011 (x2)	2.557(5)	M2 - 012 (x2)	2.537(3)
- 021 (x2)	2.738(17)	- 021 (x2)	2.545(16)
- 022 (x2)	2.552(18)	- 022 (x2)	2.696(16)
- 024 (x2)	2.636(16)	- 023 (x2)	2.656(16)
- 031	2.359(21)	- 031	2.457(24)
- 032	2.518(18)	- 032	2.459(19)
Average	2.584	Average	2.578
M3 - 013 (x2)	2.542(5)	M4 - 014 (x2)	2.585(6)
- 022 (x2)	2.617(17)	- 021 (x2)	2.625(16)
- 023 (x2)	2.741(18)	- 023 (x2)	2.555(16)
- 024 (x2)	2.537(16)	- 024 (x2)	2.772(15)
- 033	2.500(20)	- 033	2.451(22)
- 034	2.409(17)	- 034	2.345(19)
Average	2.578	Average	2.587
C1 - 011	1.325(38)	C2 - 012	1.193(32)
- 021 (x2)	1.258(21)	- 022 (x2)	1.346(20)
Average	1.280	Average	1.295
C3 - 013	1.259(36)	C4 - 014	1.332(34)
- 023 (x2)	1.316(21)	- 024 (x2)	1.270(19)
Average	1.297	Average	1.291

Mandarino *et al.* (1965) studied ancylite-(Ce) from Mont St. Hilaire and attributed the space group *Pmmm* (no systematic absences); such a space group is incompatible with the structure of ancylite, so the lack of systematic extinctions points to the *Pm* space group as the correct one. Dal Negro *et al.* (1975) have refined the structure of a crystal of ancylite-(Ce) from Mont St. Hilaire in which the disordered stacking of monoclinic domains may possibly simulate an orthorhombic symmetry in the *Pm<sub>2n</sub>* space group.

If we take into account our structural results, together with those presented by Szymanski & Chao (1986), it seems that all "ancylites" and "calcio-ancylites" are monoclinic, and that the different chemical compositions give rise to different ordering patterns among the M sites.

#### A comment on "weibyeite"

During this study, we re-examined the samples collected by Artini (1915) at Baveno which he identified as "weibyeite". The chemical composition of "weibyeite" is reported in Table 2. Our X-ray powder diffraction and chemical analyses indicate that "weibyeite" from Baveno is merely a calcio-ancylite-(Ce) with variable contents of the other REE.

From these data, it appears that the "calcio-ancylite" from Baveno shows a large compositional variation, and that both calcio-ancylite-(Nd) and calcio-ancylite-(Ce) are present.

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