



Article

Calcioancylite-(La), $(\text{La,Ca})_2(\text{CO}_3)_2(\text{OH,H}_2\text{O})_2$, a new member of the ancylite group from Gejiu nepheline syenite, Yunnan Province, China

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Abstract

Calcioancylite-(La), ideally $(\text{La,Ca})_2(\text{CO}_3)_2(\text{OH,H}_2\text{O})_2$, has been discovered from nepheline syenite of the Gejiu alkaline complex in the Honghe Hani and Yi Autonomous Prefecture, Yunnan Province, China. The mineral occurs as aggregates of subhedral grains, and the size of single crystals varies between 5–20 μm . Calcioancylite-(La) is colourless to pale pinkish grey and has transparent to translucent lustre. It is brittle with a Mohs hardness of 4. The calculated density is 4.324 g/cm^3 . The mineral is biaxial (–), with $\alpha = 1.662$, $\beta = 1.730$, $\gamma = 1.771$, $2V_{\text{meas.}} = 70^\circ(1)$ and $2V_{\text{calc.}} = 73^\circ$. Electron microprobe analysis for holotype material yielded an empirical formula of $(\text{La}_{0.58}\text{Ce}_{0.55}\text{Pr}_{0.14}\text{Nd}_{0.10}\text{Ca}_{0.39}\text{Sr}_{0.20}\text{K}_{0.04})_{\Sigma 2.00}(\text{CO}_3)_2[(\text{OH})_{1.25}\text{F}_{0.06}\cdot 0.69\text{H}_2\text{O}]_{\Sigma 2.00}$. Calcioancylite-(La) is orthorhombic, with space group *Pmcn*, $a = 5.0253(3)$ Å, $b = 8.5152(6)$ Å, $c = 7.2717(6)$ Å, $V = 311.17(4)$ Å³ and $Z = 2$. By using single-crystal X-ray diffraction, the crystal structure has been determined and refined to a final $R_1 = 0.0652$ on the basis of 347 independent reflections ($I > 2\sigma$). The seven strongest powder X-ray diffraction lines [d in Å (I) (hkl)] are: 2.334 (100) (013), 2.970 (80) (121), 4.334 (75) (110), 3.678 (68) (111), 2.517 (55) (200), 2.647 (47) (031) and 2.077 (44) (221). Calcioancylite-(La) is the La-analogue of calcioancylite-(Ce) and is a new member of ancylite-group minerals. The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2021-090).

Keywords: calcioancylite-(La); new mineral; ancylite group; REE carbonate mineral; crystal structure; nepheline syenite; Gejiu alkaline complex

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Introduction

Ancylite-group minerals are hydrous carbonates that contain rare earth elements (REE), Ca, Sr and Pb as major cations. The general chemical formula for the ancylite-group minerals is: $(\text{REE})_x(\text{M}^{2+})_{2-x}(\text{CO}_3)_2(\text{OH})_x(2-x)\text{H}_2\text{O}$ ($Z = 2$), where $1 < x \leq 2$ (Dal Negro *et al.*, 1975; Sarp and Bertrand 1985; Bulakh *et al.*, 1998; Miyawaki *et al.*, 2000). The crystal structure of ancylite-(Ce) was first solved by Dal Negro *et al.* (1975). Larsen *et al.* (2002) performed the structure refinement for two species of ancylite-(Ce) within the space groups *Pmcn* and *Pmc2*₁. Belovitskaya *et al.* (2013) studied the crystal structure of calcioancylite-(Ce) by the Rietveld method and showed that most minerals of the ancylite group were regarded as orthorhombic, and that the whole structure of ancylite-group minerals can be derived from orthorhombic carbonates by adding hydroxyl

groups that are positioned on the mirror planes and bonded to the heavy cations. However, the ancylite group of minerals has been controversial on the issue of crystallographic system. Some previous studies have shown that ancylite minerals are monoclinic, but metrically nearly orthorhombic (Szymanski and Chao 1986; Orlandi *et al.* 1990).

During a systematic investigation of rare minerals from the Gejiu nepheline syenite, some La-rich carbonate phases, corresponding to the formula $(\text{La,Ca})_2(\text{CO}_3)_2(\text{OH,H}_2\text{O})_2$ were identified. Further detailed chemical and crystallographic studies confirmed the first finding of the La-dominant member of the calcioancylite series, thus allowing the proposal of the new mineral species calcioancylite-(La). The new mineral and its name (symbol Canc-La) have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2021-090, Wang *et al.*, 2022). The type material is deposited at the Geological Museum of China, No. 16, Yangrou Hutong, Xisi, Beijing 100031, People's Republic of China, under catalogue number M16129. In this paper, the description of calcioancylite-(La) is reported including a detailed description of the mineral

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paragenesis, Raman spectroscopy, chemical composition, and crystal-structure refinements for this new member of the ancylite group.

Occurrence and physical properties

The new mineral calcioancylite-(La) was found from the Gejiu alkaline intrusive complex, Honghe Hani and Yi Autonomous Prefecture, Yunnan Province, China (23°29'40"N, 103°4'41"E). The intrusion forms an irregular ellipse body that is generally elongated in the S–N direction, covering ~28 km². The Gejiu alkaline complex yielded emplacement ages of 80–82 Ma and intruded into Triassic sandstone and carboniferous rocks (Zhang, 2013; Huang *et al.*, 2018; Wang *et al.*, 2021). The pinkish feldspathoid syenite is a massive, medium- to coarse-grained rock and contains the feldspathoid minerals nepheline and sodalite as well as dark alkaline minerals.

Calcioancylite-(La) is found in association with calcioancylite-(Ce), ancylite-(La), ancylite-(Ce), britholite-(Ce), fluorcalcio-britholite, La-dominant fluorcalcio-britholite, moxuanxueite, bobtrillite, catapleite, baddeleyite, jadeite, zircon, magnetite, andradite, orthoclase and albite (Fig. 1). As it is always veined and/or occurs on the edges of other zirconium silicates, the

crystallisation of calcioancylite-(La) may be related to the late carbonation. Calcioancylite-(La) forms aggregates of subhedral grains with pseudo-octahedral dipyrnidal crystal habit {111} with {110}, elongated along the *b* axis. The veinlets and aggregates are between 10 to 200 µm in size, and the size of individual crystals varies from 5 to 20 µm. Calcioancylite-(La) is colourless to pale pinkish grey with a white streak and vitreous lustre. The Mohs hardness is 4 and the mean Micro-indentation hardness is VHN₅₀ = 175 kg/mm² (range from 165 to 185 kg/mm²). It is brittle with an irregular fracture. The density of 4.324 g/cm³ was calculated based on the empirical formula and unit cell volume refined from single-crystal X-ray diffraction (XRD) data. Optically, it is biaxial (–), with $\alpha = 1.662$, $\beta = 1.730$, $\gamma = 1.771$, $2V_{\text{meas.}} = 70^\circ(1)$, $2V_{\text{calc.}} = 73^\circ$ and dispersion $r < v$.

Raman spectroscopy

The Raman spectrum of calcioancylite-(La) (Fig. 2) was recorded on a LabRAM HR Raman microscope with a 532nm laser (20 mW, 1 µm) in the spectral range from 100 to 4000 cm⁻¹ at the Raman Laboratory of the Tianjin Center, China Geological Survey. The Raman spectrum was collected *in situ* on the crystal used for the single-crystal XRD study from the polished thin section with a 50× objective.

Chemical data

The chemical composition was determined using a JXA-8100 electron microprobe microanalyser (EPMA) at the Beijing Research Institute of Uranium. Experimental conditions were wavelength dispersive spectroscopy mode, accelerating voltage = 15 kV, beam current = 10 nA and beam diameter = 1 µm. The standards include: phlogopite for K and Fe; plagioclase for Ca; celestine for Sr; albite for Al; monazite for La, Ce, Pr, Nd and Sm; and fluorapatite for F. H₂O was calculated by stoichiometry in order to achieve the charge balance, and the hydrous nature was confirmed by the presence of the OH stretching vibration absorption in the Raman spectrum. The chemical analysis results are reported in Table 1.

X-ray crystallography and structure determination

The crystal for XRD analysis was extracted from the polished thin section by using an FEI Helios NanoLab 600i dual beam system equipped with a Focused Ion beam (FIB). The phases were re-checked by scanning electron microscope (SEM). Both powder and single-crystal X-ray studies of calcioancylite-(La) were carried out using a Rigaku XtaLAB Synergy diffractometer (CuK α radiation). The powder X-ray diffraction data were recorded using the Gandolfi technique in powder mode at 50 kV and 1 mA. The pattern was indexed on the basis of the powder spectra and calculated on the basis of cell parameters determined by single-crystal XRD using CHEKCELL software (Laugier and Bochu, 2004). The refined lattice parameters yielded from the powder patterns are $a = 5.0332(20)$ Å, $b = 8.5238(33)$ Å, $c = 7.2799(28)$ Å and $V = 312.32(36)$ Å³. The observed and indexed powder diffraction data for calcioancylite-(La) are listed in Table 2.

Single-crystal X-ray studies were performed using a Rigaku XtaLAB Synergy diffractometer equipped with a Hybrid Pixel Array Detector and CuK α radiation at 50 kV and 1 mA from a colourless platy fragment of calcioancylite-(La) (~16 × 7 × 5 µm) at the Laboratory of Crystal Structure, Central South University,

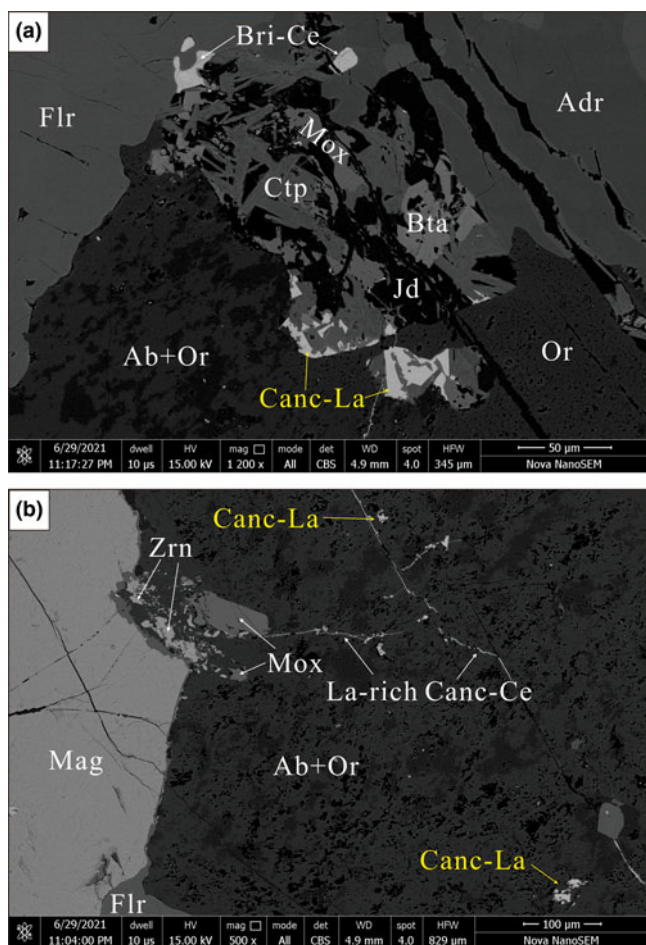


Fig. 1. SEM images of calcioancylite-(La) in aggregates of other minerals. Mineral symbols are from Warr (2021): Canc-La – calcioancylite-(La); Canc-Ce – calcioancylite-(Ce); Bri-Ce – britholite-(Ce); ADR – andradite; Mox – moxuanxueite; Bta – bobtrillite; Ctp – catapleite; Jd – jadeite; Ab – albite; Flr – fluorite; Or – orthoclase; Mag – magnetite; and Zrn – zircon. Specimen # 18CL18-5.

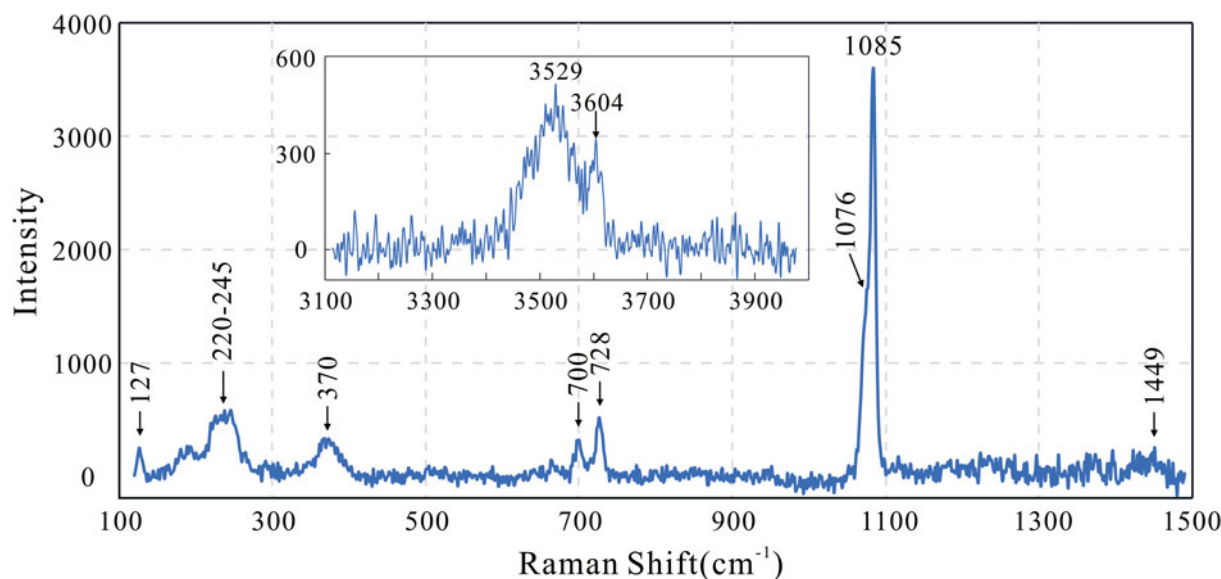


Fig. 2. The Raman spectra of calcioancylite-(La).

China. The intensity data were corrected for X-ray absorption using the multi-scan method. Empirical absorption correction was performed using *CrysAlisPro* software spherical harmonics (Rigaku Oxford Diffraction, 2015), which was implemented in the *SCALE3 ABSPACK* scaling algorithm. The crystal structure was determined and refined using the *SHELX* (Sheldrick, 2015) and *Olex2* software (Dolomanov *et al.*, 2009). The refined unit-cell parameters are $a = 5.0253(3)$ Å, $b = 8.5152(6)$ Å, $c = 7.2717(6)$ Å, $V = 311.17(4)$ Å³ and space group *Pmcn*. We also tried to refine the structure under a monoclinic system. However, the attempt yielded a worse refinement result. The following neutral scattering curves, taken from the *International Tables for Crystallography* (Wilson, 1992), were initially used: La vs. Ca at the *M* site, and C at the *C* site. The final anisotropic full-matrix least-squares refinement on F^2 with 347 unique reflections ($I > 2\sigma(I)$) converged at $R_1 = 6.52\%$ and 6.79% for all 360 data. The goodness-of-fit was 1.258. The details of the data collection and the final structure refinement are provided in Table 3. Site occupancies, atomic coordinates, and displacement parameters are given in Table 4, and selected bond distances are in Table 5. The bond-valence sums (BVS), calculated using the bond-valence parameters of Brese and O’Keeffe (1991), are shown in Table 6. A view of the structure is presented in Fig. 3. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Results and discussion

Raman spectroscopy

The characteristics of calcioancylite-(La) are comparable to that of calcioancylite-(Ce) from Mont Saint-Hilaire, Rouville County, Quebec, Canada (RRUFF R130005, <https://rruff.info/>) and ancylite-(Ce) from Bear Lodge, Wyoming, USA (Chakhmouradian *et al.*, 2017). In general, the major Raman bands of calcioancylite-(La) at 1085 cm⁻¹ and a shoulder band at 1076 cm⁻¹ can be confidently identified as symmetric C–O stretching modes (ν_1). The bands at 700 cm⁻¹ and 728 cm⁻¹ are assigned to O–C–O in-plane

bending (ν_4) modes. A very low-intensity band at 1449 cm⁻¹, which is commonly observed in bastnäsite-group minerals can be assigned to the ν_3 (CO₃)²⁻ asymmetric stretching mode (Frost and Dickfos, 2007). The bands observed at 3529 cm⁻¹ and 3604 cm⁻¹ are assigned to H₂O molecules and hydroxyl groups, respectively. A number of low wavenumber bands are observed at 127 cm⁻¹, 370 cm⁻¹ and between 220 and 245 cm⁻¹ could be described as lattice translation modes.

Chemical formula

The empirical formula of calcioancylite-(La) (average of 5 EPMA spot analyses) calculated on the basis of C = 2 atoms per formula unit, (OH + F + H₂O) = 2 atoms per formula group [apfu] is (La_{0.58}Ce_{0.55}Pr_{0.14}Nd_{0.10}Ca_{0.39}Sr_{0.20}K_{0.04})_{Σ2.00}(CO₃)₂(OH_{1.25}F_{0.06}·0.69H₂O)_{Σ2.00}. Note that the unusual presence of Al in the EPMA data (average: 1.34 wt.% Al₂O₃) could be caused by sub-microscopic ingrowths or thin films of Al hydroxides (i.e. gibbsite, boehmite, nordstrandite or amorphous Al(OH)₃). These phases are commonly associated with ancylites in late, low-temperature hydrothermal alkaline rocks. The ‘alien’ nature of Al in calcioancylite-(La) is indirectly but evidently confirmed by the wide variation of its content in the EPMA data, ranging from 0.41 to 2.69 wt.% Al₂O₃. As the presence of Al has not been reported for ancylites in the literature so far and as Al³⁺ strongly differs in ionic radius and electron shell structure from large cations such as REE, Ca, and Sr, the empirical formula was calculated without Al. The ideal compositions for the ideal boundary formula (LaCa)_{Σ2}(CO₃)₂(OH·H₂O) and (La_{1.5}Ca_{0.5})_{Σ2}(CO₃)₂(OH_{1.5}·0.5H₂O) are shown in Table 1 for comparison.

Crystal structure description

The structure of calcioancylite-(La) is identical to that of the calcioancylite-(Ce) reported by Pekov *et al.* (1997) and other members of the ancylite group (Dal Negro *et al.*, 1975; Sarp and Bertrand 1985; Miyawaki *et al.*, 2000, 2003), in which the REE³⁺ and divalent cations are situated at the centre of a ten-vertex

Table 1. Compositional data for calcioancylite-(La).

	Mean (wt.%)	Range	S.D. (σ)	Element	Apfu	Ideal-I (wt.%)	Apfu	Ideal-II (wt.%)	Apfu
K ₂ O	0.51	0.10–0.83	0.30	K	0.04				
CaO	5.62	5.17–5.98	0.29	Ca	0.39	16.79	1	7.32	0.5
SrO	5.39	3.98–7.17	1.37	Sr	0.20				
FeO	0.06	0.01–0.10	0.03	Fe	0.00				
Al ₂ O ₃	1.34	0.41–2.69	0.91						
La ₂ O ₃	24.59	23.52–26.58	1.17	La	0.58	48.77	1	63.81	1.5
Ce ₂ O ₃	23.32	22.61–24.53	0.76	Ce	0.55				
Pr ₂ O ₃	5.78	5.15–6.13	0.37	Pr	0.14				
Nd ₂ O ₃	2.49	2.19–2.74	0.21	Nd	0.10				
Sm ₂ O ₃	0.06	bdl–0.16	0.06	Sm	0.00				
CO ₂ *	22.86			C	2.00	26.35	2	22.99	2
F	0.31	0–0.16	0.07	F	0.06				
F \equiv O	–0.13								
H ₂ O [†]	6.16			H ⁺	2.63	8.09	3	5.88	2.5
Total	98.36					100		100	

Note: S.D. = standard deviation, and bdl = below detection limits.

*Calculated by C = 2 apfu; †the number of OH group was calculated from the stoichiometry; the number of water molecules was calculated from the difference of (OH + F + H₂O) = 2 apfu. The ideal boundary formula for I and II is (LaCa)₂₂(CO₃)₂(OH·H₂O) and (La_{1.5}Ca_{0.5})₂₂(CO₃)₂(OH_{1.5}·0.5H₂O), respectively.

polyhedron formed by O(1), O(2) and O(3) oxygen atoms. The O(1) and O(2) positions are occupied by oxygen atoms, whereas the O(3) position is statistically filled with (OH) groups and H₂O molecules. The chains of this ten-vertex polyhedron are stretched along the *c* axis and connected by shared O(2)–O(3)–O(2) faces. The chains are interconnected into a three-dimensional framework via (CO₃) triangles. In calcioancylite-(La), the REE share their positions with relatively light Ca and Sr atoms, with La > Ce and Ca > Sr and are bonded to eight oxygen atoms (O(1)^{×2}, O(2)^{×6}) belonging to the CO₃ group and two hydroxyls and water molecules (O(3)^{×2}). The occupancy of the cationic position *M* was 0.66(4) and 0.34(4) for La and Ca cations, respectively. The resulting occupancy of La_{0.66}Ca_{0.34} yields a site scattering of 44.4 *e*[−] which is consistent with the calculated value of 47.7 *e*[−] based on the empirical formula. The *M*–O distances range from 2.576 to 2.765 Å for the oxygen atoms, whereas the shorter *M*–O distances involving the hydroxyls vary between 2.465 and 2.496 Å. The mean *M*–O bond distance of 2.609 Å is comparable to the mean *M*–O distance of ancylite-(Ce) (2.61 Å) (Dal Negro *et al.*, 1975), and is slightly longer than the mean *M*–O bond length in calcioancylite-(Nd) (2.585 Å), which contained no strontium at the *M* site (Orlandi *et al.*, 1990). The C–O bond distances are consistent with values

Table 2. Powder X-ray diffraction data (*d* in Å) for calcioancylite-(La).

<i>l</i> _{meas}	<i>l</i> _{calc}	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>h k l</i>
23	61	5.5708	5.5357	0 1 1
75	100	4.3218	4.3340	1 1 0
68	47	3.6926	3.6780	1 1 1
30	38	3.3400	3.3475	0 1 2
80	92	2.9564	2.9696	1 2 1
19	10	2.7706	2.7678	0 2 2
47	41	2.6396	2.6468	0 3 1
55	37	2.5197	2.5166	2 0 0
100	55	2.3353	2.3339	0 1 3
32	18	2.1341	2.1309	0 4 0
44	64	2.0773	2.0769	2 2 1
42	50	2.0123	2.0116	2 1 2
11	32	1.9447	1.9449	1 2 3
39	32	1.8445	1.8452	0 3 3

Note: the strongest lines are in bold, and the *d*_{calc} were refined on the basis of single-crystal data using CHEKCELL software (Laugier and Bochu, 2004).

reported in the literature. The bond valences were calculated from the interatomic distances following the procedure of Brown and Altermatt (1985). The bond-valence sums for the *M* site and C positions are 2.711 and 3.966 valence units (vu), respectively, which agrees with the expected values given that various cations occur at the same sites. The BVS for the O(1), O(2) and O(3) positions are 1.919, 2.007 and 0.744 vu, respectively. The lower BVS for O(3) implies a mixed occupancy by (OH) group and water molecules at the O(3) site, consistent with the chemical data and Raman

Table 3. Information on structural refinement for calcioancylite-(La).

Crystal data	
Structural formula	(La _{1.32} Ca _{0.68})(CO ₃) ₂ (OH _{1.32} ·0.68H ₂ O)
Formula weight	726.26
Crystal size (μm)	16 × 7 × 5
Crystal system	orthorhombic
Space group	<i>Pm</i> <i>cn</i> (#62)
Unit cell dimensions (Å)	<i>a</i> = 5.0253(3) <i>b</i> = 8.5152(6) <i>c</i> = 7.2717(6)
Volume (Å ³)	311.17(4)
<i>Z</i>	2
Density (calculated) (g/cm ³)	3.876
Data collection	
Instrument	Rigaku Synergy
Radiation, wavelength (Å)	CuKα, 1.54184
Temperature (K)	296.15
<i>F</i> (000)	330
2θ range (°)	16.028 to 153.58
Total reflections	1054
Unique ref (all)	360
Unique ref [<i>I</i> > 2σ(<i>I</i>)]	347
<i>R</i> _{int}	0.0526
<i>R</i> _σ	0.0494
Range of <i>h, k, l</i>	−6 ≤ <i>h</i> ≤ 3, −10 ≤ <i>k</i> ≤ 10, −9 ≤ <i>l</i> ≤ 7
Refinement	
<i>R</i> [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.0652
<i>R</i> [all data]	0.0679
<i>wR</i> (on <i>F</i> _o) [*]	0.1532
Goodness-of-fit	1.258
Data/restraints/parameters	360/0/36
Δρ _{max} , (e [−] Å ^{−3})	1.99 [0.90 Å from Ca]
Δρ _{min} , (e [−] Å ^{−3})	−1.80 [1.51 Å from O3]

**w* = 1/[σ²(*F*_o) + (0.0428*P*)² + 16.9132*P*], where *P* = (*F*_o² + 2*F*_c²)/3

Table 4. Atomic coordinates and equivalent isotropic displacement parameters (in Å²) for calcioancylite-(La).

Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
<i>M</i> [*]	¾	0.66003(18)	0.8522(2)	0.0174 (7)	0.0137(9)	0.0210(10)	0.0175(9)	−0.0009(6)	0	0
C	¼	0.811(2)	0.687(3)	0.016(4)	0.010(8)	0.015(9)	0.022(10)	0.004(8)	0	0
O1	¼	0.681(2)	0.777(3)	0.032(4)	0.028(9)	0.033(9)	0.036(10)	0.012(8)	0	0
O2	0.472(3)	0.8784(13)	0.6465(15)	0.029(3)	0.029(6)	0.035(6)	0.022(6)	−0.005(5)	0.002(5)	−0.004(5)
O3	¾	0.586(2)	0.524(2)	0.036(5)	0.049(11)	0.042(10)	0.018(8)	0.017(7)	0	0

**M* = La_{0.66(4)}Ca_{0.34(4)}

spectroscopy results. As shown in Table 6, all calculated BVS values are comparable to ideal values, and basically match the charge-balance requirement.

Relation between the *M* site and additional anion site

The chemical formula of ancylite-group minerals can be defined as: $(REE_x^{3+}M_{2-x}^{2+})(CO_3)_2[(OH)_x \cdot (2-x)H_2O]$ (*M* = Ca, Sr and Pb; *Z* = 2). REE^{3+} and M^{2+} occupy the same crystallographic site and the formula is charge-balanced through the following substitution mechanism: $REE^{3+} + OH^- \rightarrow M^{2+} + H_2O$. The excess positive charge of the REE^{3+} is compensated by the incorporation of $(OH)^-$, and the number of hydroxyl ion and water molecule are equivalent to those of REE^{3+} and M^{2+} , respectively. In our case, combined structure refinement and bond-valence calculations verify that the substitution mechanism for the material studied is $(\frac{2}{3}REE^{3+} + \frac{1}{3}M^{2+}) + (\frac{2}{3}OH^- + \frac{1}{3}H_2O)$. According to the predominant cation on the M^{2+} site, the ancylite-group minerals can be subdivided into ancylite, calcioancylite, gysinite and kozoite species (Hatert and Burke, 2008; Belovitskaya *et al.*, 2013). Additionally, the primary *REE* component is also identified by a hyphenated suffix that appears in parentheses on each distinct mineral species, e.g. ancylite-(Ce) (Levinson, 1966; Bayliss and Levinson, 1988). On the basis of the composition, the minerals of the ancylite group can be described as solid solutions among ancylite, calcioancylite, gysinite and kozoite (Sarp and Bertrand, 1985; Miyawaki *et al.*, 2000). Miyawaki *et al.* (2000) constructed a ternary composition diagram for the ancylite-group minerals and plotted available published mineral analyses. The results indicate that the value of *x* in the general formula of nearly all published mineral analysis exceeds 1. The sum of $(REE^{3+} + M^{2+})$ is usually ~2 apfu, which indicates that the ancylite-group minerals are probably not intermediate solid solutions between $REE^{3+}(CO_3)(OH)$ and $M^{2+}(CO_3) \cdot H_2O$ (Sarp and Bertrand, 1985; Miyawaki *et al.*, 2000). Without quantitative

chemical analysis and clear boundaries of mineral species, members of solid-solution series cannot be identified precisely. On the issue of boundaries, Miyawaki *et al.* (2000) discussed the value of *x* in the general formula exceeding 1.5 that is the boundary between kozoite and calcioancylite. The ratios between the divalent elements and *REE* range from 1:1 to 1:3, indicating $1 < x < 1.5$, in the ancylite–calcioancylite–gysinite isomorphous series (Larsen *et al.*, 2002).

Conclusions

Although the ancylite-mineral group has only been informally defined, the chemical formula of ancylite-group minerals can be defined as $(REE_x^{3+}M_{2-x}^{2+})(CO_3)_2[(OH)_x \cdot (2-x)H_2O]$ ($1 < x \leq 2$ and *Z* = 2). It is worth noting that significant differences are present in the published general formulas within valid mineral species belonging to the ancylite group (e.g. calcioancylite-(Ce): (Ce,Ca,Sr)(CO₃)(OH,H₂O), Belovitskaya *et al.*, 2013; Calcioancylite-(Nd): Nd_{2.8}Ca_{1.2}(CO₃)₄(OH)₃·H₂O, Orlandi *et al.*, 1990). Without better understanding of this group of minerals, it is not easy to understand whether rare earth elements and divalent cations occupy the same crystallographic sites or independent sites. For example: chemically, some REE minerals can be written as Ce₂Sr(CO₃)₃(OH)₂·H₂O or Ce₃Sr(CO₃)₄(OH)₃·H₂O. Thus, the ratio of Ce to Sr is 2:1 or 3:1, which is obviously different from the simplified formula of ancylite-(Ce) in the IMA list (Pasero, 2023). The two mineral formulas apparently represent two potential new mineral species but are actually intermediate between the end-members (Ce,Sr)₂(CO₃)₂(OH,H₂O)₂ [ancylite-(Ce)] and Ce₂(CO₃)₂(OH)₂ [potential Ce-analogue of kozoite-(Nd)]. Considering that the ancylite group has not yet been formally approved by the IMA, an ancylite-group nomenclature proposal is in preparation to clarify the above aspects. The well-defined

Table 5. Selected bond distances (Å) and angles (°) of calcioancylite-(La).

<i>M</i> –O3	2.465(17)	O1–C–O2	120.0(9)
<i>M</i> –O3	2.496(17)	O2–C–O2	119.9(18)
< <i>M</i> –O3>	2.481	O1– <i>M</i> –O1	154.3(8)
		O2– <i>M</i> –O2	96.3(3)
<i>M</i> –O1 ^{×2}	2.577(4)	O3– <i>M</i> –O3	134.8(4)
<i>M</i> –O2 ^{×2}	2.576(11)		
<i>M</i> –O2 ^{×2}	2.645(12)		
<i>M</i> –O2 ^{×2}	2.765(12)		
< <i>M</i> –O2>	2.641		
C–O2 ^{×2}	1.290(15)		
C–O1	1.28(3)		
<C–O>	1.287		

Table 6. Bond-valence analysis (vu) for calcioancylite-(La).

	<i>M</i> site			Sum	Theoretical
	La	Ca	C		
O1	0.221 ^{×21→}	0.065 ^{×21→}	1.346	1.919	2
O2	0.221 ^{×21}	0.066 ^{×21}	1.310 ^{×21}	2.007	2
	0.184 ^{×21}	0.054 ^{×21}			
	0.133 ^{×21}	0.039 ^{×21}			
O3	0.299	0.088		0.744	0.667
	0.275	0.081			
Sum		2.711	3.966		
Theoretical		2.667	4		

Notes: Bond-valence sums were calculated with the site-occupancy factors given in Table 4. *M* site = $\frac{2}{3}$ La + $\frac{1}{3}$ Ca. The theoretical vu of O3 is calculated based on $\frac{2}{3}OH + \frac{1}{3}H_2O$ for charge balance. Calculations were done using the equation and constants of Brown (1977), $S = \exp[(R_0 - d_0)/b]$.

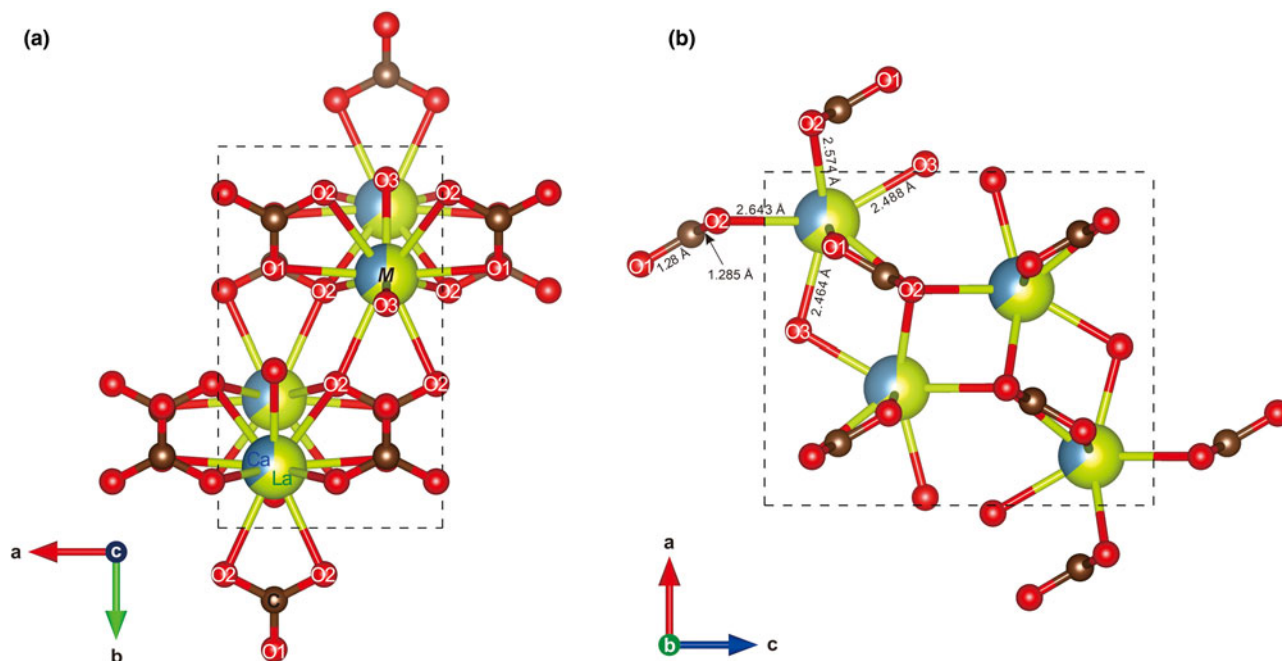


Fig. 3. The crystal structure model of calcioancylite-(La) viewed along (a) [001] and (b) [010].

mineral boundaries and a unified ideal formula, enabling the full description of the chemical variability of the informal ancylite group, will allow important chemical information to be imparted, not only to mineralogists but also to petrologists and ore geologists.

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References

- Bayliss P. and Levinson A.A. (1988) A system of nomenclature for rare-earth mineral species: revision and extension. *American Mineralogist*, **73**, 422–423.
- Belovitskaya Y.V., Pekov I.V., Gobechiya E.R. and Kabalov Y.K. (2013) Refinement of the crystal structure of calcioancylite-(Ce) by the Rietveld method. *Crystallography Reports*, **58**, 216–219.
- Breese N.E. and O’Keeffe M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Brown I.D. (1977) Predicting bond lengths in inorganic crystals. *Acta Crystallographica*, **B33**, 1305–1310.
- Brown I.D. and Altermatt D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica*, **B41**, 244–247.
- Bulakh A.G., Le Bas M.J., Wall F. and Zaitsev A.N. (1998) Ancylite-bearing carbonatite of the Sebyavr massif, Kola peninsula, Russia. *Neues Jahrbuch für Mineralogie Monatshefte*, **1998**, 171–192.
- Chakhmouradian A.R., Cooper M.A., Reguir E.P. and Moore M.A. (2017) Carbocernaite from bear lodge, Wyoming: crystal chemistry, paragenesis, and rare-earth fractionation on a microscale. *American Mineralogist*, **102**, 1340–1352.
- Dal Negro A., Rossi G. and Tazzoli V. (1975) The crystal structure of ancylite, $(RE)_x(\text{Ca,Sr})_{2-x}(\text{CO}_3)_2(\text{OH})_x \cdot (2-x)\text{H}_2\text{O}$. *American Mineralogist*, **60**, 280–284.
- Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K. and Puschmann H. (2009) A complete structure solution, refinement and analysis program. *Journal of Applied Crystallography*, **42**, 339–341.
- Frost R. L. and Dickfos M.J. (2007) Raman spectroscopy of halogen-containing carbonates. *Journal of Raman Spectroscopy*, **38**, 1516–1522.
- Hatert F. and Burke E.A.J. (2008) The IMA-CNMNC dominant-constituent rule revisited and extended. *The Canadian Mineralogist*, **46**, 717–728.
- Huang W.L., Xu J.F., Chen J.L., Huang F., Pi Q.H. and Li Z.L. (2018) Geochronology, geochemistry and genesis of the Baiyunshan alkalic rocks in Gejiu area of southeastern Yunnan Province. *Acta Petrologica et Mineralogica*, **37**, 716–732 [in Chinese with English abstract].
- Larsen A.O. and Gault R.A. (2002) Calcio-ancylite-(Ce) from syenite pegmatite at Tvedalen, Oslo Region, Norway. *Neues Jahrbuch für Mineralogie-Monatshefte*, **2002**, 411–423.
- Laugier J. and Bochu B. (2004) *LMGP Suite of Programs for the Interpretation of X-ray Experiments*. ENSP/Laboratoire des Matériaux et du Génie Physique, France.
- Levinson A. (1966) A system of nomenclature for rare-earth minerals. *American Mineralogist*, **51**, 152.
- Miyawaki R., Matsubara S., Yokoyama K., Takeuchi K., Nakai I. and Terada Y. (2000) Kozoite-(Nd), $\text{Nd}(\text{CO}_3)(\text{OH})$, a new mineral in an alkali olivine basalt from Hizen-cho, Saga Prefecture, Japan. *American Mineralogist*, **85**, 1076–1081.
- Miyawaki R., Matsubara S., Yokoyama K., Iwano S., Hamasaki K. and Yukinori I. (2003) Kozoite-(La), $\text{La}(\text{CO}_3)(\text{OH})$, a new mineral from Mitsukoshi, Hizen-cho, Saga Prefecture, Japan. *Journal of Mineralogical and Petrological Sciences*, **98**, 137–141.
- Orlandi P., Pasero M. and Vezzalini G. (1990) Calcio-ancylite-(Nd), a new REE-carbonate from Baveno, Italy. *European Journal of Mineralogy*, **2**, 413–418.
- Pasero M. (2023) *The New IMA List of Minerals*. International Mineralogical Association. Commission on new minerals, nomenclature and classification (IMA-CNMNC). <http://cnmnc.units.it/>
- Pekov I.V., Petersen O.V. and Voloshin A.V. (1997) Calcio-ancylite-(Ce) from Ilimaussaq and Narssárssuk, Greenland, Kola peninsula and Polar Urals,

- Russia; ancylite-(Ce)-calcio-ancylite-(Ce) an isomorphous series. *Neues Jahrbuch für Mineralogie, Abhandlungen*, **171**, 309–322.
- Rigaku Oxford Diffraction. (2015) *CrysAlisPro Software system, version 1.171.38.43*. Rigaku Corporation.
- Sarp H. and Bertrand J. (1985) Gysinite, $\text{Pb}(\text{Nd,Lu})(\text{CO}_3)_2(\text{OH})\cdot\text{H}_2\text{O}$, a new lead, rare-earth carbonate from Shinkolobwe, Shaba, Zaïre and its relationship to ancylite. *American Mineralogist*, **70**, 1314–1317.
- Sheldrick G.M. (2015) SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallographica*, **A71**, 3–8.
- Szymanski J.T. and Chao G.Y. (1986) The crystal structure of monoclinic ancylite. *American Crystallographic Association, Annual Meeting, Hamilton*, Abstract Paper PA2.
- Wang Y., Dong G., Santosh M., Liu C., Chen W., Liang J. and Zhang Y. (2021) Alkaline magmatism on Neo-Tethyan extensional domains: Evidences from the Gejiu complex in Yunnan, China. *Geological Journal*, **56**, 4331–4348.
- Wang Y., Gu X., Dong G., Hou Z., Yang Z., Fan G., Wang Y., Tang C., Cheng Y. and Qu K. (2022) Calcioancylite-(La), IMA 2021–090. CNMNC Newsletter 65. *Mineralogical Magazine*, **86**, 354–358.
- Warr L.N. (2021) IMA–CNMNC approved mineral symbols. *Mineralogical Magazine*, **85**, 291–320.
- Wilson A.J.C. (1992) *International Tables for Crystallography. Volume C*. Kluwer, Dordrecht, The Netherlands.
- Zhang Y., Huang Z.L., Luo T.Y., Qian Z.K., Zhang J.W. and Sun, J.B. (2013) The geochemistry and SIMS U-Pb zircon dating of the Jiasha gabbro-monzonitic intrusion in Gejiu district, Yunnan Province. *Geochimica*, **42**, 523–543 [in Chinese with English abstract].