



Article

Nomenclature of the ancylite supergroup

Mineralogy, petrology and geochemistry of pegmatites: Alessandro Guastoni memorial issue

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Abstract

The ancylite supergroup has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, with the general crystal chemical formula $(M_x^{3+}M_{2-x}^{2+})(CO_3)_2[(OH)_x \cdot (2-x)H_2O]$ ($1 \leq x \leq 2$, $Z = 2$). The ancylite supergroup can be divided into two groups defined by different proportions of the M cation and hydroxyl anion and/or water molecule: the ancylite group is defined for $1 \leq x \leq 1.5$; the kozoite group is defined for $1.5 < x \leq 2$. The ancylite supergroup minerals are orthorhombic with space group $Pm\bar{c}n$, or monoclinic with space group $Pm11$, and have a crystal structure with species-defining trivalent and divalent M cations ($M = La^{3+}$, Ce^{3+} , Nd^{3+} , Ca^{2+} , Sr^{2+} and Pb^{2+}) which centre ten-vertex polyhedra formed by oxygen atoms at three independent O sites. Two vertices of the triangular $(CO_3)^{2-}$ anion are oxygen atoms, whereas the third one, O(3), is statistically filled with $(OH)^-$ groups and H_2O molecules. The triangular faces of three oxygen atoms of MO_{10} coordination polyhedra join the chains of this ten-vertex polyhedron, which is extended along the c axis. The (CO_3) triangles connect chains in three dimensions. To date, eight valid mineral species with $M^{2+} = Sr^{2+}$, Ca^{2+} and Pb^{2+} belong to the ancylite group [ancylite-(La), ancylite-(Ce), calcioancylite-(La), calcioancylite-(Ce), calcioancylite-(Nd), gysinite-(La), gysinite-(Ce) and gysinite-(Nd)]. Two hydroxyl carbonates with only rare earth elements as species-defining cations, kozoite-(La) and kozoite-(Nd) are members of the kozoite group.

Keywords: ancylite supergroup; ancylite; calcioancylite; gysinite; kozoite; nomenclature; classification

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Introduction

Ancylite-type minerals, which are hydrous/hydroxyl carbonates containing rare earth elements ($REEs$), Ca^{2+} , Sr^{2+} and Pb^{2+} as major cations, commonly occur in alkaline rocks as late accessories or, in some types of carbonatites, as rock-forming minerals and important concentrators of light rare earth elements ($LREE$) and strontium (Fig. 1).

Prior to this work, neither ancylite group nor supergroup were formally approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA–CNMNC). However, the term ‘ancylite group’ appeared in the Fleischer’s Glossary of Mineral Species in 2008 (Back and Mandarino, 2008), has been repeated in subsequent editions, and is now a common term in literature.

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The general chemical formula for ancylite-group minerals was previously described as: $M_x^{3+}M_{2-x}^{2+}(CO_3)_2(OH)_x \cdot (2-x)H_2O$ ($Z = 2$), where $1 < x \leq 2$, $M^{3+} = REE^{3+}$ such as La^{3+} , Ce^{3+} and Nd^{3+} , $M^{2+} = Ca^{2+}$, Sr^{2+} and Pb^{2+} (Dal Negro *et al.*, 1975; Sarp and Bertrand, 1985; Miyawaki *et al.*, 2000). Note that there are significant differences in the formulae given in the original descriptions of valid mineral species belonging to the ancylite group, e.g. ancylite-(La): $Sr(La,Ce)(CO_3)_2(OH) \cdot H_2O$ (Yakovenchuk *et al.*, 1997); calcioancylite-(Ce): $(Ce,Ca,Sr)(CO_3)(OH,H_2O)$ (Belovitskaya *et al.*, 2013); calcioancylite-(Nd): $Nd_{2.8}Ca_{1.2}(CO_3)_4(OH)_3 \cdot H_2O$ (Orlandi *et al.*, 1990). Without detailed knowledge of the crystal chemistry of this group, it is not easy to understand whether trivalent $REEs$ and the other divalent cations occupy the same crystallographic site or independent sites. For example: chemically, formulae of some REE minerals can be written as $La_2Sr(CO_3)_3(OH)_2 \cdot H_2O$ or $La_3Sr(CO_3)_4(OH)_3 \cdot H_2O$, the ratio of La to Sr is 2:1 or 3:1, which is different from the ideal formula of ancylite-(La) $[LaSr(CO_3)_2(OH) \cdot H_2O]$ in the current IMA mineral list (Pasero, 2024). This suggests potentially two new mineral species, however they are intermediate between the end-members, $[LaSr](CO_3)_2[(OH)(H_2O)]$ (revised ideal formula, this work)

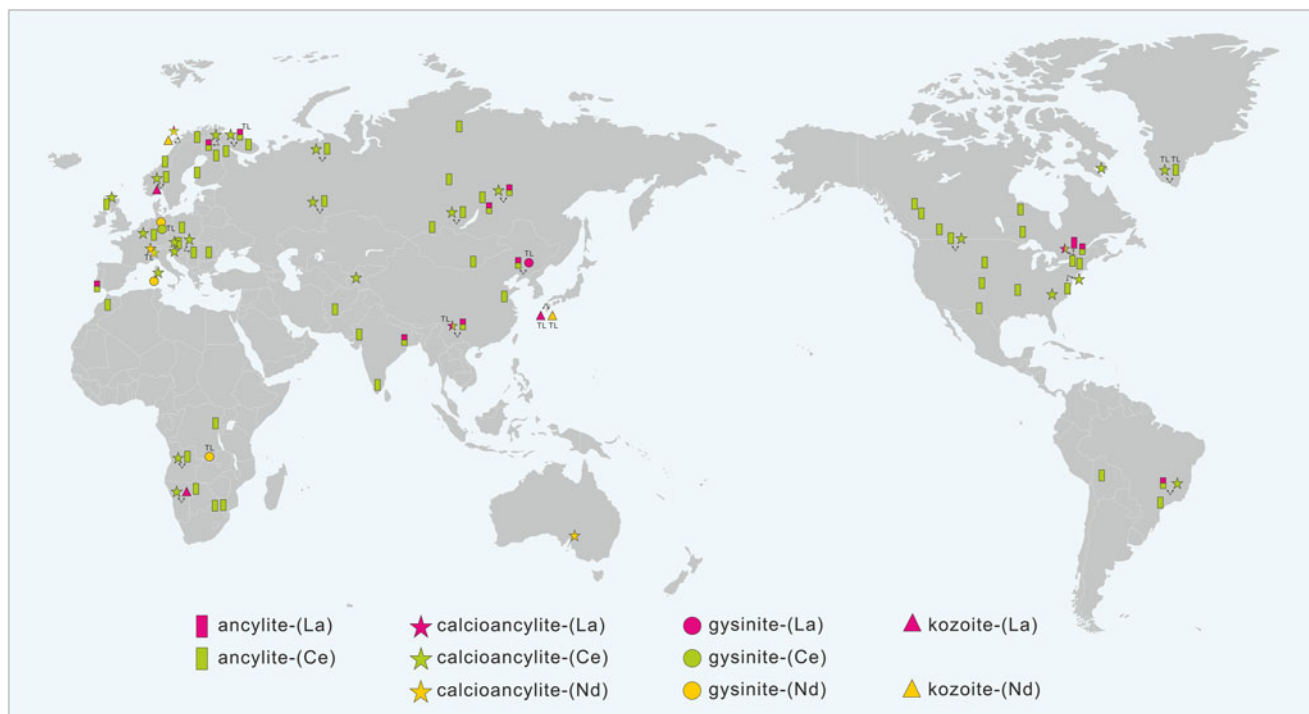


Figure 1. The localities of ancyllite supergroup minerals worldwide, following the literature records on [Mindat.org](https://www.mindat.org) (Accessed November 2023). TL = Type Locality.

[ancyllite-(La)] and $\text{La}_2(\text{CO}_3)_2(\text{OH})_2$ [kozoite-(La)]. This ambiguity is potentially confusing, not only for novices but also for expert crystallographers. The situation is additionally complicated by the specific behaviour of the $M^{3+}:M^{2+}$ ratio in the solid-solution series between ancyllite-(Ce) and calcioancylite-(Ce) (Pekov *et al.*, 1997).

These problems of inconsistent chemical formulae, the complex chemical variability of the ancyllite supergroup minerals, and vague boundaries between different hierarchies, have prompted us to formally establish the ancyllite supergroup and to recommend updating the ideal formulae of ancyllite supergroup members in the IMA–CNMNC official mineral list (Table 1). The proposal for the “*Nomenclature of the ancyllite supergroup*” has been approved by the IMA–CNMNC (Bosi *et al.*, 2024). The present work aims to not only identify and classify complex ancyllite supergroup minerals but to also convey important chemical information for mineralogists and ore geologists who are interested in alkaline complexes and REE behaviours.

Crystal structure

In the structure of the ancyllite supergroup minerals, trivalent and divalent cations (M cations), such as La^{3+} , Ce^{3+} , Nd^{3+} , Ca^{2+} , Sr^{2+} and Pb^{2+} , centre ten-vertex polyhedra, formed by oxygen atoms at three independent O sites. Two of them, at the apices of triangular $(\text{CO}_3)^{2-}$ anion, are occupied by oxygen atoms, whereas the third one, expressed as O(3) in Table 2, is statistically filled with (OH) groups and H_2O molecules. The chains of this ten-vertex polyhedral are stretched along the c axis and connected by sharing the triangular faces of three oxygen atoms of MO_{10} coordination polyhedra. The chains are interconnected into a three-dimensional framework via (CO_3) triangles (Fig. 2a).

The crystal structure of ancyllite-(Ce) was solved for the first time by Dal Negro *et al.* (1975). Belovitskaya *et al.* (2002) performed the structure refinement for two specimens of ancyllite-(Ce) within the space groups $Pm\bar{c}n$ and $Pm\bar{c}2_1$. Belovitskaya *et al.* (2013) studied the crystal structure of

Table 1. Formulae of ancyllite supergroup minerals.

Name	Formula in the current IMA list	Simplified crystal chemical formula	Recommended ideal formula
Ancyllite-(La) ¹	$\text{LaSr}(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$	$(\text{La,Sr})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{LaSr})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Ancyllite-(Ce) ²	$\text{CeSr}(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$	$(\text{Ce,Sr})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{CeSr})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Calcioancylite-(La) ³	$(\text{LaCa})(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$	$(\text{La,Ca})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{LaCa})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Calcioancylite-(Ce) ⁴	$(\text{Ce,Ca,Sr})(\text{CO}_3)_2(\text{OH}, \text{H}_2\text{O})$	$(\text{Ce,Ca})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{CeCa})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Calcioancylite-(Nd) ⁵	$\text{Nd}_{2.8}\text{Ca}_{1.2}(\text{CO}_3)_4(\text{OH})_3 \cdot \text{H}_2\text{O}$	$(\text{Nd,Ca})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{NdCa})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Gysinite-(La) ⁶	$\text{PbLa}(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$	$(\text{La,Pb})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{LaPb})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Gysinite-(Ce) ⁷	$\text{PbCe}(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$	$(\text{Ce,Pb})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{CePb})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Gysinite-(Nd) ⁸	$\text{PbNd}(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$	$(\text{Nd,Pb})_2(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_2$	$(\text{NdPb})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, $Z = 2$
Kozoite-(La) ⁹	$\text{La}(\text{CO}_3)(\text{OH})$	$\text{La}_2(\text{CO}_3)_2(\text{OH})_2$	$\text{La}(\text{CO}_3)(\text{OH})$, $Z = 4$
Kozoite-(Nd) ¹⁰	$\text{Nd}(\text{CO}_3)(\text{OH})$	$\text{Nd}_2(\text{CO}_3)_2(\text{OH})_2$	$\text{Nd}(\text{CO}_3)(\text{OH})$, $Z = 4$

References: ¹ Yakovenchuk *et al.* (1997); Petersen *et al.* (2001); ² Dal Negro *et al.* (1975); Belovitskaya *et al.* (2002); ³ Wang *et al.* (2023); ⁴ Belovitskaya *et al.* (2013); ⁵ Orlandi *et al.* (1990); ⁶ Wu *et al.* (2023); ⁷ Kampf *et al.* (2023); ⁸ Chabot and Sarp (1985); ⁹ Miyawaki *et al.* (2003); ¹⁰ Miyawaki *et al.* (2000).

Table 2. Characteristics of the ancylite supergroup described by the general formula $(M_x^{3+}M_{2-x}^{2+})(\text{CO}_3)_2[(\text{OH})_x \cdot (2-x)\text{H}_2\text{O}]$, with $Z=2$.

Group	Root name	Range	Species	Essential M cation	Essential O(3) anion/mol.	Crystal system	Space group	a (Å)	b (Å)	c (Å)	α (°)
Ancylite	ancylite	$1 \leq x \leq 1.5$	ancylite-(La)	$\text{La}^{3+}, \text{Sr}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	5.044	8.541	7.292	90
			ancylite-(Ce)	$\text{Ce}^{3+}, \text{Sr}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	5.03	8.53	7.29	90
	calcioancylite		calcioancylite-(La)	$\text{La}^{3+}, \text{Ca}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	5.0253	8.5152	7.2717	90
			calcioancylite-(Ce)	$\text{Ce}^{3+}, \text{Ca}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	5.0095	8.5006	7.2670	90
			calcioancylite-(Nd)	$\text{Nd}^{3+}, \text{Ca}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Mon.	$Pm11$	4.976	8.468	7.212	90.04
	gysinite		gysinite-(La)	$\text{La}^{3+}, \text{Pb}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	4.986	8.513	7.227	90
			gysinite-(Ce)	$\text{Ce}^{3+}, \text{Pb}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	5.0780	8.6689	7.3255	90
gysinite-(Nd)			$\text{Nd}^{3+}, \text{Pb}^{2+}$	$(\text{OH})^-, \text{H}_2\text{O}$	Orth.	$Pm\bar{c}n$	5.0028	8.555	7.2392	90	
Kozoite	kozoite	$1.5 < x \leq 2$	kozoite-(La)	La^{3+}	$(\text{OH})^-$	Orth.	$Pm\bar{c}n$	4.986	8.513	7.227	90
			kozoite-(Nd)	Nd^{3+}	$(\text{OH})^-$	Orth.	$Pm\bar{c}n$	4.9829	8.5188	7.2570	90

Note: The references are the same as in Table 1 for each mineral, respectively.

calcioancylite-(Ce) using 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 M cations. It should be noted that calcioancylite-(Nd) from Baveno, Italy, described by Orlandi *et al.* (1990) has revealed that M^{3+} and M^{2+} cations order into four M sites in the ancylite-type structure to lower the symmetry from orthorhombic ($Pm\bar{c}n$) to monoclinic ($Pm11$) with a minor deviation of α from 90° to $90.04(3)^\circ$ (Belovitskaya *et al.*, 2013). It is the only approved valid mineral species with monoclinic symmetry in the ancylite supergroup so far (Table 2). However, if the crystal structures of the polymorphs have essentially the same topology, differing only in terms of a structural distortion or in the order-disorder

relationship of some of the atoms comprising the structure, such polymorphs are not regarded as separate species (Nickel and Grice, 1998). The recommendation is that both of the ordered monoclinic and disordered orthorhombic phases be classified into a mineral species. The difference in symmetry owing to the order-disorder can be indicated by a suffix, as is the polytype distinction, e.g. calcioancylite-(Nd)- M and calcioancylite-(Nd)- O .

Nomenclature and classification of the ancylite supergroup

In the frame of the present IMA-approved nomenclature (Mills *et al.*, 2009), ancylite-type minerals are divided into two groups: the ancylite group and the kozoite group. These mineral groups compose the ancylite supergroup (named after the first adequately characterised mineral). In addition, the members are classified

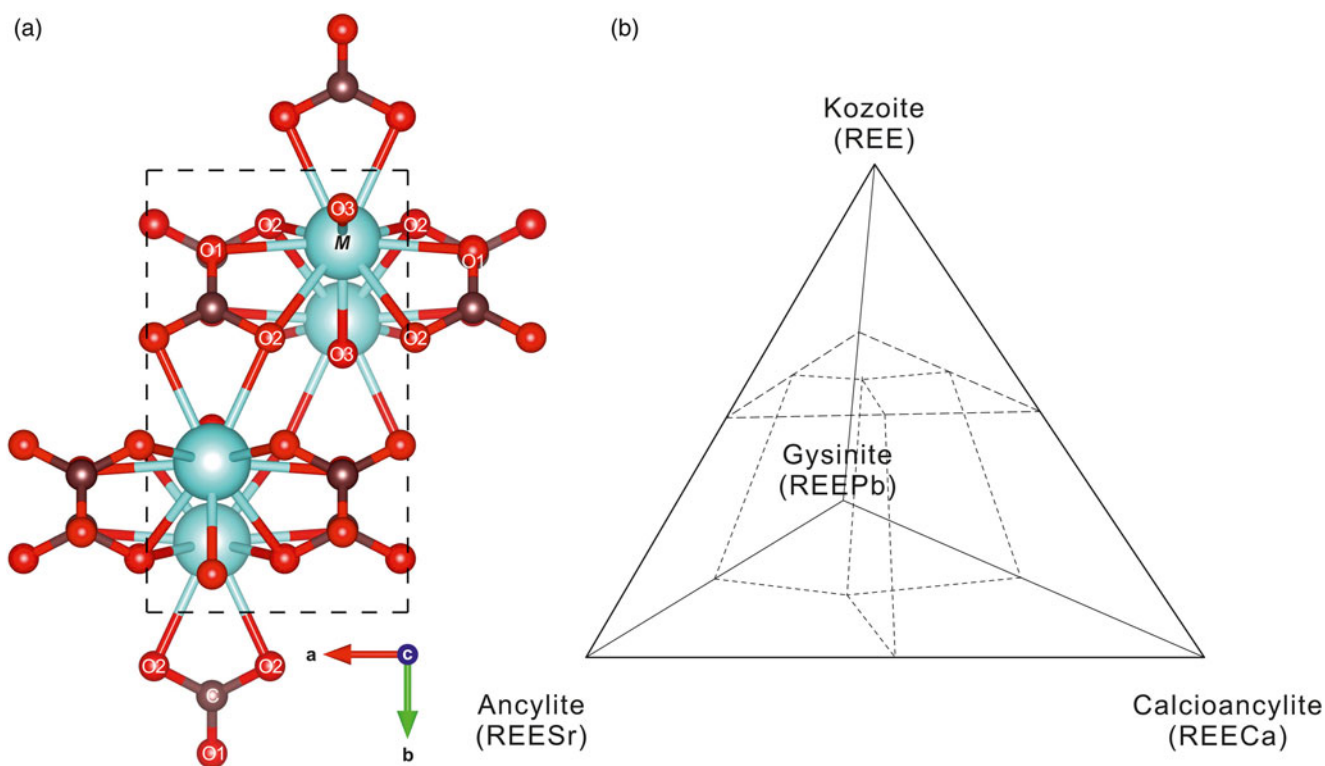


Figure 2. (a) The crystal structure of ancylite supergroup minerals viewed along [001]; (b) quaternary diagram, showing the boundaries between kozoite $\text{REE}(\text{CO}_3)(\text{OH})$, ancylite $(\text{REESr})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, calcioancylite $(\text{REECa})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$, and gysinite $(\text{REEPb})(\text{CO}_3)_2[(\text{OH})(\text{H}_2\text{O})]$. Figure 2a drawn using Vesta software (Momma and Izumi, 2011).

into root names corresponding to the essential M cations: ancylite ($REE^{3+}Sr^{2+}$), calcioancylite ($REE^{3+}Ca^{2+}$), gysinite ($REE^{3+}Pb^{2+}$) and kozoite (REE^{3+}).

The general chemical formula of ancylite supergroup minerals can be defined as $(M_x^{3+}M_{2-x}^{2+})(CO_3)_2[(OH)_x(2-x)H_2O]$ ($1 \leq x \leq 2$, $Z=2$), and different combinations of M^{3+} and M^{2+} constituents should be regarded as separate mineral species. Both M^{3+} and M^{2+} cations generally occupy the same crystallographic site, and the formula is charge-balanced through the following substitution mechanism: $M^{3+} + OH^- \rightleftharpoons M^{2+} + H_2O$. The excess positive charge of M^{3+} is compensated by the incorporation of $(OH)^-$, and the number of hydroxyl ions and water molecules are equivalent to those of M^{3+} and M^{2+} , respectively (Wang *et al.*, 2023). Taking into account the recently defined species, the boundaries between different hierarchies of the ancylite supergroup is as follows (Fig. 2b):

- (1) $1 \leq x \leq 1.5$, REE^{3+} dominant for M^{3+} : ancylite group
 - (a) Sr^{2+} dominant for M^{2+} : ancylite (root name)
 - (b) Ca^{2+} dominant for M^{2+} : calcioancylite (root name)
 - (c) Pb^{2+} dominant for M^{2+} : gysinite (root name)
- (2) $1.5 < x \leq 2$, REE^{3+} dominant for M^{3+} : kozoite group

Each distinct mineral species within the ancylite supergroup has a hyphenated suffix between parentheses, the Levinson modifier (Levinson, 1966), indicating the dominant REE constituent (Hatert and Burke, 2008; Hatert *et al.*, 2013). To date, the supergroup includes ten valid mineral species: ancylite-(La), ancylite-(Ce), calcioancylite-(La), calcioancylite-(Ce), calcioancylite-(Nd), gysinite-(La), gysinite-(Ce), gysinite-(Nd), kozoite-(La) and kozoite-(Nd) (Table 2).

Historical synopsis of the ancylite supergroup minerals

The name ancylite first appeared in literature in 1898, when this mineral was discovered in Narsaarsuk, Southern Greenland. The name is taken from the Greek word $\alpha\gamma\kappa\upsilon\lambda\omicron\varsigma$ (ankylos) for ‘curved’, in allusion to the planes of the crystals usually rounded and distorted. The formula was given by Flink (1898, 1901) as $Ce_4Sr_3(CO_3)_7(OH)_4 \cdot 3H_2O$. The La-dominant ancylite species, ancylite-(La), was discovered by Yakovenchuk *et al.* (1997) from a hydrothermal vein at the Kukisvumchorr mountain, Khibiny alkaline complex, Kola peninsula, Russia.

A brief but interesting review of the history of the discoveries and early studies of calcioancylite-(Ce) has been given by Pekov *et al.* (1997): Chernik (1904) described a Ca-dominant analogue of ancylite but without a clear locality, with the address written as “Western land of the Russian Empire” (Pekov *et al.*, 1997); the name ‘calcio-ancylite’ in literature was first mentioned by Chernik (1923), and it has been renamed to calcioancylite-(Ce) according to the revised nomenclature for the REE -bearing minerals (Nickel and Mandarino, 1987). The Nd-dominant calcioancylite was found in miarolitic cavities of Baveno granite, Italy (Orlandi *et al.*, 1990). At the same time, Orlandi *et al.* (1990) re-examined the type samples identified as ‘weibeyite’ by Artini (1915) from Baveno, and their powder X-ray diffraction and chemical analyses indicated that the material was actually a calcioancylite-(Ce). It should be noted that the term ‘weibeyite’ was first introduced by Brögger (1890) to describe a REE carbonate phase in Langesundsfjorden, Norway. If it is the same material as the ‘weibeyite’ from Baveno, it should be the first finding of the

ancylite-type mineral, but, unfortunately, Saebø (1963) discredited Broegger’s ‘weibeyite’ and the result shows that it is just a bastnäsite-(Ce) pseudomorph. Recently, the La-dominant calcioancylite species, calcioancylite-(La), was discovered from Gejiu nepheline syenite, Yunnan Province, China (Wang *et al.*, 2023).

Gysinite-(Nd), the first Pb-dominant member of the ancylite group, was discovered by Sarp and Bertrand (1985) in a specimen from the mineral collection at the Geneva Natural History Museum. The sample was originally labelled ‘schuilingite’ from Shinkolobwe, Shaba, Zaire (now the Democratic Republic of the Congo). The mineral is named after the late Professor Marcel Gysin (1891–1974) from the University of Geneva. Almost four decades later, the La-dominant mineral species, gysinite-(La), was discovered in lujavrite from the Saima alkaline complex, Liaoning Province, China (Wu *et al.*, 2023). Gysinite-(Ce), the mineral species with Ce prevailing among REE s, has recently been found in Abendröthe Mine, located in Sankt Andreasberg, Braunlage, Goslar District, Lower Saxony, Germany (Kampf *et al.*, 2023).

In 1997, a kind of pale pink REE carbonate was collected by Koichi Takeuchi from alkali olivine basalt from Hizen-cho, Saga Prefecture, Japan. Miyawaki *et al.* (1998) found that it was different from other ancylites because it was characterised by very low Ca and Sr and almost absent Pb. Several years later, two new minerals and mineral names were approved by the IMA Commission on New Mineral and Mineral Names (IMA–CNMMN, the predecessor of the IMA–CNMNC, as kozoite-(Nd) and kozoite-(La), respectively (Miyawaki *et al.*, 2000; 2003). The minerals are named in honour of the late Kozo Nagashima (1925–1985), a chemist and pioneer in the study of the crystal chemistry of rare earth minerals in Japan.

Note that if considering the extension of the solid solution of the ancylite series beyond the point $M^{2+}/M^{3+} < 0.5$, there probably exists the potential compound $Ca(CO_3)_2H_2O$ (for x close to 0 in the general formula) (Sarp and Bertrand, 1985). However, monohydrocalcite, as a mineral with the chemical formula $Ca(CO_3)(H_2O)$ that occurs in nature (Semenov, 1964), has a topology and symmetry differing from the ancylite-type series (Effenberger, 1981; Swainson, 2008). While it is not clear if that composition could be stable with the ancylite topology, previous studies that reviewed the reported chemical compositions of ‘ancylites’ and ‘calcioancylites’ from several localities showed that the value ‘ x ’ in the general formula, $(M_x^{3+}M_{2-x}^{2+})(CO_3)_2[(OH)_x(2-x)H_2O]$, always exceeded 1 (Bulakh *et al.*, 1998; Pekov *et al.*, 1997). This indicates that ancylite supergroup minerals are not intermediate solid solutions between $M^{3+}(CO_3)(OH)$ and $M^{2+}(CO_3)(H_2O)$. The end-members of this group are $M^{3+}(CO_3)(OH)$ and $(M^{3+}M^{2+})(CO_3)_2[(OH) \cdot H_2O]$ (Sarp and Bertrand, 1985; Miyawaki *et al.*, 2000). Taking into account the above reasons and the fact that no minerals having an ancylite-type topology and a chemical composition with x close to 0 (even < 0.5) have been found in Nature so far, the potential ancylite-type topology $M^{2+}(CO_3)(H_2O)$ phases are not included in this nomenclature.

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