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Gysinite, $Pb(Nd,La)(CO_3)_2(OH) \cdot H_2O$, a new lead, rare-earth carbonate from Shinkolobwe, Shaba, Zaïre and its relationship to ancylite

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Abstract

Gysinite, ideally $Pb(Nd,La)(CO_3)_2(OH) \cdot H_2O$, occurs at Shinkolobwe, Shaba, Zaïre, associated with schuilingite, malachite, cerussite, talc-chlorite, bornite, wulfenite, kasolite, native gold and garnet. The crystals, light pink to reddish pink in color, up to 1 mm in length, are euhedral with a pseudo-octahedral habit and with {111} and {110} as the most prominent forms. The streak is white to light pink. The name is to honor Professor Marcel Gysin. The crystal system is orthorhombic, space group *Pmcn*, with $a = 5.04$, $b = 8.50$, $c = 7.25$Å and $Z = 2$. $a:b:c$ ratio is 0.5929 : 1 : 0.8529. The calculated density is 4.82 g/cm^3. X-ray diffraction data are similar to those of ancylite. The mineral is biaxial negative with $2V_x = 70°$, $2V_{calc} = 72.4°$, $\alpha = 1.745$, $\beta = 1.805$, $\gamma = 1.840$, dispersion $r < v$. Optical orientation: $X = \mathbf{c}$, $Y = \mathbf{a}$, $Z = \mathbf{b}$.

Introduction

Gysinite was discovered on a single specimen from the mineral collection at the Geneva Natural History Museum. This sample, catalog #410/85, was labeled schuilingite from Shinkolobwe, Shaba, Zaïre.

The name is in honor of the late Professor Marcel Gysin, who taught mineralogy at the University of Geneva and had worked for several years in the Shaba province of Zaïre. This new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Type material, totalling about 15 mg of gysinite on the sample, is preserved in the Department of Mineralogy at the Geneva Natural History Museum.

Physical and optical properties

Gysinite is translucent, light pink to reddish pink in color, with a vitreous to greasy luster; the streak is white to light pink. The hardness could not be measured. In thin section, it is colorless to light pink. The crystals are euhedral with a pronounced pseudo-octahedral habit, elongated along **b**, and are up to 1 mm in length. The observed forms are {111} and {110}. The mineral, brittle with a lack of cleavage, occurs as isolated single crystals (Fig. 1), crystal aggregates (Fig. 2a.) and penetration twins (Fig. 2b.) on the specimen. The twin plane is (100) but it was impossible to determine the twin axis. Gysinite is soluble with effervescence in cold dilute hydrochloric acid. There is no noticeable fluorescence under both long- and short-wave ultraviolet light. It sinks in Clerici's solution. Using the Gladstone-Dale relationship with revised constants proposed by Mandarino (1981a), $K_c = 0.1634$ and $K_p = 0.1654$, indicating superior compatibility between the chemical and physical data; the calculated density is 4.82 g/cm^3. The mineral is biaxial negative with $2V_x = 70°$, indices of refraction $\alpha = 1.745$, $\beta = 1.805$, $\gamma = 1.840$ (all ± 0.005) with a perceptible $r < v$ dispersion. $2V_{calc} = 72.4°$. The optical orientation is $X = \mathbf{c}$, $Y = \mathbf{a}$, $Z = \mathbf{b}$.

X-ray crystallography

X-ray single-crystal study by the Weissenberg method shows that gysinite is orthorhombic with space group *Pmcn* as confirmed by the determination of the structure (Chabot et al., 1985). The unit-cell parameters, corresponding to the means of measurements from single crystal films, are $a = 5.04$, $b = 8.50$ and $c = 7.25$Å. The $a:b:c$ ratio is 0.5929 : 1 : 0.8529. The refined values, obtained with a four-circle automated diffractometer using Mo$K\alpha$ radiation, $\lambda = 0.7107$, are $a = 5.0028(8)$, $b = 8.555(1)$, and $c = 7.2392(8)$. The refinement is based on 35 reflections ($17.451° < 2\theta < 22.523°$) using the PARAM program (Stewart et al., 1976). The X-ray powder pattern of gysinite has been established using both Gandolfi and Guinier-Hägg cameras with Cu$K\alpha$ radiation, $\lambda = 1.5418$Å, Ni-filtered for the first one, non filtered for the second one. The values in

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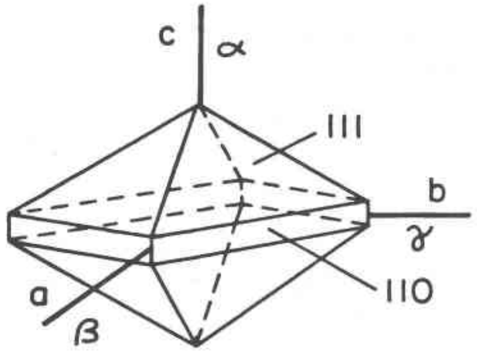

Fig. 1. Pseudooctahedral single crystal of gysinite with the position of the main optical elements.

Table 1 are from the 114.6 mm diameter Gandolfi camera. With Z = 2 and a molecular weight of 450.7 (based on the method described by Mandarino, 1981b, the calculated density is 4.82 g/cm^3. In Table 1, powder diffraction data for gysinite and ancylite, $(RE)_x(Ca,Sr)_{2-x}(CO_3)_2(OH)_x \cdot (2-x)H_2O$ (P.D.F. card 29-384) are presented. The comparison of *d*-spacing and visual intensity values shows the structural similarity between these two minerals.

Table 1. X-ray powder diffraction data of gysinite and ancylite (P.D.F. card 29-384)

Gysinite				Ancylite	
hkl	d_{calc}(Å)	d_{obs}(Å)	I_{vis}	*d*	I/I_1
011	5.516	5.54	50	5.57	50
110	4.335	4.326	100	4.34	100
021	3.667	3.676	100	3.71	100
012	3.334	3.336	40	3.36	40
102	2.943	2.950	50	2.96	100
022	2.758	2.762	5	2.78	20
031	2.639	2.640	35	2.66	40
200	2.520	2.522	30	2.53	40
122	2.420	2.431	15	2.44	20
131 013	2.338 2.325	2.336	50	2.35	80
220	2.168	2.171	<5	2.18	10
040	2.125	2.130	5	2.15	30
221	2.077	2.074	60	2.09	70
212	2.010	2.021	50	2.02	70
123	1.939	1.941	25	1.953	50
141	1.890	1.900	10	1.908	10
033	1.839	1.840	25	1.855	30
004	1.813	1.814	15	1.829	30
133	1.727	1.734	20	1.743	30
213 104	1.709 1.706	1.709	15	1.718	20
plus about 15 weak lines				plus more than 20 weak lines	

114.6 mm Gandolfi camera, CuKα radiation, Ni-filtered

Chemical composition

Gysinite was chemically analyzed with a ARL EMX-SM microprobe equipped with four wavelength spectrometers and a Tracor–Northern energy dispersive system. Wavelength scans made with Pb stearate, RAP, ADP and LiF analyzing crystals, and long counting periods with the energy dispersive system showed the presence of Pb, La, Nd and C. No other rare-earth elements were detected. The presence of water, confirmed by thermogravimetric analysis, was suggested by the behavior of gysinite under the beam. Profiles across the mineral showed slight variations in the

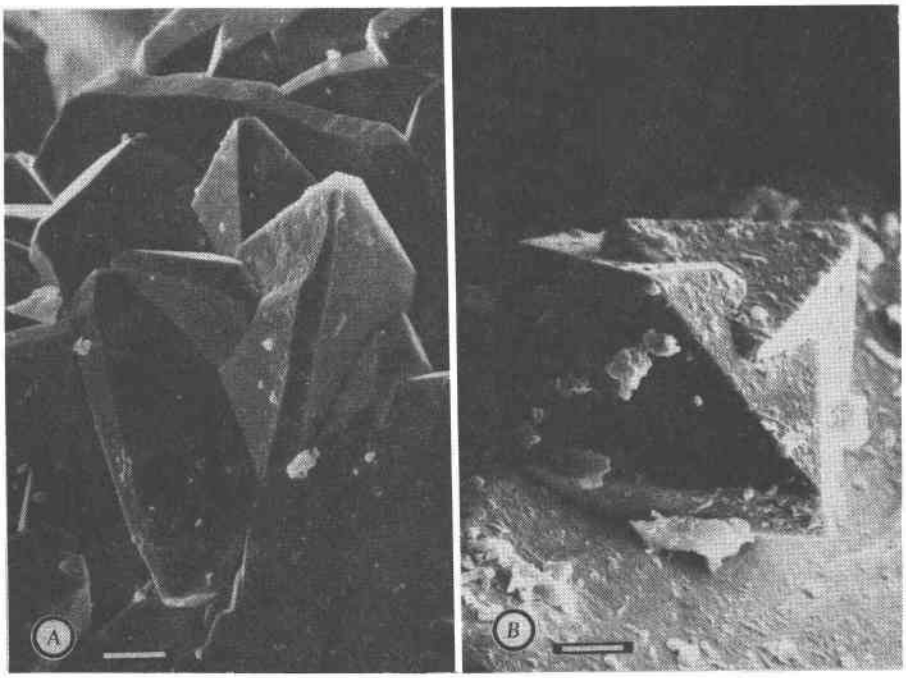

Fig. 2. Some habits of gysinite (a) Aggregate of crystals. (b) Two crystals associated by a penetration twin. SEM photomicrographs; scale bar is ~0.2 mm.

Table 2. Microprobe analyses of gysinite

	Variability†† range wt %	Mean††	Atomic††† proportions	
PbO	26.5 - 31.0	29.1	0.59	Pb
Nd_2O_3	35.0 - 43.0	38.9	1.04	Nd
La_2O_3	4.0 - 7.5	5.8	0.15	La
CO_2	17.4 - 22.3	20.1	2.05	C
H_2O†	5.6 - 6.5	6.1	3.03	H
Total		100.00		

† By difference
†† Based on 21 analyses
††† On the basis of 8 oxygen atoms

distribution of elements but without any evidence of a particular zonation. For quantitative analyses, the instrument was operated at 20 kV and 50 nA (measured on benitoite) and counting was stopped by a constant digitized beam-current. The following natural and synthetic standards were used: $PbCO_3$ for Pb and C, and two glasses of $Li_2B_4O_7$, with 5 wt.% Nd_2O_3 and La_2O_3 respectively, for Nd and La. Gysinite and the standards were coated with Ni. The beam was slightly defocussed to minimize the instability of the glasses and gysinite. The instrumental and matrix effects were corrected using a ZAF program (MAGIC). The results are given in Table 2. The amount of $CO_2 + H_2O$ determined by thermogravimetry on 10 mg of gysinite using a Mettler T.A.1 instrument is about 23 wt.%. This is in rather good agreement with the probe-measured CO_2 content and the H_2O content obtained by difference. The validity of the chemical analysis has been confirmed by the structure determination (Chabot et al., 1985). The empirical formula calculated on the basis of 8 oxygen atoms is: $Pb_{0.59}(Nd_{1.04},La_{0.15})_{\Sigma 1.19}(CO_3)_{2.05}(OH)_{0.63} \cdot 1.2\ H_2O$ or, ideally, $Pb(Nd,La)(CO_3)_2(OH) \cdot H_2O$ with Nd > La, which corresponds to the Pb–Nd analog of ancylite.

Paragenesis

Gysinite is associated with malachite, cerussite, talc-chlorite, bornite, wulfenite, kasolite, native gold, garnet and schuilingite (Piret et al., 1982; Sarp et al., 1983).

As proposed for schuilingite (Piret et al., 1982), the rare-earth elements in gysinite possibly originated from the trace elements in uraninite of the Shaba ore deposits. Monazite, which is also associated with secondary copper and uranium minerals in the oxidation zone of these deposits, is not affected by alteration processes.

Nomenclature and structure

Dal Negro et al. (1975) determined the crystal structure of ancylite and proposed the general formula $(RE)_x(Ca,Sr)_{2-x}(CO_3)_2(OH)_x \cdot (2-x)H_2O$. Depending upon the value of the Sr/Ca ratio, two varieties were defined: a strontian ancylite and a calcian ancylite. Sawyer et al. (1973) synthesized $RE(OH)CO_3$; this isostructural compound represents the end-member composition of ancylite-type structure with x = 2. Therefore, on the basis of the two known chemical compositions of the ancylite–calcioancylite series and the known composition of the phase synthesized by Sawyer et al. (1973), one can consider two ideal end-members: $(RE)_2(CO_3)_2(OH)_2$ and $(RE)(M)(CO_3)_2(OH) \cdot H_2O$, with the M site occupied by divalent cations. Extending the solid-solution beyond the point M/RE = 1.0, there exists, for x = 0, the potential compound $(Ca, Sr)_2(CO_3)_2 \cdot 2H_2O$, or more generally $(Ca,Sr)(CO_3) \cdot H_2O$. Natural $Ca(CO_3) \cdot H_2O$ occurs as the mineral monohydrocalcite; it is not isotypic with the ancylite series (Effenberger, 1981). The Sr-analogue, $Sr(CO_3) \cdot H_2O$, has not yet been found.

As $(RE)_2(CO_3)_2(OH)_2$, for x = 2, and $(RE)(M)(CO_3)_2(OH) \cdot H_2O$, for x = 1, are isostructural and because the divalent cations are missing in $(RE)_2(CO_3)_2(OH)_2$, it is apparent that the divalent cations have no significant influence on the bond connectivity of ancylite-type structures. For x = 1, divalent cations are present in the structure and ancylite, calcioancylite and gysinite, may be considered as end-members of a series of solid solutions with the general formula: $(RE)_x(M)_{2-x}(CO_3)_2(OH)_x \cdot (2-x)H_2O$. The formulas of these three mineral species are: $(Sr_{0.40}, Ca_{0.22})_{\Sigma 0.62}(Ce_{0.82}, La_{0.56})_{\Sigma 1.38}(CO_3)_2(OH)_{1.38} \cdot 0.62\ H_20$, for ancylite (Dal Negro et al., 1975), $Ca_{0.85}(Ce_{0.57}, La_{0.56})_{\Sigma 1.13}(CO_3)_2(OH)_{1.09} \cdot 0.9\ H_20$, for calcioancylite (Palache et al., 1951, p. 291) and $Pb_{0.59}(Nd_{1.04}, La_{0.15})_{\Sigma 1.19}(CO_3)_{2.05}(OH)_{0.63} \cdot 1.2\ H_2O$, for gysinite.

Chemically gysinite is the Pb–Nd equivalent of ancylite. From a structural point of view, it has a great similarity to ancylite: space group and cell parameters are very close and the estimated intensities of diffraction lines in the two powder patterns are also in good agreement. Thus gysinite is isostructural with ancylite (Dal Negro et al., 1975).

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