

Hydroxy-carbonates of the lanthanide elements

by

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ABSTRACT. — The hydrolysis of urea in hot dilute nitric acid solutions of the following trivalent lanthanide elements (Pr, Nd, Sm, Eu, Gd, Tb and Dy), produces diphasic samples which contain at least 80 % of a lanthanide hydroxycarbonate $\text{RE}(\text{OH})\text{CO}_3$, admixed with the normal lanthanide carbonate $\text{RE}_2(\text{CO}_3)_3, x\text{H}_2\text{O}$. X-ray examination of these $\text{RE}(\text{OH})\text{CO}_3$ compounds reveal that they are isostructural with the mineral species ancylite. $(\text{M}^{2+}, \text{RE}^{3+})(\text{CO}_3^{2-})_2(\text{OH}^-)\text{H}_2\text{O}$, $\text{M}^{2+} = \text{Ca}^{2+}; \text{Sr}^{2+}$; and represent the limiting composition where all the M^{2+} ions have been replaced by RE^{3+} ions.

A second polymorphic form of $\text{RE}(\text{OH})\text{CO}_3$ isostructural with the mineral bastnaesite RE.F.CO_3 is postulated to form under high pressure hydrothermal conditions.

Hydroxycarbonates des lanthanides

RÉSUMÉ. — L'hydrolyse en présence d'urée et en solution nitrique diluée à chaud des éléments trivalents suivants, Pr, Nd, Sm, Eu, Gd, Tb et Dy, fournit des échantillons biphasés qui renferment au moins 80 % d'hydroxycarbonate $\text{Re}(\text{OH})\text{CO}_3$ mélangé au carbonate normal $\text{RE}_2(\text{CO}_3)_3, x\text{H}_2\text{O}$. L'examen aux rayons X des hydroxycarbonates révèle qu'ils sont isostructuraux de l'espèce naturelle ancylite — $(\text{M}^{2+}, \text{RE}^{3+})(\text{CO}_3^{2-})_2(\text{OH}^-)\text{H}_2\text{O}$; $\text{M}^{2+} = \text{Ca}^{2+}; \text{Sr}^{2+}$ — et correspondent à la composition limite où tous les ions M^{2+} ont été remplacés par des ions RE^{3+} .

Une seconde forme polymorphique de $\text{RE}(\text{OH})\text{CO}_3$, isostructurale avec l'espèce naturelle bastnaesite, se forme par synthèse hydrothermale sous haute pression.

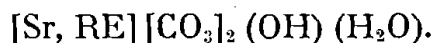
Introduction

The preparation, characterization and crystal chemistry of the various types of carbonates formed by the lanthanide elements has been the subject of much recent research and a summary of the existing data is available [1].

R. G. Charles [2] who investigated the preparation of rare earth carbonates, using a homogeneous precipitation method with the trichloroacetate ion as precipitating agent, showed that for the trivalent lanthanides Ce, Pr, Er, Tm, Yb and Lu, hydrated basic carbonates are produced, with irrational compositions but similar infrared spectra.

In the present paper the preparation of basic carbonates of the lanthanide elements by utilizing the slow hydrolysis of urea in hot dilute acid solutions of each of the following, Pr, Nd, Sm, Eu, Gd, Tb and Dy is described.

Analytical, density and X-ray powder diffraction measurements, on the samples produced by the above method, show that they contain basic carbonates $[\text{RE}(\text{OH})\text{CO}_3]$ which are similar in structure to the mineral ancylite :



Evidence is presented to show that a phase described in the literature as high pressure $\text{La}(\text{OH})_3$, may be a second polymorphic form of $\text{RE}(\text{OH})\text{CO}_3$, with a structure similar to that of the mineral bastnaesite, RE.F.CO_3 .

Experimental

Sample preparation. — The method of preparation varied slightly with different lanthanides and while only the preparation of the praseodymium compound is described here, a full description for the remaining lanthanides has been given [3].

$\text{PrO}_{2.000}$ (1.9719 g) was dissolved with heating in 1 M HNO_3 (60 ml) and then diluted to 250 ml. An aqueous solution (50 ml) containing urea (16 g) was added and the solution gently heated (80-90°C) for 5 h. The resulting pale green precipitate was allowed to stand in contact with the cold solution for 48 h, before filtering and washing with cold water (2×25 ml). The pH of the cold filtrate was 7 as estimated by pH papers. After drying at 115°C the precipitate (2.5918 g) was stored in a stoppered container.

X-ray. — The sample admixed with pure crystalline thoria for calibration purposes was examined on a Hagg-Guinier focussing camera using $\text{FeK}_{\alpha_1\alpha_2}$ radiation.

The camera case was evacuated during the exposure. Wavelength values used were $\text{Fe } \lambda_1 = 1.93597 \text{ \AA}$, $\text{Fe } \lambda_2 = 1.93991 \text{ \AA}$ and all unit cell data were obtained by a least squares method [3].

Analytical. — Each sample was analysed for RE_2O_3 , CO_2 and H_2O by conventional methods [3].

Density. — Densities were determined by measuring the weight loss on immersion in carbon tetrachloride [3].

Infrared. — The infrared spectra were recorded in the region $670\text{--}4\,000\text{ cm}^{-1}$ and are presented in a separate publication [1].

Mineral Specimens. — *Bastnaesite* RE.F.CO_3 : A single crystal fragment of bastnaesite was obtained from Diadakatany, Madagascar. X-ray examination showed only the presence of bastnaesite with unit cell dimensions very close to those reported previously (Table V). *Ancylite* $[\text{Ca, Sr, RE}][\text{CO}_3]_2(\text{OH})\text{H}_2\text{O}$: A diphasic sample consisting of ancylite intimately intergrown with alkaline earth carbonates (mainly calcite) was obtained from the Dark Star Mine Montana. Except for a slight amount of reddish material the sample was completely soluble in dilute acid and spot tests showed considerable cerium.

Results and discussion

The analytical results in table I show that all the samples prepared by the present method, have irrational compositions, in which the mole ratio of $\text{CO}_3/\text{RE}^{3+}$ varies from sample to sample but is always > 1.00 . These results are similar to those reported by R. G. Charles [2]. One

TABLE I

R. E.	Analytical Data (Analytical Data recalculated for the phases shown)	Temperature of Drying (°C)
Pr.....	$\text{Pr}_{1.000} \cdot (\text{OH})_{0.810} \cdot (\text{CO}_3)_{1.080} \cdot (\text{H}_2\text{O})_{0.045}$ { 80.6 wt. % $\text{Pr}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 19.4 wt. % $\text{Pr}_{1.000} \cdot (\text{CO}_3)_{1.50} \cdot (\text{H}_2\text{O})_{2.53}$ }	115
Nd.....	$\text{Nd}_{1.000} \cdot (\text{OH})_{0.875} \cdot (\text{CO}_3)_{1.065} \cdot (\text{H}_2\text{O})_{0.370}$ { 84.3 wt. % $\text{Nd}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 15.7 wt. % $\text{Nd}_{1.000} \cdot (\text{CO}_3)_{1.52} \cdot (\text{H}_2\text{O})_{2.96}$ }	27
Sm.....	$\text{Sm}_{1.000} \cdot (\text{OH})_{0.875} \cdot (\text{CO}_3)_{1.080} \cdot (\text{H}_2\text{O})_{0.365}$ { 84.5 wt. % $\text{Sm}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 14.1 wt. % $\text{Sm}_{1.000} \cdot (\text{CO}_3)_{1.48} \cdot (\text{H}_2\text{O})_{1.50}$; 1.4 wt. % H_2O }	27
Eu.....	$\text{Eu}_{1.000} \cdot (\text{OH})_{0.920} \cdot (\text{CO}_3)_{1.040} \cdot (\text{H}_2\text{O})_{0.315}$ { 89.4 wt. % $\text{Eu}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 9.1 wt. % $\text{Eu}_{1.000} \cdot (\text{CO}_3)_{1.50} \cdot (\text{H}_2\text{O})_{1.50}$; 1.5 wt. % H_2O }	77
Gd.....	$\text{Gd}_{1.000} \cdot (\text{OH})_{0.950} \cdot (\text{CO}_3)_{1.025} \cdot (\text{H}_2\text{O})_{0.280}$ { 92.8 wt. % $\text{Gd}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 5.7 wt. % $\text{Gd}_{1.000} \cdot (\text{CO}_3)_{1.50} \cdot (\text{H}_2\text{O})_{1.50}$; 1.5 wt. % H_2O }	
Tb.....	$\text{Tb}_{1.000} \cdot (\text{OH})_{0.920} \cdot (\text{CO}_3)_{1.040} \cdot (\text{H}_2\text{O})_{0.250}$ { 89.9 wt. % $\text{Tb}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 9.1 wt. % $\text{Tb}_{1.000} \cdot (\text{CO}_3)_{1.50} \cdot (\text{H}_2\text{O})_{1.50}$; 1.0 wt. % H_2O }	96
Dy.....	$\text{Dy}_{1.000} \cdot (\text{OH})_{0.980} \cdot (\text{CO}_3)_{1.010} \cdot (\text{H}_2\text{O})_{0.105}$ { 97.6 wt. % $\text{Dy}_{1.000} \cdot (\text{OH})_{1.00} \cdot (\text{CO}_3)_{1.00}$; } { 2.4 wt. % $\text{Dy}_{1.000} \cdot (\text{CO}_3)_{1.49} \cdot (\text{H}_2\text{O})_{1.50}$ }	27

suspects that these samples are two phase mixtures of $\text{RE}(\text{OH})\text{CO}_3$ and $\text{RE}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, but the X-ray powder patterns (particularly for the Pr and Nd samples) do not show any of the strong reflections of the normal carbonates, present as a crystalline phase (see diagram 1). Later experience with the 8-hydrate normal carbonates of Pr and Nd

have shown that these compounds become amorphous (through dehydration) either by heating at low temperatures ($< 100^\circ\text{C}$) or by placing in a vacuo, such as used in the Hagg-Guinier camera case.

If the compositions $\text{RE}(\text{OH})\text{CO}_3$ is subtracted from the sample composition, the mole ratio of $\text{CO}_3^{2-}/\text{RE}^{3+}$ remaining, is for all the samples 1.50 ± 0.02 . In calculating the weight percentages of the various phases it is assumed that all the water in the sample is present either with the normal carbonate or as a separate phase. For the normal carbonates $\text{RE}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, $x = 8$ for Pr and Nd and $x = 3$ for Sm, Eu, Gd, Tb and Dy [4].

While the presence of amorphous (dehydrated/hydrated) normal carbonates does complicate the analytical and density data, these samples do provide " Monophasic " X-ray data for the $\text{RE}(\text{OH})\text{CO}_3$ type compounds as prepared by the urea hydrolysis method.

TABLE II

*X-Ray data for various $\text{RE}(\text{OH})\text{CO}_3$ compounds
and two samples of the mineral ancylite*

Sample	a $\pm 0.003 \text{ \AA}$	b $\pm 0.004 \text{ \AA}$	c $\pm 0.002 \text{ \AA}$	Volume $\pm 0.9 \text{ \AA}^3$ (27°C)	Measured Density [g/cm^3 (*) ($^\circ\text{C}$)]	Z
Pr.....	7.266	8.522	4.988	308.9	4.25 (20)	3.63
Nd.....	7.222	8.488	4.961	304.1	4.42 (20)	3.66
Sm.....	7.131	8.465	4.918	296.8	4.64 (22)	3.65
Eu.....	7.094	8.451	4.900	293.8	4.78 (23)	3.70
Gd.....	7.068	8.441	4.879	291.1	5.06 (23)	3.79
Td.....	7.018	8.454	4.859	288.3	5.04 (22)	3.72
Dy.....	6.989	8.453	4.839	285.9	5.30 (22)	3.81
An. 1.....	7.302	8.536	5.052	314.9	—	—
An. 2.....	7.01	8.48	5.00	297.0	—	—

An. 1 : Data from a calcium-ancylite.

An. 2 : Data from a strontia-ancylite [5].

(*) Density measured on " Diphasic " samples.

The X-ray powder patterns of all the preparations are similar and were indexed by trial and error methods, in terms of an orthorhombic unit cell, which the density data indicates contains 4 RE^{3+} , 4 OH^- and 4 CO_3^{2-} . The unit cell data for each compound along with various X-ray data are given in Table II; while a representative powder pattern [for $\text{Pr}(\text{OH})\text{CO}_3$] is shown in Table III.

The systematic absences observed in the powder patterns of each of the $\text{RE}(\text{OH})\text{CO}_3$ compounds are consistent and with the axial

TABLE III

*X-Ray powder data for Pr(OH)CO₃,
indexing is for the Space Group alternative
P n a 2₁ (No. 23) (FeK_{α1})*

Intensity	<i>h k l</i>	$\sin^2 \theta \times 10^4$ Calculated	$\sin^2 \theta \times 10^4$ Observed	Intensity	<i>h k l</i>	$\sin^2 \theta \times 10^4$ Calculated	$\sin^2 \theta \times 10^4$ Observed
—	0 1 0	129.02	—	v. v. w. s.	3 3 1	3 134.88	3 133.7
—	1 0 0	177.46	—	v. v. w. s.	2 4 1	3 150.73	3 150.6
w-m. s.	1 1 0	306.48	306.0	v. w. s.	4 0 1	3 215.91	3 215.2
—	0 0 1	376.58	—	—	0 5 0	3 225.50	—
v. s. s.	0 1 1	505.60	504.7	v. v. w. s.	3 1 2	3 232.46	3 232.3
w. s.	0 2 0	516.08	515.2	m. s.	4 1 1	3 344.93	3 345.2
—	1 0 1	554.04	—	—	4 2 0	3 355.41	—
m-s. s.	1 1 1	683.06	682.0	—	2 3 2	3 377.32	—
m. s.	1 2 0	693.54	693.4	—	0 0 3	3 389.20	—
w. s.	2 0 0	709.83	709.0	—	1 5 0	3 402.96	—
m. s.	2 1 0	838.85	838.7	w. s.	0 1 3	3 518.22	3 516.9
—	0 2 1	892.66	—	—	1 0 3	3 566.66	—
w. s.	1 2 1	1 070.12	1 068.9	—	0 4 2	3 570.63	—
s. s.	2 0 1	1 086.41	1 085.6	w-m. s.	0 5 1	3 602.08	3 603.9
—	0 3 0	1 161.18	—	w. s.	3 2 2	3 619.52	3 617.7
v. v. w. s.	2 1 1	1 215.43	1 216.6	—	3 4 0	3 661.44	—
w ⁺ . s.	2 2 0	1 225.91	1 225.2	w. d.	1 1 3	3 695.68	3 694.3
m-s. s.	1 3 0	1 338.64	1 339.4	—	4 2 1	3 731.99	—
v. s. s.	0 0 2	1 506.31	1 505.5	w. s.	1 4 2	3 748.09	3 747.5
v. v. w. d.	0 3 1	1 537.76	1 536.5	—	1 5 1	3 779.53	—
—	3 0 0	1 597.12	—	—	0 2 3	3 905.28	—
m. s.	2 2 1	1 602.49	1 601.2	w. s.	2 5 0	3 935.33	3 934.4
—	0 1 2	1 635.33	—	—	4 3 0	4 000.51	—
—	1 0 2	1 683.77	—	w. s.	3 4 1	4 038.02	4 037.4
v. s. s.	1 3 1	1 715.22	1 715.3	v. w. s.	1 2 3	4 082.74	4 081.7
m. s.	3 1 0	1 726.14	1 724.7	w. s.	2 0 3	4 099.04	4 097.0
v. v. w. s.	1 1 2	1 812.79	1 813.5	—	2 1 3	4 228.06	—
w. s.	2 3 0	1 871.01	1 871.8	m. s.	3 3 2	4 264.62	4 265.6
—	3 0 1	1 973.70	—	—	2 4 2	4 280.46	—
w-m. s.	0 2 2	2 022.39	2 024.0	—	2 5 1	4 311.91	—
m. s.	0 4 0	2 064.32	2 064.4	w. d.	4 0 2	4 345.64	4 345.6
w. s.	3 1 1	2 102.72	2 103.0	—	4 3 1	4 377.09	—
v. v. w. s.	3 2 0	2 113.20	2 113.2	—	5 0 0	4 436.45	—
v. s. s.	1 2 2	2 199.85	2 199.2	w. s.	4 1 2	4 474.66	4 474.9
v. w. s.	2 0 2	2 216.15	2 214.8	—	0 3 3	4 550.38	—
w-m. s.	1 4 0	2 241.78	2 242.9	—	5 1 0	4 565.47	—
—	2 3 1	2 247.59	—	w. s.	2 2 3	4 615.12	4 613.2
s. s.	2 1 2	2 345.17	2 345.5	—	0 6 0	4 644.72	—
—	0 4 1	2 440.90	—	w. d.	1 3 3	4 727.84	{ 4 730.0 }
m. s.	3 2 1	2 489.78	2 490.2	—	0 5 2	4 731.81	{ 4 730.0 }
w. s.	1 4 1	2 618.35	2 619.6	—	5 0 1	4 813.03	—
—	0 3 2	2 667.49	—	—	1 6 0	4 822.17	—
v. w. s.	2 2 2	2 732.23	2 735.5	—	3 5 0	4 822.62	—
w-m. s.	3 3 0	2 758.30	2 758.9	—	4 2 2	4 861.72	—
—	2 4 0	2 774.15	—	w. s.	4 4 0	4 903.65	4 903.9
w. d.	4 0 0	2 839.33	{ 2 841.6 }	—	1 5 2	4 909.27	—
—	1 3 2	2 844.95	{ 2 841.6 }	v. v. w. d.	5 1 1	4 942.05	4 941.5
v. w. d.	4 1 0	2 968.35	2 967.2	—	5 2 0	4 952.53	—
—	3 0 2	3 103.44	—	—	3 0 3	4 986.33	—

v. s. s., very strong sharp; w-m. s. weak to medium sharp; v. w. d., very weak diffuse.

settings used in Table II are :

$h00$, for h even	$hk0$, none
$0k0$, for k even	$h0l$, for h even
$00l$, for l even	hkl , none
$0kl$, for $k+l$ even	

which correspond to the space group $Pna2_1$ (No. 33) or with interchange of axes to the alternative space group $Pnma$ (No. 62).

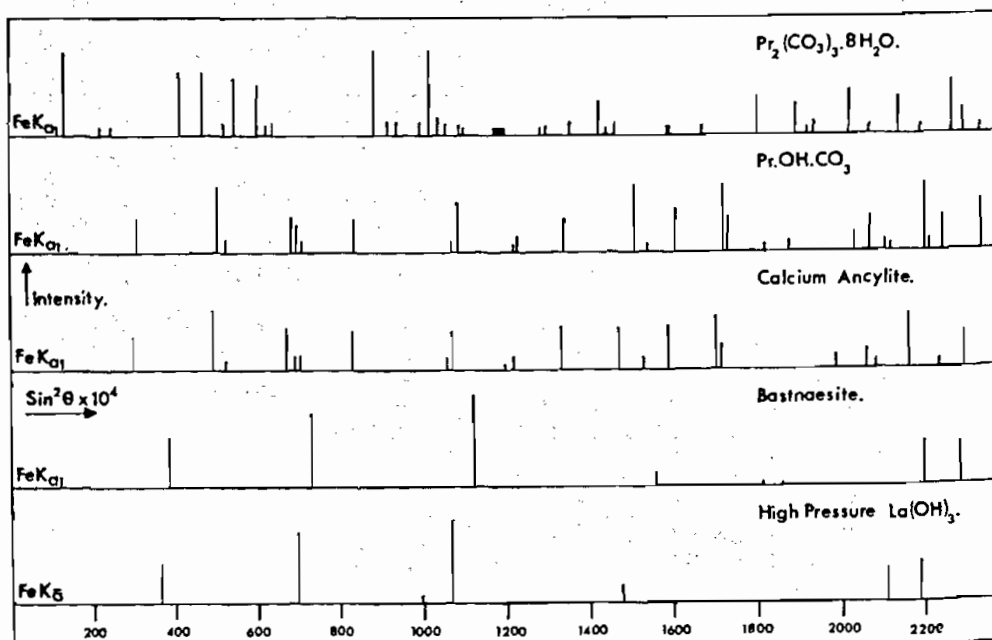


Diagram 1. — X-Ray Guinier Patterns.

While it may be necessary to determine the complete crystal structure to decide which of the alternative space groups is the correct one, some information may be obtained by considering the multiplicity of the positions available in either space group.

In $Pna2_1$ there is one set of four fold positions, while in $Pnma$ there are three sets of four fold positions and one set of eight fold positions. The density data (particularly for the Dy Sample) indicates that there are 4 RE^{3+} , 4 OH^- and 4 CO_3^{2-} per unit cell so that irrespective of which is the correct space group, the RE^{3+} , OH^- and C must all occupy 4 fold positions.

The compound $RE(OH)CO_3$ might be expected to be isostructural with the mineral bastnaesite $RE.F.CO_3$ ($r_{OH^-} \sim 1.35 \text{ \AA}$; $r_{F^-} \sim 1.36 \text{ \AA}$). X-ray powder examination of a pure sample of bastnaesite shows that this is not the case (diagram 1).

Another mineral containing RE , OH^- and CO_3^{2-} is ancylite. E. I. Semenov and M. E. Kazokova [5] report a strontia-ancylite with

TABLE IV

X-Ray powder data for a ancylite/alkaline earth carbonate sample (FeK₂₁)

Intensity	$\sin^2 \theta \times 10^4$ Observed	<i>h k l</i>	$\sin^2 \theta \times 10^4$ Calculated	<i>h k i l</i>	$\sin^2 \theta \times 10^4$ Calculated
v. v. v. w. d.	166.1	(*)	—	(*)	—
—	—	0 1 0	128.59	—	—
—	—	1 0 0	175.73	—	—
m. s.	301.3	1 1 0	304.32	—	—
—	—	0 0 1	367.09	—	—
m-s. s.	493.8	0 1 1	495.68	—	—
w. s.	512.4	0 2 0	514.27	—	—
—	—	1 0 1	542.81	—	—
w. s.	631.7	—	—	1 0 $\bar{1}$ 2	632.5
m-s. s.	670.0	1 1 1	671.41	—	—
w. s.	688.9	1 2 0	690.10	—	—
w. s.	701.7	2 0 0	702.91	—	—
m. s.	831.4	2 1 0	831.50	—	—
v. v. v. w. s.	852.3	(*)	—	(*)	—
—	—	0 2 1	881.46	—	—
v. s. s.	1 020.6	—	—	1 0 $\bar{1}$ 4	1 019.2
w ⁺ . s.	1 057.3	1 2 1	1 057.18	—	—
m. s.	1 070.4	2 0 1	1 069.99	—	—
v. v. w. d.	1 160.7	0 3 0 ?	1 157.33	0 0 0 6	1 160.1
v. v. w. s.	1 196.4	2 1 1	1 198.59	—	—
w. s.	1 216.6	2 2 0	1 217.28	—	—
m. s.	1 332.2	1 3 0	1 333.06	—	—
m. s.	1 467.2	0 0 2	1 468.35	—	—
m. s.	1 510.9	—	—	1 1 $\bar{2}$ 0	1 510.9
w. s.	1 526.6	— 0 3 1	1 524.42	—	—
—	—	3 0 0	1 581.54	—	—
m. s.	1 583.3	2 2 1	1 584.36	—	—
—	—	0 1 2	1 596.94	—	—
—	—	1 0 2	1 644.07	—	—
m-s. s.	1 699.7	1 3 1	1 700.14	—	—
w-m. s.	1 711.0	3 1 0	1 710.13	—	—
—	—	1 1 2	1 772.67	—	—
m. s.	1 800.5	—	—	1 1 $\bar{2}$ 3	1 800.9
—	—	2 3 0	1 860.24	—	—
—	—	3 0 1	1 948.63	—	—
w. d.	1 982.4	0 2 2	1 982.72	—	—
w ⁺ . d.	2 057.8	0 4 0	2 057.48	—	—
v. w. d.	2 076.5	3 1 1	2 077.22	—	—
—	—	3 2 0	2 095.91	—	—
s. s.	2 143.4	—	—	2 0 $\bar{2}$ 2	2 143.4
s. s.	2 158.4	1 2 2	2 158.44	—	—
—	—	2 0 2	2 171.25	—	—
—	—	2 3 1	2 227.32	—	—
w. d.	2 234.5	1 4 0	2 233.20	—	—
m. d.	2 300.6	2 1 2	2 299.95	—	—
—	—	0 4 1	2 424.56	—	—
w. d.	2 463.8	3 2 1	2 463.00	—	—
w. d.	2 529.9	—	—	2 0 $\bar{2}$ 4	2 530.1
m. d.	2 568.1	—	—	1 0 $\bar{1}$ 8	2 566.0
v. w. d.	2 599.8	1 4 1	2 600.29	—	—
—	—	0 3 2	2 625.68	—	—
m. d.	2 672.1	—	—	1 1 $\bar{2}$ 6	2 671.0
—	—	2 2 2	2 685.62	—	—
w. d.	2 738.3	3 3 0	2 738.87	—	—

TABLE IV (suite)

X-Ray powder data for a ancylite/alkaline earth carbonate sample (FeK_{α1})

Intensity	$\sin^2 \theta \times 10^4$ Observed	<i>h k l</i>	$\sin^2 \theta \times 10^4$ Calculated	<i>h k i l</i>	$\sin^2 \theta \times 10^4$ Calculated
—	—	2 4 0	2 760.38	—	—
—	—	1 3 2	2 801.40	—	—
w. d.	2 808.9	4 0 0	2 811.63	—	—
—	—	4 1 0	2 940.22	—	—
—	—	3 0 2	3 049.89	—	—
w. s.	3 104.7	3 3 1	3 105.96	—	—
w. d.	3 127.9	2 4 1	3 127.47	—	—
w. d.	3 177.9	3 1 2	3 178.48	—	—
—	—	4 0 1	3 178.72	—	—
—	—	0 5 0	3 214.81	—	—
—	—	0 0 3	3 303.78	—	—
v. w. d.	3 310.4	4 1 1	3 307.31	—	—
—	—	4 2 0	3 326.00	—	—
—	—	2 3 2	3 328.58	—	—
—	—	1 5 0	3 390.53	—	—
w. d.	3 433.5	0 1 3	3 432.37	—	—
—	—	1 0 3	3 479.51	—	—
—	—	0 4 2	3 525.82	—	—
w. d.	3 557.0	—	—	2 1 $\bar{3}$ 1	3 557.6
—	—	3 2 2	3 564.26	—	—
—	—	0 5 1	3 581.89	—	—
—	—	1 3 1	3 608.10	—	—
—	—	3 4 0	3 639.02	—	—
m. d.	3 652.0	—	—	2 1 $\bar{3}$ 2	3 654.4
v. v. v. w. s.	3 693.7	4 2 1	3 693.09	—	—
—	—	1 4 2	3 701.55	—	—

Plus additional indexed reflections up to $\sin^2 \theta = 0.470$

(*) Unidentified Reflections.

Calcite type phase; $a = 4.980 \text{ \AA}$, $c = 17.05 \text{ \AA}$.

Calcite; A. S. T. M., 5-0586, $a = 4.989 \text{ \AA}$, $c = 17.06, \text{ \AA}$.

the composition $\text{SrCe}(\text{CO}_3)_2 \text{OH}$, H_2O and an orthorhombic unit cell with $a = 7.01 \text{ \AA}$, $b = 8.48 \text{ \AA}$ and $c = 5.00 \text{ \AA}$.

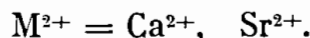
A sample of ancylite intimately intergrown with alkaline-earth-carbonates was examined on a Hagg-Guinier camera and gave the X-ray data shown in Tables IV and II and illustrated in diagram 1. The alkaline earth carbonate associated with the ancylite, is from the X-ray data very close to pure calcite, suggesting this sample from the Dark Star Mine Montana is actually a calcium-ancylite. The smaller unit cell volume for ancylite 2 (diagram 2) reported as a strontia-ancylite suggests this sample contains a high percentage of RE of small atomic radius ($\text{Sm} \rightarrow \text{Dy}$).

The intensity distributions observed for this calcium-ancylite are very similar to those for the $\text{RE}(\text{OH})\text{CO}_3$ compounds, while the systematic absences are the same (diagram 1, Tables III and IV). The isostruc-

tural relation between these compounds of different composition is explained by the fact that in the mineral, there is a random distribution of particles of approximatively the same size ($r_{\text{OH}^-} \sim 1.35 \text{ \AA}$, $r_{\text{H}_2\text{O}} \sim 1.38 \text{ \AA}$, $r_{\text{Ca}^{2+}} \sim 0.99 \text{ \AA}$, $r_{\text{Sr}} \sim 1.13 \text{ \AA}$, $r_{\text{RE}^{3+}} \approx 1.00 \text{ \AA}$) over the four sites, as shown by the formula



where



Thus in any particular mineral sample, it is the ratio of $\text{RE}^{3+}/\text{M}^{2+}$ which determines the $\text{H}_2\text{O}/\text{OH}^-$ ratio; and when all the M^{2+} ions are replaced by RE^{3+} ions the sample is anhydrous with the ideal composition $(\text{RE}^{3+})_4 (\text{OH}^-)_4 (\text{CO}_3^-)_4$.

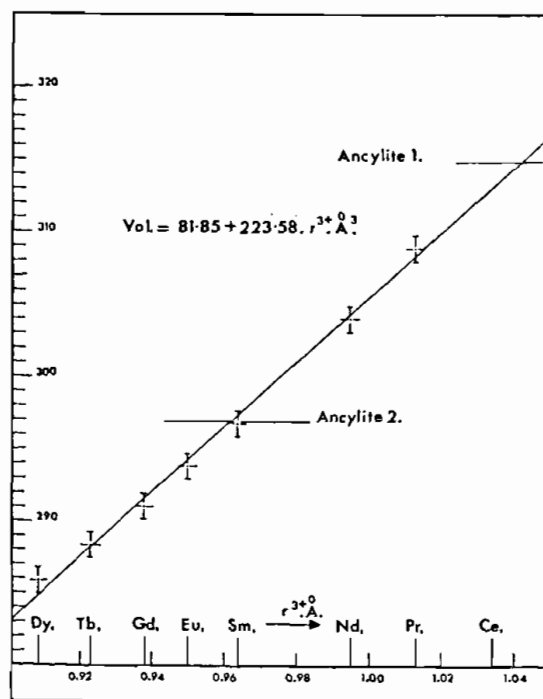


Diagram 2

Diagram 2. — Plot of cell volumes ajounst RE^{3+} radii.

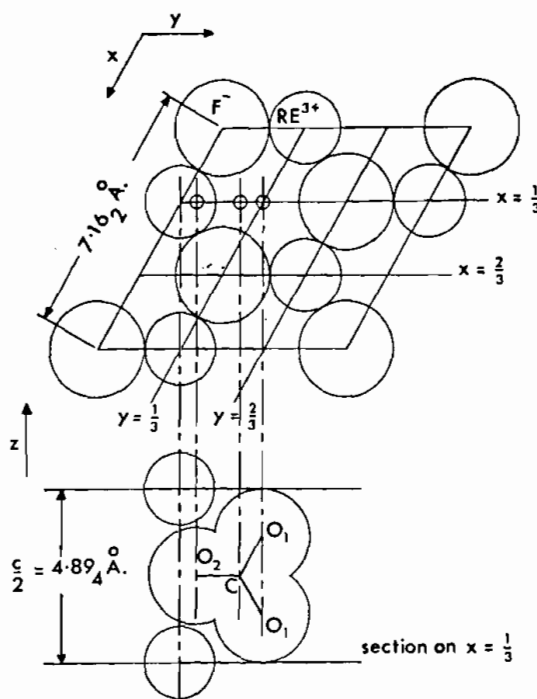


Diagram 3

Diagram 3. — The bastnaesite RE.F.CO_3 structure.

A plot of cell volumes against RE^{3+} radius for the $\text{RE}(\text{OH})\text{CO}_3$ compounds is shown in diagram 2 and the scatter of the points around the line of best fit, indicates that there may be some variability in the composition of these phases. It is suggested that these solution prepared phases may have a composition range :



and contain some structural water if there are vacancies in the cation lattice. To establish this would require additional X-ray, density, and analytical data on strictly monophasic samples.

Included in diagram 1 is a phase termed $\text{La}(\text{OH})_3$ "high pressure". This phase was reported by M. W. Shafer and R. Roy [6] and the X-ray data is from A. S. T. M. Card No. 13-84.

The close similarity between the X-ray powder patterns of high pressure $\text{La}(\text{OH})_3$ and RE.F.CO_3 is evident and suggests that a possible structural relationship exists between these compounds and should be investigated. The crystal structure of RE.F.CO_3 is known [7].

In the structure, hexagonal layers of composition $[\text{RE.F}]_n^{2n+}$ are held together by vertically orientated carbonate groups. Some important interatomic distances are shown in diagram 3. The arrangement of the $[\text{RE.F}]_n^{2n+}$ sheets alone could be described by a Hexagonal Sub Cell with $a = 4.13 \text{ \AA}$ and $c = 4.89 \text{ \AA}$, but it is the orientation of the carbonate group within the sheets which determines the final symmetry (Space Group $P\bar{6}2C$) and true unit cell of $a = 7.16 \text{ \AA}$ and $c = 9.78 \text{ \AA}$.

TABLE V

X-Ray powder data for bastnaesite ($\text{Fe.K}_{\alpha 1}$)

Inten- sity Vi- sual.	$\sin^2 \theta$ $\times 10^4$ Observed	$h k l$ True. cell.	$h k l$ Sub. cell.	$\sin^2 \theta$ $\times 10^4$ Calculated	Inten- sity Vi- sual.	$\sin^2 \theta$ $\times 10^4$ Observed	$h k l$ True. cell.	$h k l$ Sub. cell.	$\sin^2 \theta$ $\times 10^4$ Calculated
50	387.8	0 0 2	0 0 1	389.16	33	2586.1	3 0 2	1 1 1	2586.91
75	732.0	1 1 0	1 0 0	732.58	15	2932.3	2 2 0	2 0 0	2930.33
100	1121.3	1 1 2	1 0 1	1121.74	20	3317.5	2 2 2	2 0 1	3319.49
15	1557.4	0 0 4	0 0 2	1556.64	1	3500.2	0 0 6	0 0 3	3502.44
1	1809.2	2 1 1	X X X	1806.65	15	3750.5	3 0 4	1 1 2	3754.39
1	1854.7	2 0 3	X X X	1852.39	15	4234.0	1 1 6	1 0 3	4235.02
40	2198.1	3 0 0	1 1 0	2197.75	15	4483.6	2 0 6	X X X	4479.21
40	2289.5	1 1 4	1 0 2	2289.22	?	?	2 2 4	2 0 2	4486.97

Sub. cell.; $a = 4.130 \text{ \AA}$, $c = 4.907 \text{ \AA}$.

True. cell.; $a = 7.153 \pm 0.003 \text{ \AA}$, $c = 9.814 \pm 0.004 \text{ \AA}$.

X X X Superstructure reflections.

$a_{\text{true}} = 2 \cdot \cos 30^\circ \cdot a_{\text{sub}}$; $c_{\text{true}} = 2 \cdot c_{\text{sub}}$.

Single crystal data of Gabrielle Donnay and J. D. H. Donnay [7]:

$a = 7.16_2 \pm 0.02_2 \text{ \AA}$; $c = 9.787 \pm 0.02_9 \text{ \AA}$.

Because of the relatively low scattering ability of the C—O atoms of the CO_3^{2-} group, the superstructure reflections indicating the true unit cell are weak compared to the fundamental reflections (Table V). The X-ray powder data for $\text{La}(\text{OH})_3$ "high pressure" may be indexed in terms of a hexagonal sub cell with $a = 4.21 \text{ \AA}$ and $c = 5.041 \text{ \AA}$ (Table VI). This indexing accounts for all but five weak reflections of the twenty two given. The five weak reflections cannot be indexed using a hexagonal unit cell with $a = 2 \cos 30^\circ \times 4.214$ and $c = 2 \times 5.041 \text{ \AA}$;

TABLE VI

X-Ray powder data for La (OH)₃ high pressure (CuK_α)

Inten- sity	$\sin^2 \theta \times 10^4$ Observed	<i>h k l</i>	$\sin^2 \theta \times 10^4$ Calculated	Inten- sity	$\sin^2 \theta \times 10^4$ Observed	<i>h k l</i>	$\sin^2 \theta \times 10^4$ Calculated
45	231.0	0 0 1	234.0	10	2 564.0	1 0 3	2 551.2
85	442.6	1 0 0	445.2	10	2 720.0	2 0 2	2 177.0
10	630.6	?	—	5	3 120.0	2 1 0	3 116.0
100	677.4	1 0 1	679.2	20	3 359.0	2 1 1	3 350.0
20	937.1	0 0 2	936.0	5	3 457.0	?	—
40	1 335.0	1 1 0	1 335.6	5	3 726.0	?	—
50	1 386.0	1 0 2	1 381.2	5	4 006.0	3 0 0	4 007.0
35	1 571.0	1 1 1	1 569.6	10	4 059.0	2 1 2	4 052.0
20	1 780.0	2 0 0	1 781.0	5	4 202.0	?	—
20	2 017.0	2 0 1	2 051.0	10	4 246.0	3 0 1	4 241.0
20	2 276.0	1 1 2	2 272.0	5	4 945.0	3 0 2	4 943

Hexagonal sub cell.; $a = 4.21_1 \text{ \AA}$, $c = 5.04_1 \text{ \AA}$.

suggesting the sample is either diphasic or the orientation of the "CO₃²⁻ groups" between the sheets of (LaOH)_n²ⁿ⁺ is different from that in RE.F.CO₃. While the present evidence does not exclude the possibility of other ions besides carbonate ions holding the (LaOH)_n²ⁿ⁺ layers together, the distances 5.041 Å is suitable for vertically orientated carbonate groups as found in RE.F.CO₃. That La (OH)₃ "high pressure" is actually a second polymorphic form of RE (OH) CO₃ is to be investigated.

A lanthanide hydroxy carbonate isostructural with bastnaesite has recently been prepared for praseodymium ([8], [9]).

Recently it has been suggested [10] that the ancylite type hydroxycarbonate (A-RE (OH) CO₃) is connected with the aragonite variety of calcium or strontium carbonate in the same manner as the bastnaesite fluorocarbonate is related to the vaterite type of calcium carbonate [11].

The difference between the two polymorphic hydroxycarbonates will then be in the orientation of the CO₃ groups between the (REOH)_n²ⁿ⁺ layers: "planar" in the A-type and "vertical" in the B-type (for bastnaesite). The ancylite mineral may then corresponds to the same phenomenon of syntaxy which gives rises to the well known bastnaesite family of rare earth and calcium fluorocarbonates.

REFERENCES

- [1] P. E. CARO, J. O. SAWYER and Leroy EYRING, *Spectrochimica Acta*, 28 A, 1972, p. 1167.
- [2] R. G. CHARLES, *J. Inorg. Nucl. Chem.*, t. 27, 1965, p. 1489.
- [3] Leroy EYRING, P. CARO, J. SAWYER, J. KORDIS, D. BURNHAM, T. FELMLEE, G. STONE, J. WARMKESSEL and G. WEBER, Technical Prog. Report COO-1109-22, A. E. C. Contract A. T. (11-1)-1109, Arizona State University, Tempe, Arizona, 1966.