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DOVERITE FROM COTOPAXI, COLORADO

A. A. LEVINSON[1] AND R. A. BORUP, *The Dow Chemical Company, Freeport, Texas.*

ABSTRACT

Doverite, $YCaF(CO_3)_2$, the yttrium analogue of synchisite, has been found at the Henry pegmatite, Cotopaxi, Colorado, in very small amounts intimately associated with cenosite. *X*-ray powder data are similar to those of synchisite but with a significantly smaller unit cell. Wet chemical and *x*-ray emission spectrometry methods show the presence of rare-earth elements predominantly Y, Yb, Er, Dy and Gd.

INTRODUCTION

The crystallographic study by Donnay and Donnay (1953) of the cerium fluocarbonate minerals related to parisite has established the existence of bastnaesite, parasite, roentgenite and synchisite as valid species. From their work the crystal chemistry, chemical composition, and relationship of each of these species to each other is now well understood. The very common occurrence of syntaxis intergrowths of any combination except bastnaesite-synchisite was observed by them.

Yttrium analogues of the cerium fluocarbonates have been reported or suggested by Nefedov (1941), Smith *et al.* (1955, 1960), Haynes (1958), Glass *et al.* (1958), and Semenov (1959). Because of preliminary or inadequate descriptions, or intimate mixtures of contaminants in material chemically analyzed and studied by *x*-ray diffraction methods, the existence of authenticated yttrium analogues of any of the cerium fluocarbonates had not previously been unquestionably proved. Whereas the cerium fluocarbonates commonly occur as well-developed "polycrystals," almost all previously described examples of the yttrium analogues are fine-grained intergrowths or aggregates of several minerals, and pure examples have not been definitely isolated. The yttrium analogues generally appear to be restricted to late-stage alteration products of monazite, xenotime, gadolinite and other rare-earth minerals; fluorite is usually found in association.

In this paper we describe an yttrium fluocarbonate mineral which we demonstrate to be the yttrium analogue of synchisite for which Smith *et al.* (1955, 1960) have proposed the term doverite. As with previously described material, our specimen is impure, being mixed with about 10 per cent cenosite as well as a very small amount of an unidentified phase.

Several recent studies have shown that vaterite corresponds to the $CaCO_3$ member of the series bastnaesite-parisite-roentgenite-synchisite-vaterite. Donnay and Donnay (1961) correlate the optical properties of

[1] Present address: Gulf Research and Development Co., Pittsburgh, Penna.

members of the series as a function of the $CaCO_3$ (vaterite) content. They also discuss the yttrium analogues described by Nefedov (1941) and Semenov (1959) in relation to the bastnaesite-vaterite series (see below).

Other Occurrences of Yttrium Fluocarbonates

Nefedov (1941) has briefly described yttroparisite from the Adun-Cholon (Transbaikalia) pegmatites, which he reports to have a composition near parisite and synchisite but which contains much yttrium. The mineral occurs as inclusions in fluorite. Several other rare-earth minerals (xenotime, monazite, allanite) are known from the pegmatite. The mineral is uniaxial positive, with $\omega=1.643$ and $\epsilon=1.755$. Hexagonal unit cell dimensions are reported as $a=4.008\pm.03$ and $c=4.469\pm.04$ Å. Although these optical and *x*-ray data do suggest an yttrium analogue of some cerium-earth fluocarbonate, much more detailed data, including a complete chemical analysis on pure material, would be necessary to prove unquestionably the relationship of this mineral to parisite. Donnay and Donnay (1961) have discussed the relationship of this mineral to the bastnaesite-vaterite series and concluded it may be a variety of the mineral described by Semenov (1959) (see below).

Smith *et al.* (1955) described the new mineral, doverite, from Dover, New Jersey, as the yttrium analogue of synchisite. Later, after a more detailed study, they (Smith *et al.* 1960) refer to their material as a possible new mineral because the analyzed brownish-red aggregates were subsequently found to be a mixture of doverite, quartz, xenotime, hematite, bastnaesite and leucoxene. Smith *et al.* (1960) also point out that the *x*-ray powder data and unit cell dimensions show close similarity to synchisite and their doverite may actually be an yttrian synchisite. The calculations presented by Smith *et al.* (1960) in their Table 4, upon which much of their thesis rests, are based upon numerous assumptions or estimates which may be open to question.

It is our opinion that the *x*-ray spacings and unit cell dimensions presented by Smith *et al.* (1960) should be weighed more heavily in the evaluation of their data, and accordingly, doverite from Dover, New Jersey, is probably an yttrian synchisite. However, even though the original naming of the yttrium analogue of synchisite may be based on less rigorous grounds than would be desired, we feel that there is no alternative but to continue to use the name doverite. Even if future work should discredit the type doverite described by Smith *et al.* (1955, 1960), the description and nomenclature accredited to the doverite herein will permit doverite to remain a valid mineral name.

Haynes (1958) reports doverite, as well as possible yttrium analogues of additional cerium fluocarbonates, occurs as late stage fluocarbonate replacements of primary pegmatite minerals in the White Cloud pegmatite near South Platte, Colorado. Other rare-earth minerals found in the pegmatite include gadolinite, allanite and yttrofluorite. The published abstract includes no *x*-ray, optical or chemical data, but Haynes (pers. comm.) indicates further details are forthcoming in papers nearing completion.

Glass, *et al.* (1958) have briefly described the mineralogy of the yttrium-bearing Teller pegmatite, Park County, Colorado. Yttrium-containing minerals identified include gadolinite, fluorite, allanite, xenotime, monazite and an unidentified, high-yttrium, cerium-earth carbonate. This unidentified mineral, which they report occurs in small amounts and is being studied in detail, appears to be an alteration product of gadolinite. No chemical, optical or *x*-ray data are presented.

Professor E. Wm Heinrich has kindly placed at our disposal several specimens from the Snowflake pegmatite which give *x*-ray powder patterns identical to our doverite; in addition they contain fluorite and in some specimens unidentified phases which could be yttrium analogues of other cerium-earth fluocarbonates. All are dark red in color, contain high yttrium and low cerium and lanthanum, and have optical properties suggestive of yttrium fluocarbonates (uniaxial positive; $\omega = ca.$ 1.64). Unfortunately none are of sufficient purity to warrant chemical analysis. One sample from the Black Cloud pegmatite also appears to contain an yttrium analogue of a cerium rare-earth fluocarbonate other than synchisite. Both the Snowflake and Black Cloud pegmatites are in the South Platte-Lake George pegmatite district, Colorado, as are the Teller and White Cloud pegmatites (Heinrich, 1958).

Semenov (1959) has described a possible new rare-earth fluocarbonate from northern Kirghiza similar in many properties to the doverite of Smith *et al.* (1955, 1960). Semenov's (1959) mineral is found as a secondary rose-colored cryptocrystalline replacement of accessory monazite in hydrothermal and greisen deposits. The mineral occurs in aggregates which include quartz, monazite and fluorite, and from which a purified specimen could not be obtained. Accordingly, their chemical analysis on impure material does not give a conclusive answer as to whether the mineral may be identical to the yttrium analogue of synchisite (doverite). Another possibility suggested by Semenov (1959), which is encouraged by Donnay and Donnay (1961), is that the mineral corresponds to a new member of the bastnaesite-vaterite series with the formula $2CeFCO_3 \cdot 3CaCO_3$.

The optical properties of Semenov's (1959) mineral ($\omega \sim 1.63$, $\epsilon \sim 1.72$) are similar to those of the doverite described in this paper. The *x*-ray powder data presented by Semenov (1959), after elimination of some unidentified lines and lines due to fluorite, compare well also. The unit cell constants for the Russian mineral and the doverite described below are essentially identical and significantly smaller than those of synchisite.

Doverite from the Henry Pegmatite, Colorado

Location, Geology, Mineralogy. The doverite described in this paper is from the Henry pegmatite near Cotopaxi, Colorado. The exact location, detailed geology of the deposit, and the mineralogy are discussed by Heinrich, Borup and Salotti (1962). It suffices to state that the doverite is intimately associated with cenosite and both are found in the replacement unit of the pegmatite.

Physical and Optical Properties. Doverite at this occurrence is very fine grained, as are all other previously reported examples of yttrium fluocarbonates. The aggregates are reddish-brown; no other physical properties could be determined. Less than one gram of the doverite has been found, all of which is intergrown to some extent with cenosite and small amounts of iron oxides, mainly hematite.

Optical data obtained on the doverite are (Na light):

$$\omega = 1.643 \pm .002$$

$$\epsilon = 1.73 \pm .01$$

Uniaxial positive

The indices of refraction are very similar to those of synchisite, but slightly lower. Lower indices would be expected for the yttrium analogues of cerium minerals on the basis of ionic refractivities (Donnay and Donnay, 1961).

Chemical Analysis. A 30-mg sample was used for the analysis (Table I). The original analysis, which totalled 101.7 per cent, yielded 3.2 per cent SiO_2 which is present as admixed cenosite (detected on the *x*-ray films and observed optically). The analysis presented in Table I is recalculated eliminating 10.8 per cent cenosite, as calculated from the 3.2 per cent SiO_2 in the original analysis, as well as 1.0 per cent Fe_2O_3. (For analysis of cenosite associated with doverite see Heinrich *et al.*, 1962.) Mr. J. A. Greear, who made the analysis by wet chemical methods, indicates the good summation is somewhat fortuitous; some of the figures in Table I, therefore, are not considered to be of the highest accuracy. On the rare-earth oxide precipitate, Borup determined yttrium and the order of abundance of the other rare-earth elements by *x*-ray emission methods. The results, on a 100 per cent rare-earth oxide basis, are:

Y_2O_3 = 52% (quantitative)
Yb_2O_3, Er_2O_3, Dy_2O_3 = each about 10% (order of magnitude)
Gd_2O_3 = about 5% (order of magnitude)
Oxides of: Ce, Nd, Sm, Tm, Ho = remainder of about 13%

TABLE I. ANALYSIS OF DOVERITE, HENRY PEGMATITE, COLORADO, AND THEORETICAL DOVERITE ANALYSIS

	A	B		C
CaO	18.3%	18.5%		19.2%
RE_2O_3	45.1%	46.1%	$Y_2O_3=24\%$ (quantitative) Others = 22.1% (by difference)	46.9%
CO_2	29.0%	31.4%		30.1%
F	5.1%	5.7%		6.5%
SiO_2	3.2%	—		—
Fe_2O_3	1.0%	—		—
	101.7%	101.7%		102.7%
O≡F	−2.1%	−2.4%		−2.7%
	99.6%	99.3%		100.0%

A = Original analysis of doverite with admixed cenosite.
Note: RE_2O_3 = total rare-earth oxides.
B = Doverite analysis recalculated from original sample (A) with 10.8% cenosite and 1.0% Fe_2O_3 eliminated; see text.
C = Theoretical doverite, $YCaF(CO_3)_2$, with Y:Dy = 2:1.

The other rare-earth elements, particularly Lu and Tb, may be present in small amounts, but their presence cannot be confirmed.

For the rare-earth calculations (other than yttrium) in Table I, we used the atomic weight of Dy, as it appears to be close to the average of the remaining 22.1% rare-earth oxides. The atomic ratio of Y to the other rare earths is about 2:1. The atomic ratio of Ca:RE is exactly 1:1. The ratio Ca:F is 1:0.9, indicating a slightly low value for fluorine. Nevertheless, this mineral is most likely the yttrium analogue of synchisite rather than another of the fluocarbonates with different atomic ratios. The formula for the mineral is ideally $YFCO_3\cdot CaCO_3$ or $YCaF(CO_3)_2$.

X-*Ray Diffraction Studies. X*-ray powder diffraction studies yield patterns similar to those of synchisite but with a measurable shifting of the lines, indicative of a smaller unit cell. The *d*-spacings recorded from the analyzed material, with three or four of the main cenosite lines deleted, are presented in Table II. It is assumed that doverite will have the same *C*-centered orthorhombic (or monoclinic) symmetry found by Donnay and Donnay (1953) for synchisite. On the basis of the orthorhombic cell, for synchisite $a=4.10$ Å, $b=7.10$ Å, $c=9.12$ Å. From the powder pattern of doverite, the cell constants are $a=4.00$ Å, $b=6.92$ Å, and $c=9.00$ Å based on $d_{(200)}=2.00$ Å, $d_{(040)}=1.73$ Å and $d_{(004)}=2.25$ Å. The only unambiguously indexable reflections are $\{00l\}$ with $l=1, 2, 3, 4$ and 7. The stated unit cell was obtained and the interplanar spacings

Table II. Powder X-Ray Data on Doverite, Cotopaxi, Colorado
(Filtered Iron Radiation. Camera Diameter 143.2 mm.)

I	d(Å) Observed	d(Å) Calculated		hkl
5	9.0	9.000		001
0.5	5.6		extraneous	
5	4.50	4.500		002
7	3.47	3.465		020
		3.464		110
1	3.22	3.233		021
		3.233		111
4	3.00	3.000		003
8	2.75	2.745		022
		2.745		112
1	2.62		extraneous	
3	2.25	2.250		004
0.5	2.04		extraneous	
9	2.00	2.000		130
		2.000		200
10	1.89	1.887		024
		1.886		114
1	1.86		extraneous	
9	1.83	1.827		132
		1.827		202
2	1.73	1.732		040
		1.732		220
1	1.70	1.701		041
		1.700		221
1	1.66	1.664		133
		1.664		203
0.5	1.64		extraneous	
6	1.62	1.616		042
		1.616		222
6	1.49	1.494		134
		1.494		204
0.5	1.46		extraneous	
0.5	1.39		extraneous	
9	1.37	1.372		044
		1.372		224
1	1.34	1.338		135
		1.337		205
1	1.31	1.309		150
		1.309		240
		1.309		310
0.5	1.28	1.285		007
7	1.26	1.257		152
		1.257		242
		1.257		312
4	1.20	1.200		153
		1.200		243
		1.200		136
		1.200		313
		1.200		206

were calculated (Table II) by taking the entire powder diffraction data into consideration and utilizing the pseudo-hexagonal symmetry. There are seven very weak lines which are extraneous. These represent an unidentified impurity other than cenosite in the analyzed material, but the extremely weak intensities of the lines indicate only a small amount of the phase; this should not detract from the validity of the theme of this paper.

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