MINERALOGIA POLONICA
Vol. 2 — 1971

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SYNCHYSITE FROM FOSSIL BONES

UKD 549.744.12:[568.19:591.471.33](517.3)

A b s t r a c t. Synchysite $CeCaF(CO_3)_2$ was found in the Havers canals of dinosaur ribs from Mongolia. It occurs there in the form of very fine yellow-brown anhedral grains. X-ray diffraction pattern of the bone containing 0.57 wt. % Ln_2O_3 contains strong reflections of the main constituent — francolite — accompanied by a series of weaker peaks characteristic of synchysite. The calculated cell parameters $a = 7.12$ Å and $c = 9.12$ Å are concordant with those reported by Smith for cerium synchysite. Since the chemically separated lanthanide oxides contains 57.0 per cent light earths (La — Gd) and 43.0 per cent heavy earth (Y, Tb — Lu), it is supposed that elements of the latter group occur as isomorphic substitutions in francolite.

INTRODUCTION

Synchysite is an uncommon mineral of the group of Ln-, Ca-fluoro--carbonates. This group includes such minerals as bastnäsite $LnFCO_3$, parisite $Ln_2CaF_2(CO_3)_3$, roentgenite $Ln_3Ca_2F_3(CO_3)_5$ and synchysite $LnCaF(CO_3)_2$. The symbol Ln in these formulas stands for the rare earth elements. The occurrence of synchysite was reported in rather few localities, being connected with pegmatitic and hydrothermal crystallization products.

It was discovered by Flink (1900) in syenitic pegmatites of Narsarsuk, Greenland. It was also found in pegmatites associated with aegirine rocks in Quincy (Massachussets) and Ravalla (Montana) (Palache, Warren 1911), being often described as parisite. Moreover synchysite occurs in hydrothermal Alpine veins of Val Nalps (Parker, Brandenberger 1946) and Oberaar (Iitaka, Stalder 1961). In the latter locality there occurs a rare paragenesis of four rare earths minerals: synchysite, bastnäsite, monacite and xenotime associated with other minerals typical of the so called dry Alpine fissures. Recently Weibel (1964) found synchysite and scheelite in the La Bianca summit (Tavetsch) associated with quartz, adularia, muscovite and hematite.

It should be emphasized that some authors considered the name synchysite and parisite to be synonymous because they neglected negligible differences in physical,

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crystallographic and chemical properties of these minerals. The problem was solved by Oftedal's (1931) X-ray examination of samples from Narsarsuk and Quincy, who determined crystal structures of parisite, bastnäsite, synchysite and cordylite. As follows from these data, particularly parisite and synchysite represent separate minerals. Nevertheless Söhnge (1944) in his description of minerals accompanying cassiterite in the tin mine Zaitplaats, Potgietersrust (Transvaal) mentions parisite displaying physical properties of synchysite. Finally, detailed crystallographical examinations of all the members of this rare earths fluoro-phosphates group, carried out by G. Donnay and J. Donnay (1953), clearly proved the existence of all the above mentioned minerals of this group. In these authors opinion, all the controversial conclusions in this respect are due to the occurrence of formerly unknown intergrowths of these minerals.

Yttrium equivalent of synchysite — doverite — was found in the Scrub Oaks mine in Dover, New Yersey (W. L. Smith et al. 1955). It occurs as brownish red aggregates consisting of fine-grained mixture of doverite, hematite, xenotime and quartz (E. I. Smith et al: 1960). Moreover, doverite in association with cenosite was found to form fine-grained reddish brown aggregates in Henry pegmatite in Cotopaxi, Colorado (Levinson, Borup 1962). Finally, a mineral displaying physical properties of doverite was reported by Semenov (1959) in greisen rocks of northern Kirgisia.

RARE EARTH ELEMENTS IN FOSSIL BONES

The occurrence of rare earth elements in fossil bones was established when examining the variation of heavy elements contents with geological age. Spectrochemical investigations of bones ranging in age from Neogene to Permian (Lavrov 1956) have shown some enrichment in them in Y, Ce, La and Pb which are lacking in contemporaneous bones. Kochenov and Zinovyev (1960) and later Bloch (1961) have determined the rare earth elements contents in phosphatic debris of Oligocene and Miocene fishes, as well as of Devonian fishes from the Russian platform. It was found that the average content of these elements in them amounts to 1 per cent, whereas in the phosphatic debris of Devonian fishes — up to 4.7 per cent. Bone fragments from Wyoming ranging in age from Late Cretaceous to Pleistocene have been analyzed for Y, Fe, Sr, Mn, As and other heavy elements by Toots (1963) showing a systematic variation of their content with age. According to this author's X-ray studies, no other minerals except hydroxyl-apatite and sometimes calcite are present in these fossil bones.

CHEMICAL AND MINERALOGICAL STUDY

Chemical examinations

Rare earth elements were determined in bones of dinosaur from the Nemegt valley in Mongolia collected by the Polish Palaeontological Expedition. The bone material, approximately 100 grams in weight, was dissolved in nitric acid and pure lanthanide oxides were separated by several alternating precipitations of oxalates and hydroxides. Depending on their structure, these bones contain from 0.03 to 0.5 per cent Ln_2O_3.

It was established that the ribs of these reptiles are particularly enriched in rare earth elements.

The obtained mixture of lanthanide oxides was separated by ion-exchange chromatography using Brunisholz's method (Brunisholz, Quinche 1960; Moret, Brunisholz 1961). The result of this analysis is as follows:

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Y	Dy	Ho	Er	Tm	Yb	Lu
26.9	5.7	3.8	14.3	1.6	1.7	3.0	0.5	33.4	3.5	0.9	2.3	0.2	1.6	0.6

The enrichment in rare elements of the phosphatic bone mass consisting essentially of francolite took place unquestionably during diagenesis of bone-bearing sediments. It is supposed that alteration of amorphous collophane, occurring in living organisms, into fluor-apatite and francolite was accompanied by isomorphic substitutions of rare earth elements for calcium.

X-ray examinations

X-ray diffractometer pattern was obtained by means of Rigaku-Denki apparatus using filtered CuK_α-radiation. Detailed inspection of the diffractogram of a sample of dinosaur rib, containing the highest amount of lanthanide oxides (0.57 per cent), has shown that characteristic francolite reflections on it are accompanied by strongest reflections of synchysite.

Table 1 contains interplanar spacings of synchysite calculated from diffractogram of dinosaur rib and those reported in Smith's and Mikheiev publications. Some reflections corresponding to this mineral coincide with strongest reflections of francolite, the main bone constituent. The calculated cell parameters of synchysite $a = 7.12$ Å and $c = 9.12$ Å are concordant to those of E. I. Smith et al. (1960) and correspond to the data reported by G. Donnay and J. Donnay (1953) i. e. $a = a' \sqrt{3} = 7.107$ Å and $c = 9.120$ Å.

Optical examinations

Detailed microscope observations of thin sections have shown that apart from the main mineral component of bone matter — francolite — there occur fine-grained aggregates of isometric crystals filling the Haver's canals. These crystals are either subhedral and colourless or anhedral and pale yellow brownish. Examination of powdered sample in immersion liquids has shown that the colourless crystals display refractive index corresponding to that of fluorapatite. On the other hand yellowish crystals represent anhedral platy fragments oriented perpendicularly or nearly perpendicularly to optical axis. Their refractive index amounts to 1.64, corresponding fairly well to that of synchysite. The values of refractive indices of this mineral reported by different authors are detailed in Table 2.

The above orientation of synchysite fragments is due to its preferred parting according to *(0001)*. The size of isometric synchysite grains (measured in thin section) varies from 0.008 to 0.01 mm.

Table 1

X-ray powder data for synchysites and doverite

Synchysite from dinosaur bones			Synchysite (after Smith et al. 1960)			Synchysite (after Mikheiev 1957)			Doverite (after Smith et al. 1960)		
hkil	d (Å)	*I*	*hkl*	d (Å)	*I*	*hkil*	d (Å)	*I*	*hkl*	d (Å)	*I*
			001	9.1	*s* 10				001	9.1	*ms*
0002	4.55	2	002	4.55	*m* 8				002	4.55	*m*
$11\bar{2}0$	3.56	10	110	3.56	*s* 10	$11\bar{2}0$	3.56	6	110	3.53	*s*
$11\bar{2}1$	3.31	10	111	3.31	*m* 8				111	3.30	*wb*
0003	3.087	7	003	3.07	*w* 5				003	3.05	*wb*
	(3.053)*			3.04	*w* 5						
$11\bar{2}2$	(2.81)*		112	2.81	*s* 10	$11\bar{2}4$	2.807	9	112	2.80	*s*
$11\bar{2}3$	2.292	2	113	2.31	*w* 5				113	2.30	*vf*
0004	2.276	2	004	2.28	*w* 5				004	2.28	*wb*
$30\bar{3}0$	2.052	2**	200	2.05	*ms* 9	$30\bar{3}0$	2.051	9	200	2.04	*ms*
$0\bar{3}31$	1.996	1***	131	2.002	*w* 5				131	1.995	*vvf*
$11\bar{2}4$	1.926	10**	024	1.918	*m* 8	$11\bar{2}8$	1.922	6	024	1.916	*ms*
$0\bar{3}32$	1.873	7**	132	1.87	*ms* 9	$30\bar{3}6$	1.868	7	132	1.863	*m*
$2\bar{2}40$	1.783	3**	040	1.781	*w* 5	$2\bar{2}40$	1.775	2	040	1.772	*m*
			221	1.749	*w* 5				221	1.727	*f*
			203	1.704	*w* 5				203	1.689	*f*
			042	1.658	*m* 8	$2\bar{2}44$	1.653	7	042	1.647	*w*
						00012	1.525	5			
						$11\bar{2}.12$	1.404	6			
						$4\bar{1}50$	1.343	3			
						$4\bar{1}52$	1.288	9			

* Coincidence with $d = 3.055$ and 2,79 Å of francolite.

** Slightly visible splitting of the peak might be due to coincidence of synchysite and francolite reflections.

*** Coincidence with $d = 2.001$ Å of fluorapatite.

Table 2

Refractive indices of synchysites

Refractive index	Iitaka, Stalder 1961	Levinson, Borup 1962	Semenov 1959	Łoziński
n_α	1.649	1.643	1.673	1.64
n_γ	1.750	1.73	1.769	n.d.

Rare earth elements are lithophylic and during fractional crystallization of magma concentrate in residual igneous differentiates. Consequently they appear in larger amount in pegmatitic stage. In hydrothermal stage the presence of rare earth elements depends on the concentration of fluorides and phosphates. The largest concentration of these elements are connected with carbonatites where parisite and bastnäsite are fairly abundant. However, these are not the commonest rare earth minerals. The most widespread seems to be monacite, frequent accessory constituent of leucogranites and alkali syenites as well as of pegmatites connected with the latter rocks. The tendency of rare earth elements to concentrate in association with phosphorous and fluorine is manifested not only in late-magmatic and hydrothermal environment but also in sedimentary rocks — namely in fossilized debris of bone tissue.

Separation of a mixture of lanthanides and yttrium obtained from the dinosaur ribs by means of ion exchange chromatography using Brunisholz method has been shown that it consists of 57.0 per cent of light earths (La — Gd) and 43.0 per cent of heavy yttrium earths (Y, Tb — Lu). Since the reflections recorded on the X-ray diffraction pattern correspond not to doverite but to synchysite sensu stricto, it is concluded that a part of rare earth elements — the light cerium group — precipitated in Haver's canals to form a separate mineral — synchysite, whereas yttrium and other elements of this group substituted calcium in the francolite structure.

Acknowledgements. The author wishes to thank Doc. R. Gradziński for supplying him with samples of dinosaur fossil bones and to Professors A. Gaweł and T. Wieser for critically reading the manuscript.

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SYNCHISYT W KOŚCIACH KOPALNYCH

Streszczenie

Synchisyt $CeCaF(CO_3)_2$, minerał występujący w stosunkowo nielicznych punktach litosfery i związany zwykle z fazą pegmatytową lub utworami hydrotermalnymi, został znaleziony w kopalnych kościach dinozaura z Mongolii. W kanałach Haversa kości tworzy on bardzo drobne anhedralne ziarna barwy żółtobrunatnej. Dyfraktogram proszkowy kości zawierającej 0,57% Ln_2O_3 wykazuje obok refleksów głównego składnika, frankolitu, wiele refleksów charakterystycznych dla synchisytu (tabl. 1). Obliczone stałe sieciowe $a = 7{,}12$, $c = 9{,}12$ Å są zgodne z podanymi przez E. I. Smitha i in. (1960) i odpowiadają także wartościom $a = a' \sqrt{3} = 7{,}107$, $c = 9{,}120$ Å wyznaczonym przez G. Donnay'a i J. Donnay'a (1953). Rozdzielenie za pomocą chromatografii jonowymiennej metodą Brunisholza mieszaniny tlenków lantanowców i itru wydzielonej z żebra dinozaura wykazało, że składa się ona z ziem cerowych (La—Gd) w 57,0%, ziem itrowych (Y, Tb—Lu) w 43,0%. Ponieważ dyfraktogram wykazuje refleksy charakterystyczne dla synchisytu *(sensu stricto)*, a nie dowerytu (synchisytu itrowego), należałoby przyjąć, że część pierwiastków ziem rzadkich, zwłaszcza grupa cerowa, utworzyła odrębny minerał synchisyt w kanałach Haversa kości, itr zaś i pierwiastki ziem itrowych weszły w skład frankolitu jako podstawienia diadochowe wapnia.

Ян ЛОЗИНЬСКИ

СИНХИЗИТ В ИСКОПАЕМЫХ КОСТЯХ

Резюме

Синхизит — $CeCaF(CO_3)_2$, редкий минерал, встречающийся в нескольких пунктах литосферы, связанный, как правило, с образованиями пегматитовой или гидротермальной фаз, был обнаружен в ископаемых костях динозаура из Монголии. В каналах Хаверса костей он образует мельчайшие ангедральные зерна желтовато-бурого цвета. Порошковая дифрактограмма кости, содержащей 0,57% Ln_2O_3, кроме рефлексов главного компонента — франколита, показывает ряд рефлексов, характерных для синхизита (табл. 1). Вычисленные параметры ячейки $a = 7{,}12$, $c = 9{,}12$ Å совпадают с данными, приведенными Смисом и др. (1960), а также соответствуют значениям $a = a' \sqrt{3} = 7{,}107$, $c = 9{,}120$ Å, определенным Доннейем и Доннейем (1953). Ионообменный хроматографический анализ методом Брунисхольца смеси окислов лантанидов и иттрия, извлеченной из ребра динозаура, показал, что эта смесь состоит из цериевых земель (La—Gd) в 57,0% и иттриевых земель (Y, Tb—Lu) в 43,0%. Так как на дифрактограммах отмечаются рефлексы характерные именно для синхизита, а не доверита (иттриевого синхизита), следует заключить, что часть редкоземельных элементов, особенно цериевая группа, образовала самостоятельный минерал синхизит, развитый в каналах Хаверса в костях, а иттрий и элементы иттриевых земель вошли в состав франколита, замещая диадохически кальций.