THE OCCURRENCE OF CRANDALLITE IN A SINKHOLE NEAR FLORZE (BELGIAN CONDROZ)

P. BUURMAN en L. VAN DER PLAS[1])

ABSTRACT

Crandallite has been found in a sinkhole near Florzé where recently also halloysite was discovered. The mineral occurs in a pocket in a residual clay derived from Visean limestones. The clay is found on top of *Om* and *Onx* deposits and below Pleistocene solifluction material. X-ray diffraction patterns, D.T.A.-traces, specific density separation, refractive indexes, X-ray fluorescence patterns and chemical composition have been determined and are reported. The samples are rich in uranium.

INTRODUCTION

Crandallite has been found in a large dolina near Florzé and Aywaille, Belgium (topographical map 49, x = 241.500 y = 130.780), 35 km. SE of Liège. It occurs as a constituent of rather inhomogeneous material enclosed by residual clays derived from Visean and probably also Tournaisian limestones. The outcrop of this pocket in the heavy residual clay moves slowly with the clay along the steep wall of a sandpit. The pocket is filled with various materials, of which a description is given below. The origin of this material is not known as yet; its association with carbon-rich compounds and amorphous silica and alumina compounds points to a – at least partial – relationship with organic accumulations.

[1]) Department of Soil Science - Agricultural University, Wageningen.

The bottom of the pit consists of sands and gravels of the *Om* and *Onx*-formations belonging to the Upper Oligocene period. Above these deposits the clay with the crandallite-pocket occurs which is overlain by the following formations (from top to bottom):

- a colluvial toplayer of loessy material with pebbles
- a markedly bedded colluvium
- a deposit of rebedded loessy material with a fresh water fauna
- a solifluction layer with remnants of an Eemian soil formed on limestone
- a deposit of clay with chert (solifluction).

The clay-with-chert deposit is a remnant of Tertiary soil formation from Carboniferous limestones. Its occurrence on the Upper Oligocene sediments indicates that it is not in its original position. The presence of a formation of Eemian age in the overlaying material excludes the possibility of displacement during the Würm period. There are indications that the movement took place during the early Riss time; therefore, the clay with crandallite was formed before this period. Residual clays of limestone weathering in the Belgian Condroz generally do have their origin in the Tertiary epoque.

The clay in which the crandallite occurs, the deposits of clay-with-chert and an Eemian soil fill a gully in the underlying deposits. The three layers on top of these cover the gully and its banks.

TABLE 1

Summarizing table on Data about Crandallite

Loughlin & Schaller, 1917

Locality: Provo, Utah; Formula: $CaAl_4(PO_4)_2(OH)_8.H_2O$; optical: hexagonal; -elong; n =1.585-1.595 1.605-1.62; habit: platy. clear fracture planes. fibrous aggregates. white-light grey-yellowish brown. opaque, transparent; association: quarz, barite, pyrite, evansite, galena, sphalerite; has a crust of tenorite; genesis: alteration of goyazite. Al_2O_3 35%; CaO 4.88%; SrO 1.44%; P_2O_5; 17.61%; SO_3 2.47%; W.12.26%.

Larsen, 1942

Locality: Fairfield, Utah; Formula: $CaAl_3(PO_4)_2(OH)_5.H_2O$, $Ca(Ca,Al)Al_2(PO_4)_2(OH)_{4-5}.H_2O$; optical: rhomboedr. n=1.618-1.627 n=1.640-1.650; habit: yellow fibers. glassy crusts, yellow aggregates; association: in variscite nodules in combination with deltaïte.

van Tassel, 1956

Locality: Belgium, canal Mont-Blaton (Mons) Bioul, Sirault; optical: n=1.614-1.623; habit: nodules, fibrous aggregates; association: with kaolin, pyrite and gypsum and destinézite in phtanites of Visean-age.

Greenberg, 1958

Locality: Gardner Mine Ridge Lawrence C, Indiana; optical: wavy extinction n=1.625-1.630; habit: fibrous; association: with allophane-rich variety of brown halloysite.

Owens, 1960

Locality: Homeland, Florida; optical: n=1.59-1.60; association: microcrystalline in phosphorite ass. with millisite; genesis: formed by lateritic leaching of Al phosphates 0.03% U descending amounts Al, Si, Ca, P, Fe, Na, Ti, Mg, Ba, Pb, Sr, Cu, B, V, Zr, Ga, Ni, Y, Mn, Sc, Yb, Be.

Stadler, 1962

Locality: Ruhrgebiet, Westphalien A-C; Formula: $CaAl_3(PO_4)_2(OH)_5.H_2O$; habit: nodules; association: in coal layers and caolin-claystones. ass. with apatite; genesis: formation when deficient Ca for Apatite.

Cowgill, 1963

Locality: Guatemala, Trop. Swamp; Formula: $(Ca, Sr, Pb)_2Al_7(PO_4)_3(OH)_{16}.H_2O$ between $Ca_2Al_6(PO_4)_4(OH)_{10}.3H_2O$ and $Ca_2Al_6(PO_4)_3(OH)_{14}.3H_2O$.

Trueman, 1965

Locality: Christmas Island; association: lateritic weathering of guano, combined with cations of underlying rocks as limestones and volcanic rocks. In cavites of underlying rock. Surface layer of apatite deposits.

Wilson, 1966

Locality: Derbyshire, England; optical: n=1.624; association: in Rowhurst Tonstein, Westphalien. ass. with caolin, apatite, pyrite, quarz, illite; supposed formation from soil colloids. combination lateritic leaching and accumulation in swamps. Al and P from plants (Lycopodium).

DESCRIPTION OF THE MATERIAL

Besides a bulk sample, the following seven samples of different appearance were selected for investigation.

A: soft, white material
B: black, resinous material
C: ditto, with marked shrinking cracks when dry
D: grey, powdery concretions
I: white, glassy crusts
II: grey, powdery material with black spots
III: yellow, transparent glassy crusts.

DESCRIPTIONS IN LITERATURE OF CRANDALLITE DEPOSITS

The earlier descriptions of crandallite deposits are compiled in table 1. X-ray diffraction patterns, if mentioned are presented in table 2. The impressions gathered from the literature, may be generalized as follows:

1. Crandallite is associated with ore deposits as well as with organic material in sediments and soils.
2. Its genesis in most cases is related to alteration processes near the earth's surface.
3. Hexagonal, ditrigonal, orthorhombic and triclinic structures are reported. Optical properties are given as isotropic with a rather varying index of refraction. The crystallographic properties are not well known, or else the material occurs in various forms.
4. The chemical composition does not lead to one type of formula. The two main types are:

$$CaAl_4(PO_4)_2(OH)_8.H_2O$$
$$CaAl_3(PO_4)_2(OH)_5.H_2O$$

5. It seems to have an attraction for rare elements such as: Be, B, Sc, Ti, V, Ga, Ge, Sr, Y, Zr, Yb and U.
6. The reported X-ray diffraction patterns are consistent but for the pattern reported by Cowgill c.s. (1963), adopted by the A.S.T.M. (16-162). According to our experience with patterns of wardite and variscite this pattern may be contaminated with lines of these crystalline phases.

TABLE 2

X-ray diffraction patterns.

Cowgill ASTM 16-162	Wilson	Owens	van Tassel	ASTM 5-615	Florzé G957a	Florzé G958b	Florzé G997c	Leiden St.80104 G960c
9.45								
7.00	6			6.73				
6.51								
6.24				6.05	6.06			
5.75	5.70	5.68	5.72	5.70	5.70	5.69	5.71	5.67
5.47								
5.37								
5.06	4.88	4.86	4.85	4.86	4.84	4.84		4.82
4.77								
4.42					4.48	4.47		
3.53					4.37	4.36		
3.42	3.50	3.49	3.52	3.50	3.50	3.50	3.51	3.49
3.40								
3.30								
3.19								
3.16								
3.08				3.09				
2.97	2.95	2.98	2.96		2.98	2.98	2.99	2.98
2.88	2.84	2.95		2.94	2.94	2.93	2.94	2.93
2.79				2.87				2.85
2.77								2.83
2.73								
2.68		2.70	2.67	2.69	2.69	2.70		2.69
2.60					2.59	2.58		2.57
2.58				2.52	2.56	2.56		2.53
2.45	2.43		2.44	2.43	2.50	2.42		
2.29					2.42			
2.27		2.24			2.39		2.26	
2.21	2.21		2.22	2.23	2.34	2.20	2.21	2.21
2.18	2.17		2.19		2.20			2.20
2.15			2.15	2.16	2.16	2.16	2.16	2.16
2.10				2.11				
2.01								
1.97		1.99		1.99		1.97		1.98
1.95								
1.93				1.93				
1.91								
1.90	1.89	1.89	1.89	1.93	1.89	1.89	1.90	1.89
1.87								
1.85				1.84				1.83
1.75	1.75	1.75	1.75	1.80	1.75	1.77	1.78	1.80
1.69				1.75				1.79
1.66				1.67				1.75
1.64							1.65	1.72
1.63							1.63	1.68
1.61				1.60	1.61			1.64
1.59								1.62
1.58								1.60
1.56								1.56
1.54							1.55	1.55
1.53								1.53
1.53								
1.51			1.52	1.51	1.50	1.49	1.51	1.51
1.49			1.49	1.49	1.49	1.46	1.49	1.51
1.48								1.49
1.47			1.46	1.47	1.47	1.47	1.47	1.48
1.42								
1.41								
+ 5 additional			+ 14 add.	+ 9 add.	1.40	1.42	+ 3 add.	+ 3 add.

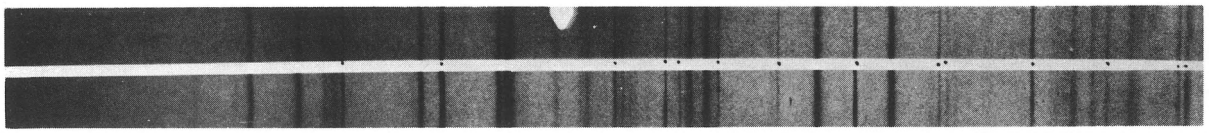

Fig. 1
X-ray diffraction pattern of density-fraction d = 2.5-2.7, G957a, Black dots indicate quartz-lines. Co-K-alpha radiation.

PROCEDURES

In the investigation of this material X-ray diffraction, X-ray fluorescence, Specific Density Separation, D.T.A. and chemical analysis have been used. The refractive index was determined with a series of liquids of known r.i. X-ray diffraction has been carried out with a quadruple Guinier-De Wolff camera, using iron-filtered Co-K-alpha radiation. X-ray fluorescence was performed with a Philips apparatus using Ag-radiation and LiF and P.E. crystals.

For D.T.A. a Du Pont-900 apparatus was used. The samples were analysed in a N_2 atmosphere when burning of organic substances had to be prevented. Specific Density Separation was done in two ways. The first one, a linear density gradient separation, was carried out by Drs. G. Halma using bromoform and decaline (H a l m a, 1969a, 1969b). In this separation the limits were d = 1.7-2.6. The second separation was done in four steps, using the same liquids. The steps were: d 2.0; 2.0-2.2; 2.2-2.4; 2.4-2.6.

Refractive index

The refractive index of sample III is 1.492-1.496. According to the values given in table 1 this is rather low, probably due to impurities. Sample III is isotropic.

TABLE 3

Interpretation of X-ray diffraction patterns

Sample	
A	crandallite + several lines of unknown material
B	a strong 4.84 Å line, characteristic for crandallite
C	weak lines of crandallite
D	weak crandallite pattern + several lines of unknown material unlike A
I	as A
II	weak crandallite pattern
III	ditto

X-ray diffraction

According to Guinier-De Wolff photographs the samples consist of a bulk of amorphous material with various amounts of crandallite in varying degrees of crystallinity. Three X-ray patterns are given in table 2, together with a crandallite from Fairfield. Utah (Collection Geological Museum, Leyden, St. 80104).

G957a, pattern given as fig. 1, is a specific density fraction of the bulk sample, d = 2.5-2.7. The lines indicated by black spots belong to quartz which is a constituent of this fraction.

G997c gives the pattern of sample II.

G958b gives the pattern of the specific density fraction d = 2.4-2.6.

The patterns leave no doubt about the presence of crandallite. The X-ray patterns of the seven samples previously listed are given in table 3.

Thermal analysis

D.T.A. traces of all the reported samples have been made and are shown in fig. 2. The traces are made of samples that for a few days were kept in relative humidity of 50% at 25 °C. The traces show an endothermic reaction at approximately 160 °C, sometimes followed by a second reaction at a slightly higher temperature. The dark coloured samples give an exothermic oxidation reaction which does not occur in runs made in N_2 atmosphere. An exothermic reaction occurs at approximately 1000 °C with the exception of sample A that shows two such reactions.

The quantity of crandallite in the various samples as indicated by the X-ray analysis shows no relationship to the results obtained by thermal analysis.

We made one TGA of sample D in order to find out if the reactions shown in the DTA were closely associated with a weight loss, but found that this was not the case.

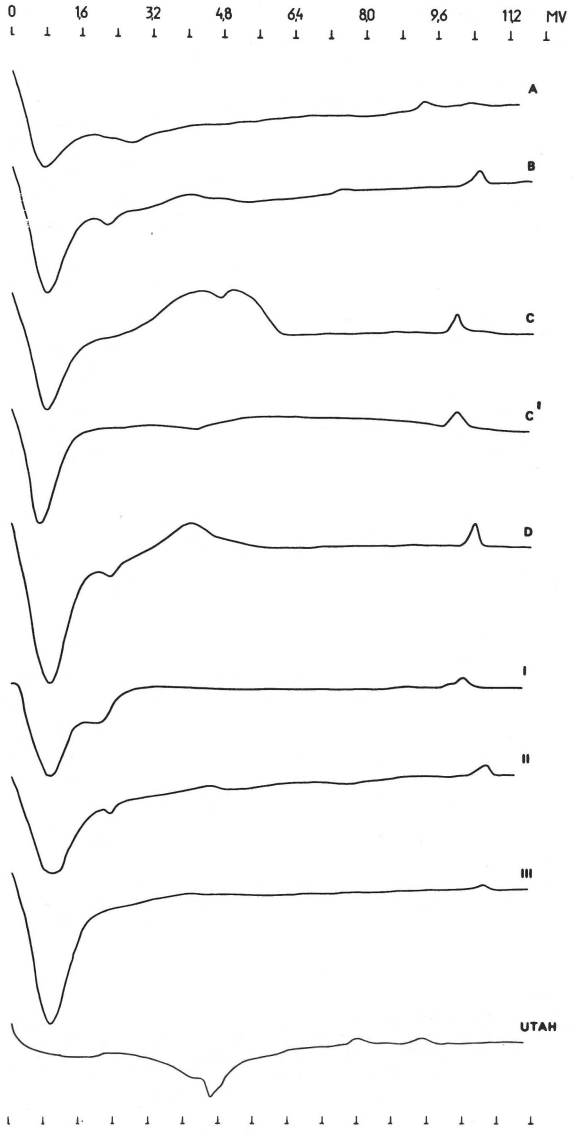

Fig. 2
D.T.A.-traces of 7 crandallite-samples from Florzé and a crandallite-sample from Utah (Leyden, St. 80104); Pt-PtRh thermocouples. Trace C^1 in N_2 atmosphere. The others in O_2-atmosphere. Heating rate 20 °C/min.

Specific density separation

Only the fraction 50-200 microns of the ground bulk sample was subjected to specific density separation. Gradients ranging from density 1.7-2.6 showed several concentrations of different materials. X-ray patterns show a marked increase in intensity of the crandallite lines with increasing density. This points to an association of crystalline crandallite (d = 2.7-2.8) with amorphous material of a lower density, and agrees with the chemical analysis (see below).

TABLE 4

Chemical analysis of the bulk sample.

SiO_2	36.91%
Al_2O_3	33.49%
Fe_2O_3	.86%
TiO_2	.32%
MnO	.05%
CaO	.18%
MgO	.38%
P_2O_5	4.71%
Na_2O	.30%
K_2O	1.56%
Loss on ignition	18.55%
	97.31%

Chemical analysis

One chemical analysis of the bulk sample was carried out and is shown in table 4. If the amount of crandallite is calculated from the amount of P_2O_5, using the formula:

$2CaO.3Al_2O_3.2P_2O_5.7H_2O$ or
$2CaAl_3(PO_4)_2(OH)_5.H_2O$

the result is 11 wght % of crandallite. The remainder is assumed to be amorphous material because the X-ray analysis shows only a very small amount of quartz. A calculation of a "norm composition" of the remainder after the substraction of crandallite leaves only 1 % of quartz and a compound of SiO_2 and Al_2O_3. The proportions of the oxides in this compound would allow the formation of halloysite.

X-ray fluorescence

The seven samples listed were investigated with X-ray fluorescence. For this purpose, they were ground to about 50 microns and pressed to tablets of about 2½ cm ϕ. They were investigated with P.E. and LiF analysing crystals. Elements with atom numbers up to 12 cannot be detected with this method. Relative amounts of the elements are given in table 5.

TABLE 5

Relative amounts of various elements found in the crandallite deposit of Florzé. Strongest lines used.

Scale: + less than 500 counts per second more than background
1 500–1000 ...
2 1000–2000 ...
3 2000–5000 ...
4 5000–10000 ...
5 over 10000 ...

sample	element													
	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cu	Zn	Sr	Y	U
A	3	3	3	+	+	+	5	+	3	-	1	5	2	2
B	3	2	3	+	+	1	5	2	2	-	2	5	1	+
C	4	4	1	1	+	3	4	2	3	1	+	2	2	2
D	2	3	3	+	+	2	5	2	3	-	1	5	1	1
I	3	3	2	+	+	+	5	+	1	-	1	5	1	3
II	2	3	+	+	+	2	4	1	3	-	1	+	1	2 J
III	3	3	2	+	+	2	4	1	5	-	3	2	3	+

In all samples traces of V, Cr and Ni. have been found.

Quantitative measurements of Sr, Y and U were carried out by Mr. P. G. J. M. Anten of the Vening Meinesz Laboratory, Utrecht. They are shown in table 6.

Conclusions:

No conclusions have been drawn about the genesis of the crandallite bearing material. It may have been a part of the carboniferous limestone and associated rocks just as in the case described by S t a d l e r (1962) and v a n T a s s e l (1956). It may also have originated from leaching processes in the breccia forming the contact between the Visean and Tournaisian limestones where the Florzé sinkhole is situated.
L e g r a n d (1957) reports Uranium-bearing iron phosphates from this contact breccia near Visé.

Crandallite has been reported as a product of tropical soil formation by C o w g i l l c.s. (1963) and by T r u e m a n (1965). Tropical soil forming processes (lateritic leaching of limestones during the Tertiary epoque) may have favoured the accumulation of phosphates and of uranium.

The occurrence of uranium does not seem to be restricted to the crandallite-rich samples. Judging from the X-ray patterns (especially samples A and I) it is possible that compounds akin to Ca- or Sr-Uranyl-phosphates are also present.

In arriving at a possible formula for the crandallite under investigation we considered the following factors. Other elements were substituted for Ca, as there was insufficient Ca in the bulk analysis to form crandallite from the P_2O_5 available. L a r s e n (1942) reports the possible substitution of Al by Ca. It is also possible that the amount of Sr in the sample is related to the amount of phosphates. c.f. table 5.

According to general substitution rules as well as

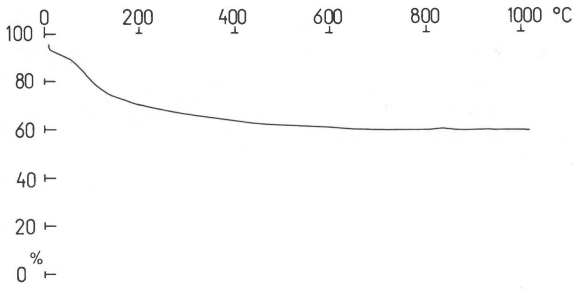

Fig. 3
T.G.A.-trace of sample D. N_2-atmosphere. Heating rate 20 °C/min. Chromel Alumel thermocouples.

TABLE 6

Quantities of Y and U in ppm.; of Sr in wgt. % or ppm.

Element	Sample							
	A	B	C	D	I	II	III	bulk
Sr	0,33%	ca. 1.2%	80 ppm.	0,43%	1650 ppm.	10 ppm.	130 ppm.	n.d.
Y	150	110	180	100	50	90	380	n.d.
U	740	100	410	300	1010	590	250	130

to the reported analyses, c.f. table 1, the formula may be generalized:

$(Ca,Sr,Pb,Cu,Zn)\,(Al,Y)_3(PO_4)_2(OH,Cl)_5 \cdot H_2O$

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