

PHYSICAL AND CHEMICAL DATA FOR CRANDALLITE FROM ALACHUA COUNTY, FLORIDA

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ABSTRACT

Crandallite in a crandallite-clay quartz sandstone was determined by scanning electron microscope and by electron probe microanalysis. Extrapolation of this information to similar rocks facilitates the distinction in thin section between crandallite and associated minerals in the phosphatic sediments from Florida.

The crandallite used in this study was found to be a strontian variety intermediate between crandallite and goyazite ($Cn_{70}Gz_{30}$), and probably much of the crandallite in Florida is of a similar composition. Crandallite was formed from the elements in carbonate fluorapatite and clay minerals and during the process Sr has been enriched many times over its concentration in the source mineral (apatite).

INTRODUCTION

The occurrence of crandallite (pseudowavellite), $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$, in Florida (phosphatic deposits near Bartow, Polk County) was apparently first reported by Hill, Armiger, and Gooch (1950). Altschuler *et al.* (1956) discussed the origin of crandallite and other secondary phosphate minerals (millisite and wavellite) which occur in the Bone Valley Formation in central Florida. Espenshade and Spencer (1963) listed crandallite as a minor constituent of weathered phosphatic sediments in the phosphorite unit of the Hawthorn Formation (upper Hawthorn) of northern Florida. Except for partial X-ray data published by Owens *et al.* (1960), the literature dealing with phosphate minerals from Florida does not include a study of the physical and chemical properties of crandallite itself and it is my purpose to present the results of work on crandallite from a specific occurrence in Florida.

Crandallite is a member of the plumbogummite group which includes the minerals plumbogummite, gorceixite, goyazite (Gz), crandallite (Cn), and florencite, with characteristic cations of Pb, Ba, Sr, Ca, and Ce respectively. Palache *et al.* (1951) include deltaite in the group, but Elberty and Greenberg (1960) have shown that deltaite is a mixture of crandallite and hydroxyapatite. Minerals of the plumbogummite group are considered to be isostructural, with an alunite-type structure, and have the general formula $XAl_3(PO_4)_2(OH)_5 \cdot H_2O$, where $X = Pb, Ba, Sr, \text{ or } Ca, \text{ or } CeAl_3(PO_4)_2OH_6$ (florencite). Considerable solid solution exists between members of this group and be-

tween members of the plumbogummite, alunite, and beudandite groups. The crandallite described in this report has the approximate formula $Cn_{70}Gz_{30}$ and is thus essentially a strontian crandallite, intermediate between crandallite and goyazite.

OCCURRENCE

Poorly-indurated to well-cemented sandstones and sandstone nodules occur in numerous exposures of the Hawthorn Formation from Ocala, Florida to the Florida-Georgia border. Where present at relatively shallow depth, many of these sandstones are composed dominantly of quartz grains in a matrix or a cement of clay (dominantly kaolinite) and/or wavellite. Less commonly crandallite is present and rarely small amounts of variscite (Blanchard and Denahan, 1967) can be detected. Where crandallite is present it is generally cryptocrystalline and is virtually inseparable from associated phosphate and clay minerals. Because of small crystallite size, association with other minerals (especially phosphates), and because of a lack of detailed information on crandallite, it is difficult to identify (with a reasonable degree of certainty) crandallite in thin section. During preliminary X-ray analysis of a large number of samples of these sandstones, one group of samples was found to consist of quartz grains in a matrix of crandallite with minor clay minerals and no other detectable phosphate minerals. This provided an opportunity to study the crandallite without the danger of confusion between characteristics and properties of crandallite and other phosphate minerals, and it is this concentration of crandallite which was used in this study.

The exposure, a small road bank on U. S. 441 near Micanopy, Alachua County, Florida, is dominantly unconsolidated sand with sparse nodules of white to light-gray to light-tan poorly-indurated quartz and crandallite, and with well-indurated nodules containing quartz, wavellite, and crandallite. In hand specimen the quartz-crandallite nodules have the appearance of an argillaceous sandstone and, disregarding degree of induration, they are megascopically indistinguishable from the much more abundant wavellite-cemented sandstones of the Hawthorn Formation.

DATA

Crandallite was separated from most of the associated quartz by gentle crushing and dry sieving at 325 mesh and by disaggregation with a magnetic stirrer and wet sieving at 325 mesh. Concentrates of crandallite (-325 mesh) were used for X-ray and chemical analysis, for measurement of optical properties, and for differential thermal analysis. Thin sections and polished thin sections of the nodules were prepared for petrographic study and for electron probe microanalysis, and small fragments of the nodules were coated with gold-palladium for examination with the scanning electron microscope.

Chemical Analysis

Qualitative X-ray fluorescence analysis of the -325 mesh fraction of the crandallite-bearing rock showed the presence of essential

amounts of Ca, Al, P, Sr, and Fe and minor to trace amounts of As, Y, Ce, Ti, and K.

Qualitative electron probe microanalysis of part of a polished thin section of a crandallite nodule was made in order to correctly identify the phases seen in optical examination of thin sections and in order to establish the mineralogical location of the iron and strontium found in the X-ray fluorescence analysis and in the quantitative chemical analysis. Analysis for Al, Si, P, Ca, Fe, and Sr was made along an 1125 micron traverse. A specimen current image for the area around the traverse is shown in Figure 1, along with a photomicrograph of the same part of the polished thin section. A scan for the $K\alpha$ line of each of the elements listed above (except Fe) is shown in Figure 1. In the microprobe scans quartz shows up as high counting rates for Si and background for the other elements. Crandallite is characterized by high counting rates for Ca, Al, P, Sr, and Fe, and low counting rates for Si. Regions along the traverse which show high counting rates for Si, Al, Fe, and low counting rates or background for P, Ca, and Sr are interpreted as clay, probably (at least in part) kaolinite and/or montmorillonite.

The results of the microprobe analysis show that (1) crandallite is the dominant isotropic or very nearly isotropic mineral visible in thin section and the dominant birefringent material (excluding quartz) is clay, (2) in many places in the thin section crandallite and clay are physically separate and optically distinguishable from one another, but in a few places the two are intimately mixed, and (3) Sr is confined to the crandallite, whereas Fe is present in both crandallite and clay.

A quantitative chemical analysis of the -300 mesh fraction of the crandallite-bearing rock is given in Table 1. This material is dominantly crandallite, clay, and minor quartz. Because the composition of the clay mineral or minerals is unknown and because the proportion of the clay to quartz is unknown it is not possible to obtain from the data a complete composition for the crandallite. The most striking, and unexpected, aspect of the analysis is the rather high percentage of SrO. From the microprobe analysis it is clear that essentially all the Sr and Ca are in the crandallite, and from the chemical analyses for Sr and Ca this leads to a composition of $Cn_{68.5}Gz_{31.5}$ (wet chemical) or $Cn_{70}Gz_{30}$ (X-ray fluorescence) for the crandallite.

X-Ray Analysis

X-ray analyses of the whole-rock sample show strong lines for quartz and crandallite and the crandallite concentrate shows addi-

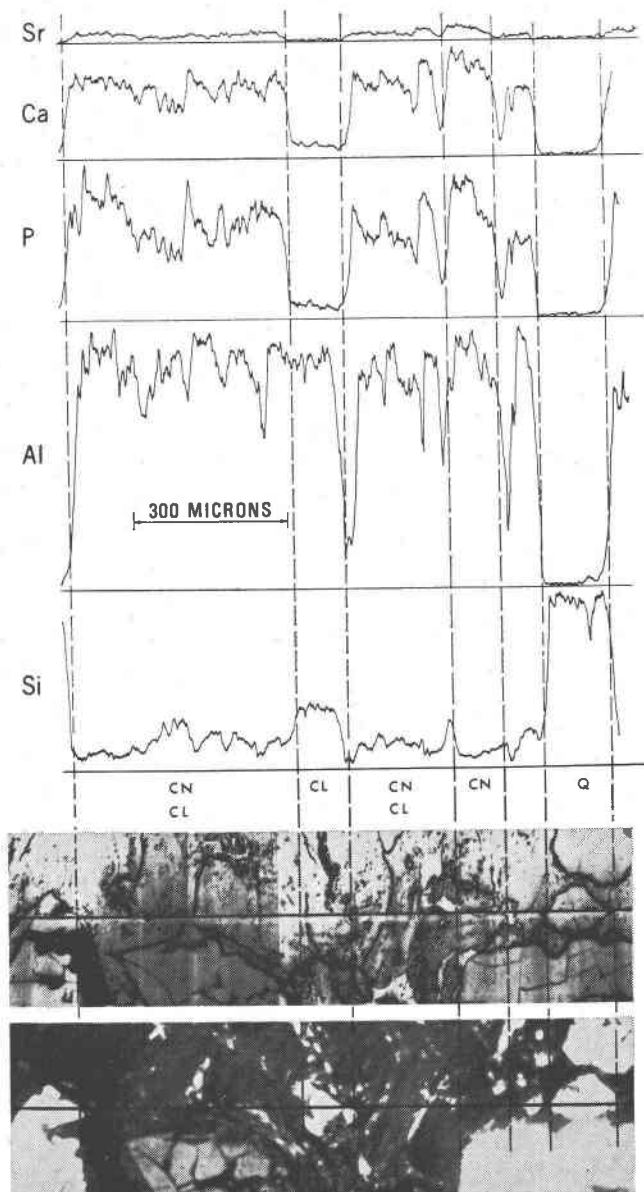


FIG. 1. Electron microprobe analysis for Sr, Ca, P, Al, and Si. Scans for $K\alpha$ lines of elements (top), specimen current image (middle), and thin section photomicrograph with crossed polars (bottom). Crandallite (Cn), clay (Cl), and quartz (Q).

TABLE 1
 CHEMICAL ANALYSIS OF THE -325 MESH
 FRACTION OF A CRANDALLITE-QUARTZ-CLAY NODULE

	Calculated Composition for Crandallite-Goyazite			Crandallite (with quartz and minor clays) from Florida	
	Cn ¹	Cn ₇₀ Gz ₃₀	Gz ²	Wet Chemical	X-Ray Fluorescence
CaO	13.55	9.16		5.29	5.84
SrO		7.26	22.45	4.51	4.67
Al ₂ O ₃	36.93	35.73	33.12	26.86	
P ₂ O ₅	34.29	33.13	30.77	21.84	
H ₂ O ³	15.23	14.72	13.66	16.72	15.41
SiO ₂				17.62	
Fe ₂ O ₃				1.53	
MgO				0.31	
K ₂ O				0.15	
Na ₂ O				0.09	
H ₂ O ⁴				1.62	2.36
Cn-Gz (determined from SrO:CaO mol. fraction)				Cn _{68.5} Gz _{31.5}	Cn ₇₀ Gz ₃₀

¹CaAl₃(PO₄)₂(OH)₅·H₂O

²SrAl₃(PO₄)₂(OH)₅·H₂O

³Between 120° and 990° C.

⁴Below 120° C.

tional weak lines corresponding to the strongest lines for kaolinite, montmorillonite and what is probably a mixed-layer clay. X-ray analyses of the partially separated and sedimented clay minerals yielded the expected strong lines for oriented kaolinite, montmorillonite and a 21-angstrom line which may result from a mixed-layer clay. No other phases were identified although an unidentified sharp line is

present at $d = 6.08$. The observed and calculated d -spacings corresponding to reflections from crandallite, along with similar data for crandallite from Fairfield, Utah, are given in Table 2. There is a close correspondence between the two sets of diffraction lines, however, the data does not correspond closely with either of the two A.S.T.M. cards for crandallite.

Lattice parameters for the crandallite were determined from diffractometer charts using Ni-filtered Cu-radiation, a scanning speed of $0.2^\circ 2\theta$ per min., a time constant of 4 sec., 1° beam slit, MR soller slit, and a 0.02° detector slit. The reflections listed in Table 2 were used in refinement of lattice parameters using the least squares method and

TABLE 2. POWDER DIFFRACTION DATA

Line	hkl ¹	Crandallite-Florida			Crandallite-Fairfield, Utah		
		Observed $d\text{\AA}$ ⁰	Calculated $d\text{\AA}$ ²	I relative	Observed $d\text{\AA}$	Calculated $d\text{\AA}$ ³	I relative
1	101	5.698	5.692	41	5.695	5.688	34
	003	Not observed	5.417		Not observed	5.397	
2	012	4.869	4.866	20	4.866	4.859	29
3	110	3.511	3.508	54	3.509	3.508	35
	104	Not observed	3.378		Not observed	3.368	
4	021	2.984	2.987	44	2.983	2.985	50
5	113	2.945	2.945	100	2.941	2.941	100
	015	2.862	2.866	5	2.858	2.857	6
	202	Not observed	2.846		Not observed	2.844	
7	006	2.710	2.709	9	2.699	2.698	17
8	024	2.435	2.433	7	2.430	2.430	4
	211	Not observed	2.274		Not observed	2.274	
	205	Not observed	2.220		Not observed	2.215	
9	122	2.209	2.210	19	2.207	2.209	16
10	107	2.1684	2.1688	28	2.1624	2.1615	36
	116	Not observed	2.1440		Not observed	2.1387	
	300	Not observed	2.0255		Not observed	2.0252	
11	214	2.0009	1.9994	3	1.9964	1.9973	2
	018	Not observed	1.9364		Not observed	1.9200	
12	303	1.8972	1.8973	28	1.8960	1.8961	27
	125	Not observed	1.8757		Not observed	1.8731	
13	027	1.8441	1.8448	2	1.8417	1.8402	6

¹All possible hkl values listed for hexagonal-rhombohedral

²Calculated for $a = 7.017$, $c = 16.252$ (refined for observed reflections to $50^\circ 2\theta$, CuK α)

³Calculated for $a = 7.013$, $c = 16.196$ (refined for observed reflections to $50^\circ 2\theta$, CuK α)

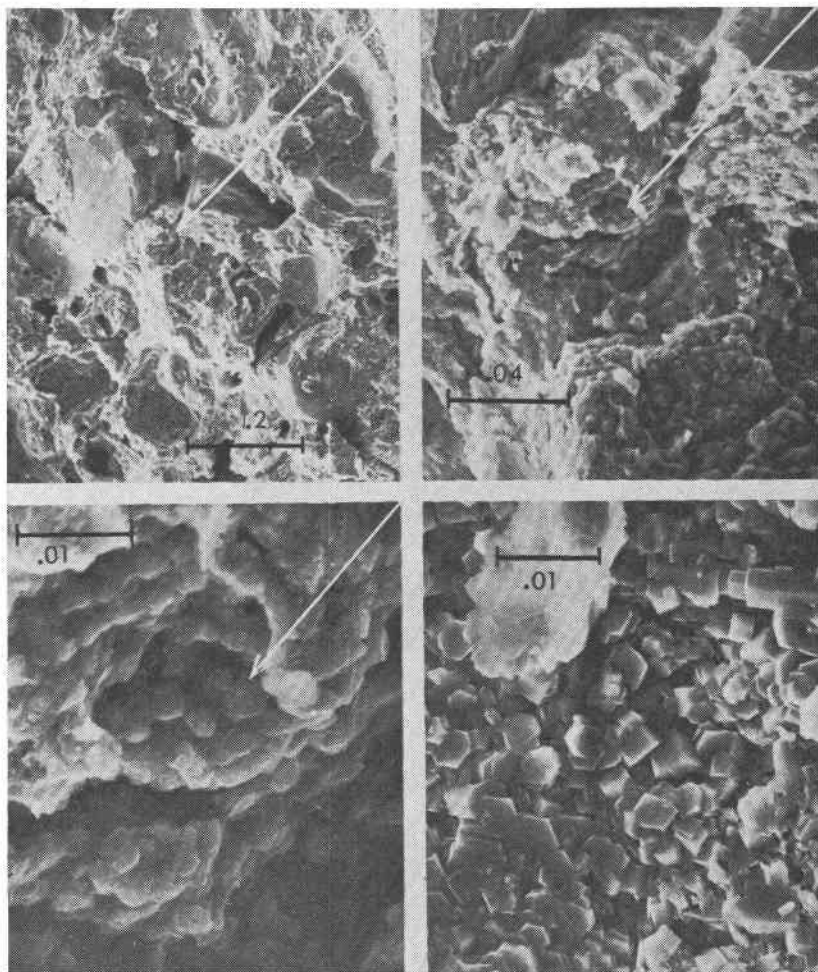


FIG. 2. Electron micrographs (scanning electron microscope). Crandallite-bearing rock (Florida) with arrows pointing to crandallite (upper and lower left). Crandallite from Fairfield, Utah (lower right). Scales in mm.

the computer program of Appleman and Evans (1967). The results are:

$$\begin{array}{ll}
 a = 7.017 (\pm .001) & c = 16.252 (\pm .004) \text{ (Florida)} \\
 a = 7.013 (\pm .0008) & c = 16.196 (\pm .003) \text{ (Utah)}
 \end{array}$$

The slightly larger unit cell volume of the material from Florida may result from the substitution of the larger Sr^{2+} for the smaller Ca^{2+} .

Electron Microscopy

Samples of the crandallite-bearing rock were examined with the scanning electron microscope and electron micrographs were compared with those taken of a sample of well-crystallized pure crandallite from Fairfield, Utah (Fig. 2). The crandallite from Fairfield occurs as platy hexagonal crystals and as equant pseudocubic rhombohedral crystals, averaging 3 to 6 microns across (Fig. 2, lower right). This habit is similar to that described by Palache *et al.* (1951) for goyazite, but is somewhat different from the habit described as typical for crandallite. This may be because macrocrystalline crandallite is rare and because the crystal habit of crandallite has not been investigated by electron microscopy. Comparison of the electron micrographs of Fairfield crandallite with those of the crandallite-bearing sandstone from Florida, and consideration of the nature of the Florida crandallite as seen in thin section, suggest that the crandallite from Florida can be recognized by its crystal habit (Fig. 2, lower left). The individual crystals of Florida crandallite are platy, hexagonal, and average about 2.5 microns in maximum dimension. The crystals tend to occur (at least in part) in pockets approximately 100 microns across (Fig. 2, upper). In order to confirm the identification of this material as crandallite, the X-ray emission spectrum from a similar region of platy hexagonal crystals was examined using non-dispersive optics and a multichannel analyzer. $\text{CaK}\alpha$, $\text{AlK}\alpha$ and $\text{PK}\alpha$ lines were strong, precluding the possibility of the material being a clay mineral.

Light Microscopy

In thin section the crandallite from Florida is isotropic or very nearly isotropic, pale brown, and stands out with low to moderate relief (Fig. 3). It constitutes the chief matrix mineral of the rock and it is mostly physically separate from the occasional particles of darker brown anisotropic clay. The measured refractive index of crushed fragments of the crandallite is approximately $1.596 \pm .002$. The smaller crushed fragments are colorless and isotropic or nearly so, while the larger aggregates are brown and show very weak birefringence. The optical properties and general appearance in thin section are very similar to the carbonate fluorapatite (francolite) which occurs in phosphorites and phosphatic sediments of Florida, and it seems probable that crandallite may be easily mistaken as francolite.

Differential Thermal Analysis

Differential thermal analyses of fractions (100 mg) of the crandallite concentrate in silica crucibles were made from room temperature

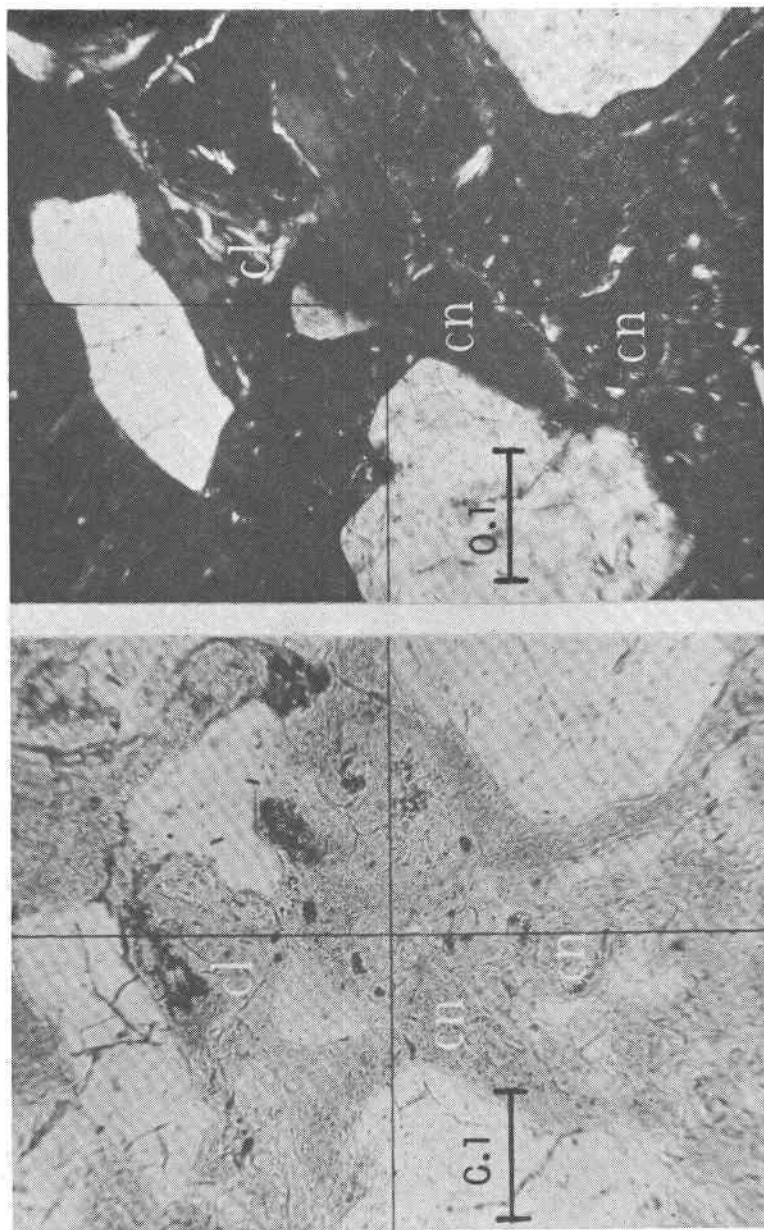


FIG. 3. Photomicrographs of thin section of crandallite-bearing rock. Crandallite (Cn) and clay (Cl). Left plain light, right crossed polars. Scale in mm.

to about 1100°C at 5°, 10°, and 25° per minute. After the analysis the furnace was cooled to 500°C and the heated crandallite concentrate was replaced with a 100 mg sample of quartz; the temperature of the furnace was then raised at the same heating rate used in the analysis. This procedure gave a calibration check on the furnace temperature (quartz inversion at 573°C) and provided a reference for DTA peak magnitudes.

A typical thermogram for the crandallite concentrate is shown in Figure 4. Interpretation of the reactions was facilitated by comparison with the thermogram of pure crandallite (Blanchard, 1971) and by heating samples of the crandallite concentrate to temperatures just above prominent DTA reactions (150°, 250°, 440°, 540°, 620°, 800°, 850°, 1030°, and 1090°); X-ray diffraction patterns were then made from each of these heated samples in order to identify the phases present.

The endothermic reaction at 125° results from loss of adsorbed water. The endotherm at 180° probably results from loss of inter-layer water in montmorillonite. Below this temperature the mont-

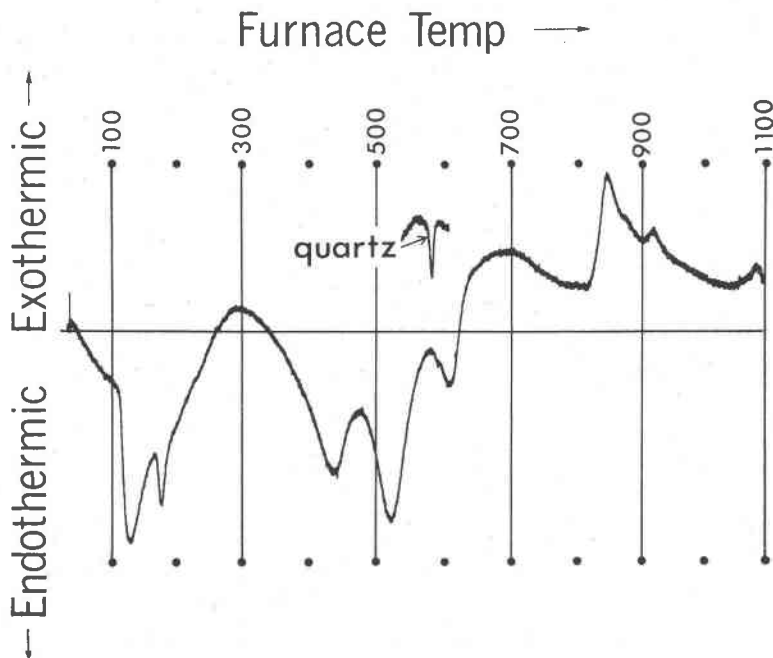


FIG. 4. Thermogram of crandallite concentrate heated at 25°C per minute.

morillonite shows a poorly developed 15 Å diffraction line; after heating to 250° the montmorillonite line has shifted to about 9 Å. The endotherm at 435° corresponds to the disappearance of diffraction peaks for montmorillonite. The endotherm at 525° corresponds to dehydration of crandallite and disappearance of the crandallite structure. The endotherm at 605° is associated with the disappearance of the kaolinite lines. The diffraction pattern between 620° and 800° shows only quartz as well-crystallized and shows a broad hump in the range of 20 to 30° 2θ (Cu-radiation) suggesting the presence of considerable amorphous material. At 845° a sharp exothermic reaction corresponds with the crystallization of AlPO_4 and possibly incipient crystallization of apatite (both produced from the dehydrated crandallite) and at 920° the exothermic reaction corresponds with crystallization of apatite. Actually between 845 and 1030° there appears to be more or less continual crystallization and recrystallization of apatite and AlPO_4 . The exothermic reaction at 1085° is associated with the first appearance of corundum (Al_2O_3 from the dehydrated crandallite residue). The chief difference between the thermal behavior of the crandallite-clay-quartz mixture from Florida and the thermal behavior of pure crandallite from Fairfield, Utah is that in the latter AlPO_4 and apatite appear immediately with the dehydration of crandallite, whereas in the material from Florida the crystallization of AlPO_4 and apatite does not occur until a higher temperature is reached.

DISCUSSION

It is well established that the crandallite in Florida phosphorite is a secondary mineral formed during weathering of phosphatic (apatitic) clayey sediments. Aluminum in the crandallite is derived from clay minerals, while P and Ca are derived from apatite. In addition the apatite seems to be the only available mineral to supply the Sr (and Ce) found in the crandallite. The concentration of SrO in the crandallite is several percent, whereas analyses of four apatite or apatite-rich samples from Florida show only 0.03 to 0.20 percent SrO. Furthermore, the sample showing the highest percentage (up to 0.20 percent) contains appreciable crandallite associated with the apatite. Apparently, during the weathering of apatite, Sr is preferentially taken up in the crandallite resulting in a twenty- to one hundred-fold enrichment of SrO. The ability of alunite-type structures to concentrate Sr has been described by Frondel (1958), and this occurrence of crandallite seems to be an excellent example.

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REFERENCES

- ALTSCHULER, Z. S., E. B. JAFFE, AND CUTTITTA (1956) The aluminum phosphate zone of the Bone Valley Formation, Florida, and its uranium deposits. *U. S. Geol. Surv. Prof. Pap.* 300, 495-504.
- APPLEMAN, D. E., AND H. R. EVANS, JR. (1967) Experience with computer self-indexing and unit cell refinement of powder data (abstr.). *Geol. Soc. Amer. Spec. Pap.* 115.
- BLANCHARD, F. N. (1971) Thermal analysis of crandallite. *Quart. J. Fla. Acad. Sci.* 34, 1-9.
- AND S. A. DENAHAN (1967) Variscite from the Hawthorn Formation. *Quart. J. Fla. Acad. Sci.* 29, 163-170.
- ELBERTY, W. T., AND S. S. GREENBERG (1960) Deltaite is crandallite plus hydroxylapatite (abstr.) *Geol. Soc. Amer. Bull.* 71, 1857.
- ESPENSHADE, G. H., AND C. W. SPENCER (1963) Geology of phosphate deposits of northern Florida. *U. S. Geol. Surv. Bull.* 1118.
- FRONDEL, C. (1958) Geochemical enrichment of strontium in minerals of the alunite structure type (abstr.) *Geol. Soc. Amer. Bull.* 69, 1567-1568.
- HILL, W. L., W. H. ARMIGER, AND S. D. GOOCH (1950) Some properties of pseudowavellite from Florida. *Min. Eng.* 187, 699-702.
- OWENS, J. P., A. S. ALTSCHULER, AND R. BERMAN (1960) Millisite in phosphorite from Florida. *Amer. Mineral.* 45, 547-561.
- PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) *The System of Mineralogy of . . . Dana 7th Ed.*, vol. 2, Wiley, New York.