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The Mineralogy and Chemistry of Urinary Stones from the United Arab Emirates

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هدف هذه الدراسة هو تمييز حصى الكلى من دولة الإمارات العربية المتحدة بواسطة التقنيات المستخدمة في دراسة المعادن ومقارنة أنسجتها مع الصخور في الطبيعة . لقد تم دراسة ستة وعشرين من حصى الكلى بتعريضها للتحاليل الكيميائية والأشعة السينية والحرارية والمجهر المستقطب . وقد بينت النتائج أن الحصى تتكون من ٤ مجموعات هي : مجموعة الفوسفات (ستر وفيت ، يهرنيت ، بودوليت ، وفوسفات آمونيا الكالسيوم المائية) وتشكل ما نسبته ٥ , ١١٪ من مجموع الحصى ، مجموعة الاكسالات (وهولايت وقليل من الودلايت) وتشكل ٥ , ٣٨٪ ، ثم مجموعة اليوريا (يوريكيت) وتشكل ٥ , ١١٪ من المجموع ثم مجموعة مشتركة التركيب وتشكل ٥ , ٣٨٪ . أن التقنيات المستخدمة في دراسة المعادن مثل استخدام المجهر المستقطب والتحليل الحراري قد قدمت نتائج دقيقة ومفصلة أكثر مقارنة مع طرق التحليل الكيميائي للحصى . لقد تم مناقشة عوامل التغذية والمناخ وتأثيرها على تكون الحصى في دولة الإمارات العربية المتحدة .

Key Words: Mineralogy, Urinary stones, Chemsitry, X-ray, DTA, TGA, Texture, United Arab Emirates

ABSTRACT

The purpose of this study is to characterize urinary stones from the United Arab Emirates using mineralogical techniques and compare it with stones in nature. Twenty six urinary calculi were subjected to chemical analysis, XRD, DTA, TGA and polarizing microscopy. The results show that the calculi belong to one of the four groups; namely phosphate (struvite, dehrenite, podolite, and ammonium calcium phosphate hydrate) making 11.5 % of the stones. Oxalate (whewellite and minor weddellite) 38.5%, urates (uricite) 11.5 %, and mixed type 38.5 %. Common mineralogical methods like the use of polarizing microscopy and thermal analysis proved to be a sensitive tool in the investigation of urinary calculi and gave more information than chemical analysis. The role of dietary factors and climate are discussed in relation to renal stones in the United Arab Emirates.

INTRODUCTION

Urinary stones have become increasingly common in most parts of the world [1-3]. Calculous disease of the urinary tract is common in the United Arab Emirates [4], but reports on the disease are scarce. Several studies have examined the factors predisposing to the formation urinary and kidney stones [5-9]. The analysis of urinary calculi only by chemical methods is rather unsatisfactory [10,11]. Polarized light microscopy has found application in many fields of scientific study but has been little used in solving medical problems. It is extensively used by mineralogists in the identification of natural and synthetic minerals and rocks and their textural relations. Calculi are closely analogous to natural minerals and their study by physical methods can shift the problem from the time-consuming chemical assaying to simple inspection of a stone thin section [10,11]. Common mineralogical methods include the use of polarizing microscopy, thermal analysis and X-ray diffraction

METHOD OF STUDY

Laboratory work have been carried out on 26 calculi samples obtained from the Department of Urology, Tawam Hospital. Analyses have been carried out at the Central laboratories of the Egyptian Geological Survey and Mining Authority (Cairo) . Mineralogical studies include X-ray diffraction (XRD), thermal analysis (TA), polarizing microscopy, and scanning electron microscopy (SEM). XRD analyses were carried out using a Phillips X-ray diffraction equipment model PW/1710 with Ni-filter, Cu-radiation at 40 kV, 30 mA and scanning speed of 0.02 degree/s. The reflection peaks between $2\phi = 2$ and 60 degree were determined. The corresponding spacing (d,A) and relative intensities (I/Io) were acquired and compared with standard data (A.S.T.M. Cards). The results are recorded in Table 1. Scanning electron microscopic photographs were obtained for 2 calculi samples (C-1 and C-3) using SEM model JEOL, JEM-T20, with accelerating voltage 19 KV, magnification 35X up to 10000X and resolution 200A. Thermal analysis (differential thermal DTA, and thermogravimetric TGA) were done by means of Shidadzu DTA-50 and TG-50. Four powdered stone samples were heated, by 10°C/min, up to 1000°C for DTA and TG with Al2O3 as a reference material. Chemical analysis of P2O5 were carried out by gravimetric method using citro ammonium molybedate. CaO and MgO were determined by titration against EDTA. Na2O, K2O, Fe2O3 and MnO were analyzed by using atomic absorption (Perkin Elmer 1100). Determination of C, H and N were determined for 7 samples using HERAEUS equipment. Thin sections were prepared in longitudinal and transverse orientations after impregnation of samples with araldite resin under vacuum. Some of the stones were large enough to carry out all necessary investigations (e.g. C-1 to C-5, C-9, C-16, C-18, C-22 and C-24) while others were too small to fulfil the task. In the latter case, the available amounts were used mainly for X-ray diffraction analysis.

RESULTS

X-Ray Diffraction

Powder diffraction and megascopic descriptions of the investigated stones are given in Table 1. According to these results, the stones can be divided into the following groups:

1- Phosphate stones (Samples C-2, C-15, and C-22):

These stones consist mainly of struvite, dehrenite and podolite (A.S.T.M. card No. 15-762, 569, and 570 respectively). Ammonium calcium phosphate hydrate is present as a trace (A.S.T.M card No. 22-35). These represent 11.5 % of the investigated calculi.

2- Oxalate stones (Samples C-1, C-5, C-6, C-9, C-10,C-12, C-18, C-20, C-21, and C-25).

The stones represent up 38.5 % of the investigated calculi. They consists only of whewellite (A.S.T.M. card No. 20-231). Weddellite (A.S.T.M. card No. 17-762) was observed as minor mineral only in one sample.

3- Urate stones (Samples C-8, C-11, and C-16)

Uricite (A.S.T.M. card No 28-2016) forms the major mineral in these stones, whereas whewellite occurs as a minor or as a trace mineral. They represent 11.5% of the investigated stones. It is noteworthy to mention that stones C-11 and C-16 belong to the same patient. C-11 passed from the patient two years before C-16. However, both have the same major mineralogical composition (uricite) but differ in the amount of whewellite which was more concentrated in C-16 (Table 1).

4- Mixed stones (Samples C-3, C-4, C-7, C-13, C-14, C-17, C-19, C-23, C-24, and C-26)

These stones are a mixture of group 1 and 2 and represent 38.5 % of the total stones.

PETROGRAPHY

1- Phosphate stones (Samples C-2, C-15, and C-22, Figs. 1A-1D)

The stones range from a creamy white and chalky to buff or brown (Fig. 1a) and are characterized by zoned texture composed of alternating colorless and thin brownish layers (Fig. 1B). The concretion is built around a non-crystalline reddish brown core. Similarly, the brown layers are isotropic and non-crystalline while the colorless layers are distinctly crystalline and consist of radial crystals of struvite and/or podolite. The brown layers are mainly ammonium calcium phosphate hydrate as evident from X-ray powder diffraction study.

2- Oxalate stones (Samples C-1, C-5, C-6, C-9, C-10,C-12, C-18, C-20, C-21, and C-25)

Most of these stones are brown in color and vary in shape from spheroidal to irregular-shaped masses (Figs. 2A, Table 2). The stones are dense and hard. They show well developed colloform texture with alternating pale brown and colorless laminae of whewellite (Figs. 2B). The laminae are concentrated around a deep red brown amorphous core. The crystals are mostly fibrous. Crystallization increases toward the rim of the stones.

3- Urates (Samples C-8, C-11, C-16)

The urate stones are small and tend to have an oblate or near spheroid shape (Fig. 3A). The grains have prismatic shape with interlocking texture (Fig. 3B). The uricite crystals may show distinct parting. The periphery consists of alternating thin laminar films with radial striations.

4- Mixed types (Samples C-3, C-4, C-7, C-13, C-14, C-17, C-19, C-23, C-24, and C-26).

Some stones are of mixed composition (phosphate + oxalate). They are formed mainly of whewellite which occurs either as colorless radial crystals or brown amorphous to microcrystalline grains. The interspaces between whewellite laminae are filled with brown microcrystalline phosphate mainly podolite and/or dehrenite which form the cementing material. The texture is mainly colloform. Spindle shape texture was observed in one sample (Fig. 4A). The crystalline form of whewellite commonly replaces the amorphous portions.

Differential Thermal Analysis (Dta) And Thermogravemtric Analysis (TGA)

The thermal and thermogravimetric characteristics of 2 representative samples are given in Figures 5 and 6. Temperatures of the endothermic and exothermic reactions are characterized by the temperature at the crest of their peaks. In the phosphate stones (struvite, podolite and ammonium calcium phosphate hydrate), a symmetric broad endothermic DTA peak occurs at 128.2°C. In the oxalate stones (whewellite), two endothermic peaks are found; one is small and symmetric and occurs at 64.2°C, and the second is large, symmetric and occurs at 204.7°C. These peaks are accompanied by a slight loss in weight as represented by the TGA curves. Peaks which occur at temperature below 150°C are mostly due to the loss of hygoscopic water. The second endothermic peaks in the oxalate stones are mainly due to the loss of water of crystallization. These peaks occur at a temperature range of 338.1°C to 381.1°C in the phosphate stones and are mainly due to the loss of ammonia and water of crystallization. The presence of three peaks is due to the presence of three different phosphates (struvite, podolite and ammonium calcium phosphate). Two small exothermic DTA peaks occur at the temperature range 446.7°C to 698.1°C in the phosphate stones. The first one represents dehydration and the second represents recrystallization of Mg-hydrogen phosphate to Mg-pyrophosphate. Most of loss in weight corresponds to the endothermic peaks, whereas loss in weight due to the exothermic peaks is minor. Three exothermic peaks occur at 408°C to 501.4°C in the oxalate stone. These peaks represent a structural change of anhydrous Ca-oxalate to Ca-carbonate and loss of CO gas. All Ca-oxalate change to Ca-carbonate at 652.8°C. The decomposition of Ca-carbonate is represented by large asymmetric endothermic peak at 779.8°C. The loss in weight is gradual and in different stages

CHEMICAL ANALYSIS

The results of chemical analysis (Table 3) confirm the mineralogical results. Chemical analysis of the phosphate calculi indicates that the stones consist mainly of P2O5, MgO, CaO, C, H, and N. They belong to the non-infection stones (Category I) of Abdel-Halim [12]. Mineralogically, these stones consist of struvite, podolite and amounium calcium phosphate. In comparison, the oxalate calculi are poor in P2O5, MgO and rich in CaO and C. The mixed calculi are mainly oxalate and are rich in CaO and P2O5 whereas MgO is relatively low. The oxalate and the mixed types calculi belong to the infection stones (Category II) of Abdel-Halim [12]. The urate calculi are rich in C and N, similar to uric acid stones (UrI4) described by Abdel-Halim [12].

DISCUSSION

Table 1. shows that the major component of urinary stones from the United Arab Emirates (UAE) is calcium oxalate (pure and mixed types ~ 77 %), confirming Sutor's [13] observation that urinary stones in the developing countries have the same composition as those in industrialized countries where calcium oxalate constituted 55-75 % of the urinary stones. However, the percentage incidence of phosphate, urate and oxalate stones is lower than that reported in Saudi Arabia [14-15], Iraq [16], Jordan [17], Egypt [18] and similar to that reported from western countries [10, 11, 20, 21]. Oxalate stones and mixed type of oxalate-phosphate stones seem to be the most common type which is in agreement with other reports from industrialized countries [20, 21]. Anderson [23] suggested that in the developing countries there appears to be a direct relationship between the overall incidence of urinary stones and the rise in the standard of living. Epidemiological observations suggested that dietary changes especially an increase in the intake of both animal proteins (fish and meat) and refined carbohydrates, lead to an increase of urinary stones, mainly oxalate and urate [24, 25]. The diet of the people of the UAE is rich in protein , carbohydrates, oxalate and sugar. The increase in the intake of animal proteins and carbohydrates (over the past 30 years) in the UAE may lead to an increase of oxalate and urate stones . However, the climatic conditions undoubtedly have some bearing on the high incidence of urinary stones in the UAE. The climate is very hot and humid and the temperature may exceed 50oC in summer. It seems likely that this climate plays a major role in the incidence of urolithiasis [22, 23, 25].

This study suggests that urinary stones in the UAE can be attributed to better socioeconomic status approaching a pattern similar to that of industrialized counties. Finally, a high ambient temperature and dehydration are probable causative factors. The triggering mechanism, however, may lie in enzyme disorder, bacterial infection and/or heredity. The effect of these factors need a detailed medical study.

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Table 1. Results of X-ray diffraction study in the investigated samples.

Sample No.	Mineralogy Major	Minor	Trace	Morphology
			1-Phosphate	
C-2	struvite	podolite	ammonium calcium phosphate	pale yellow to white, fine-grained, massive, rounded to sub-rounded, 5 cm in size, smooth outer surface
C-22	struvite	dehrnite podolie	....	similar to C-2, 2 cm in size
C-15	podolite	struvite	....	white with yellow staining, very fine- grained, irregular shape, smooth surface, 0.1 to 1 cm in size.
			I1- Oxalates	
C-1	whewellite	....	....	pale brown to yellow, granulated, 0.5 cm in size
C-5	whewellite	....	....	yellow to brown, star-shaped with more than 6 arms, 3 cm in size.
C-6	whewellite	....	....	pale brown, massive, 0.5 cm in size
C-9	whewellite	....	....	pale yellow to white, botryoidal structure, 0.2 to 0.4 cm in size
C-10	whewellite	....	....	pale brown to white, oval, 0.3 to 0.6 cm in size.
C-12	whewellite	....	....	pale brown to white, rugged surface, 0.1 to 0.3 cm in size
C-18	whewellite	....	....	white with yellow patches, finegrained, rugged surface, 0.4 cm in size
C-20	whewellite	weddellite	....	pale brown, granulated to shreds, 0.1 to 0.2 cm in size
C-21	whewellite	....	....	yellow to white, smooth surface, 0.9 cm in size
C-25	whewellite	....	....	white, smooth surface with dark brown patches, 1 cm in size
			II1- Urates	
C-8	uricite	whewellite	....	pale brown to white, elongate, 1 cm in size
C-11	uricite	....	whewellite	pale yellow, circular, smooth surface 0.2 to 0.5 cm in size
C-16	uricite	whewellite	....	white, rounded to oval, smooth surface, 0.1 to 0.4 cm in size

Sample No.	Mineralogy Major	Minor	Trace	Morphology
1V -Mixed type (Phosphat - Oxalates - Urates)				
C-3	whewellite	....	dehrnite podolite	pale brown with white patches, fine to coarse-grained, ellipsoidal with botryoidal structure, uneven surface.
C-4	whewellite	whewellite	struvite	fine-grained white, 2 cm in size with hair-growth 4 cm long, pale brown.
C-7	whewellite	....	weddellite dehrnite Struvite	pale yellow, elongate with angular outline, 1 cm in size.
C-13	whewellite	whewellite dehrnite	....	white, yellow spots, rugged surface, 0.1 to 1 cm in size
C-14	whewellite	dehrnite whewellite	....	pale brown to white, shapeless, 1.5 cm in size with rugged surface
C-17	whewellite	dehrnite	whewellite	pale brown, conical, rugged surface, fine-grained, massive sub-rounded with rugged surface, 0.6 cm
C-19	whewellite whewellite	podolite	dehrnite podolite	pale brown, fine to medium-grained, rugged surface, 0.5 cm in size
C-23	whewellite	dehrnite	....	very paleyellow to white, fine to medium-grained,
C-24	whewellite	weddellite		rugged surface, 0.5 cm in size
C-26	dehrnite	whewellite whewellite	....	yelloish to white, rugged surface shapeless, 1 cm in size.

Struvite : NH4MgPo4.6H20

Dehrnite : (Ca, Na, K) 5 (PO4, CO3) 3 (OH)

Podolite : (Ca10 (PO4) 6CO3. H20

Ammonium calcium phosphate: NH4Ca2H3 (P207) 2H20

Whewllite: C2CaO4. H20

Weddellite C2CaO4. 2H20

Uricite C4 (NH) O2C(NH)20

Table 2. Physical and optical properties of detected phases.

Mineral	whewellite monohydrate	weddellite dihydrate	struvite	dehrnite	dehrnite
System	momclinic	tetragonal	orthorhombic	monoclinic	orthorhombic
Habit	equitant to anhedral	pyramidal or short prismatic	equant, wedgey globular	massive, reniform	granular, prismatic
Twin	common, heart-shaped prismatic	....	common (001)	common (1121)	parting
Cleaveage	good (101)	....	good (001)	poor (0001)	good
Fracture	conchoidal	conchoidal	conchoidal	conchoidal	conchoidal
Hardness	2.5-3.0	4	2	5	2.5
Specific gravity	2.23	1.94	1.711- 1.07	2.9-3.1	1.9
color	colorless or brown	colorless to yellowish	colorless	colorless to pale yellowish brown	colorless
Extinction angle	31	0	0	0	0
Interference figuyr	biaxial +	uniaxial	biaxial +	uniaxial -	?
Birefrengence	high	low	werylow	low	high

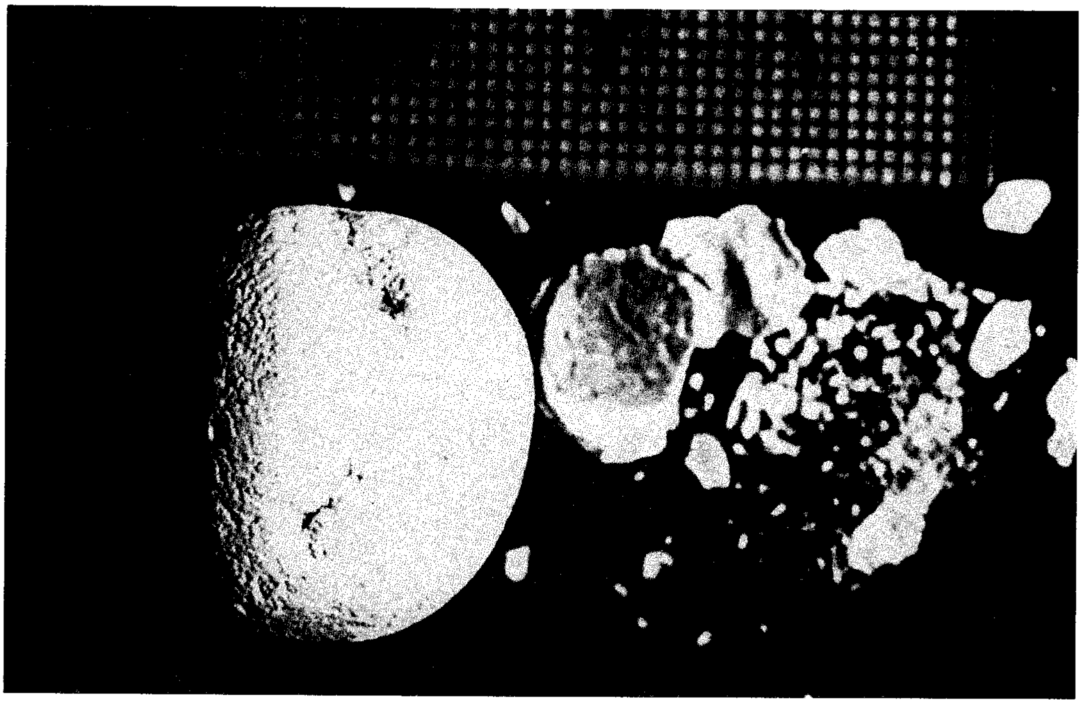

Fig. 1 A

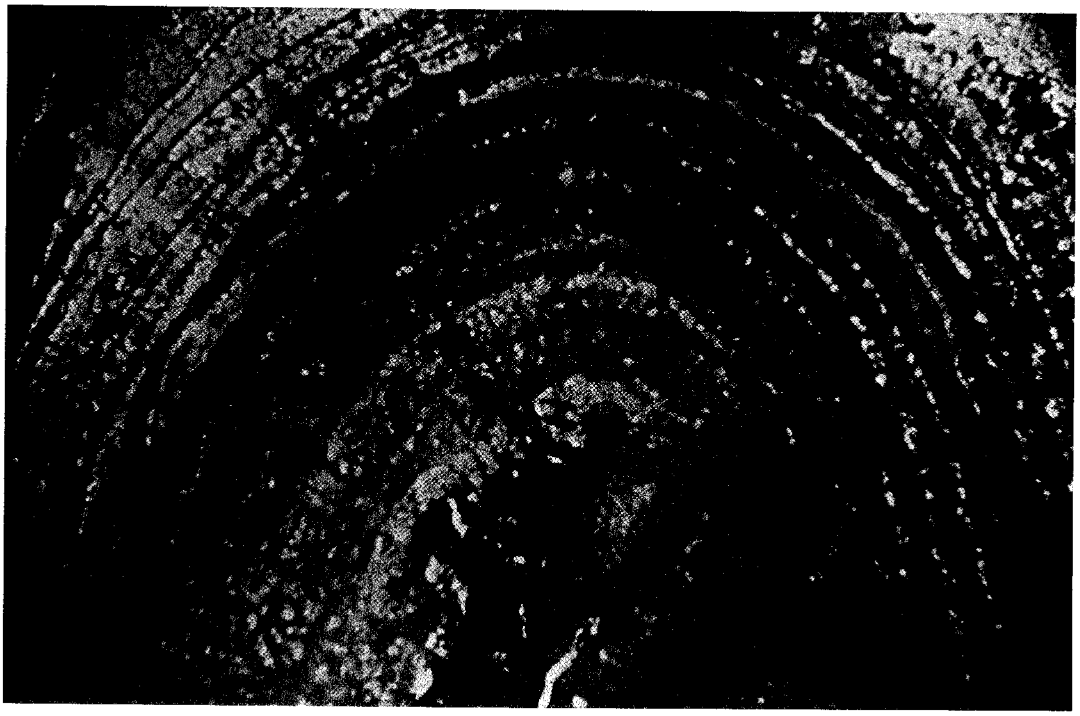

Fig. 1 B

Fig. 1. Phosphate calculus. A, struvite calculus with smooth surface. B, photo micrograph of the struvite calculus under plane polarized light showing zonal texture (X 12.5).

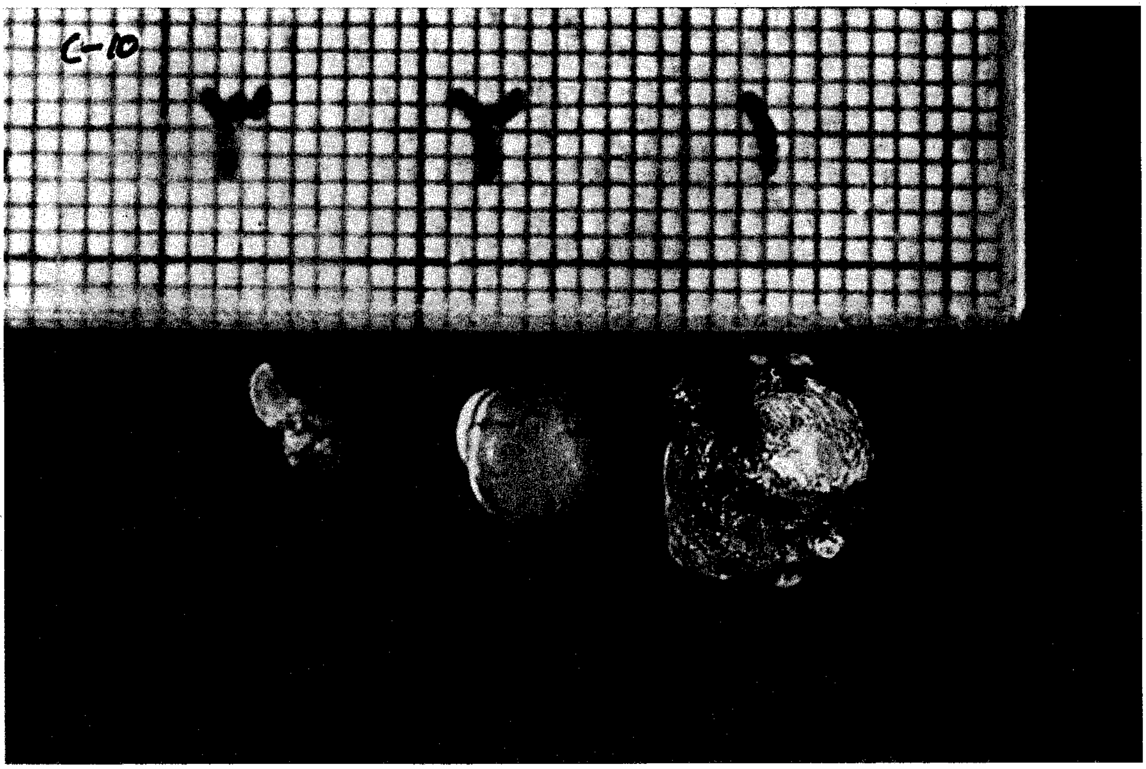

Fig. 2 A

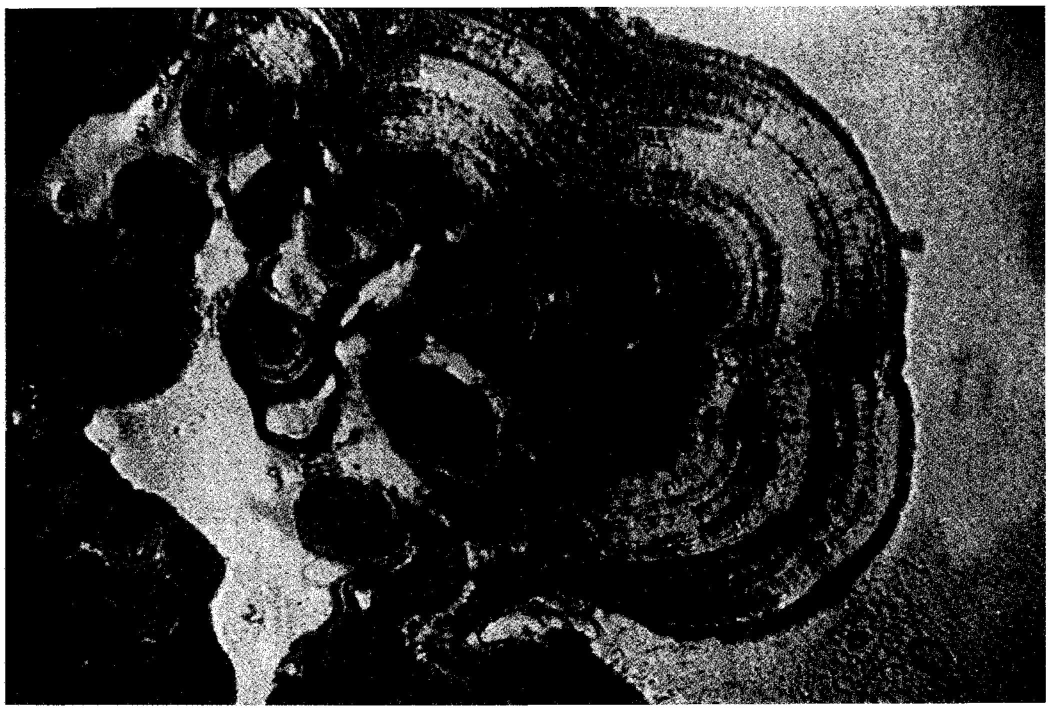

Fig. 2 B

Fig.2. Oxalate calculus. A, ellipsoidal whewellite calculi with botroidal structure B, photomicrograph of the same calculus showing colloform texture with alternating laminae of whewellite (X 12.5).

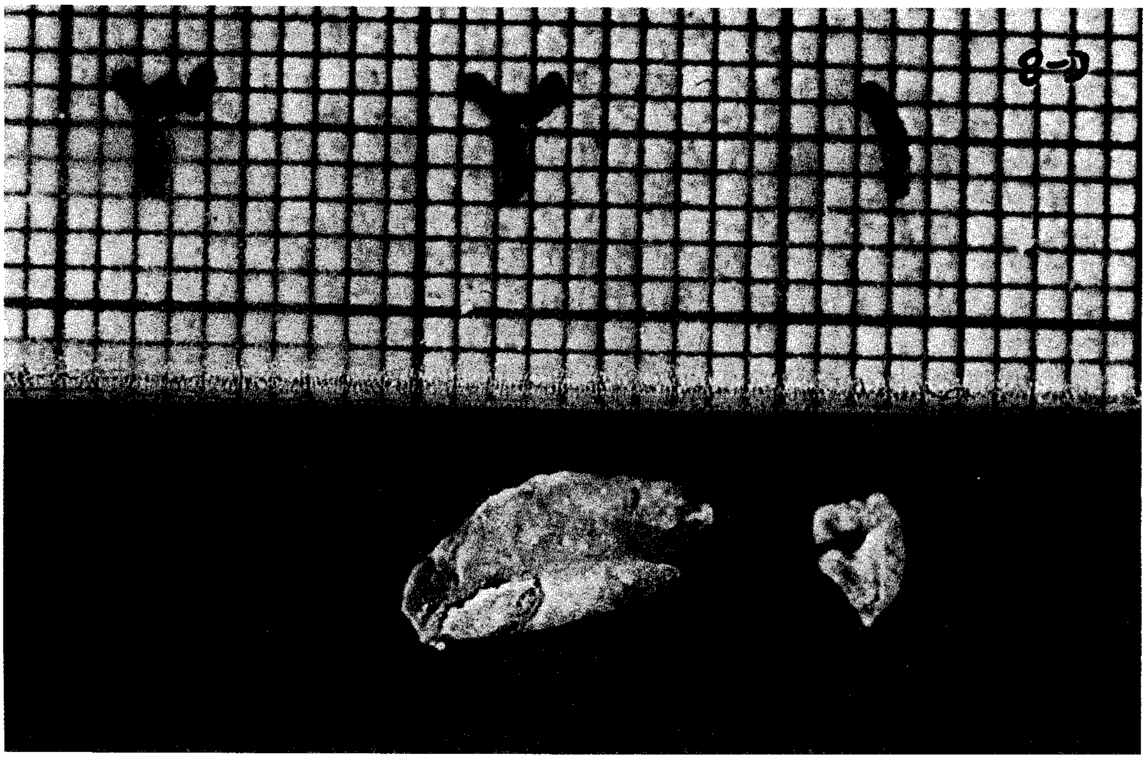

Fig. 3 A

Fig. 3 B

Fig.3. Urate calculus. A, white rounded to oval shaped uricite calculus. B, Photomicrograph of the same calculi showing interlocking crystal intergrowth (X 39).

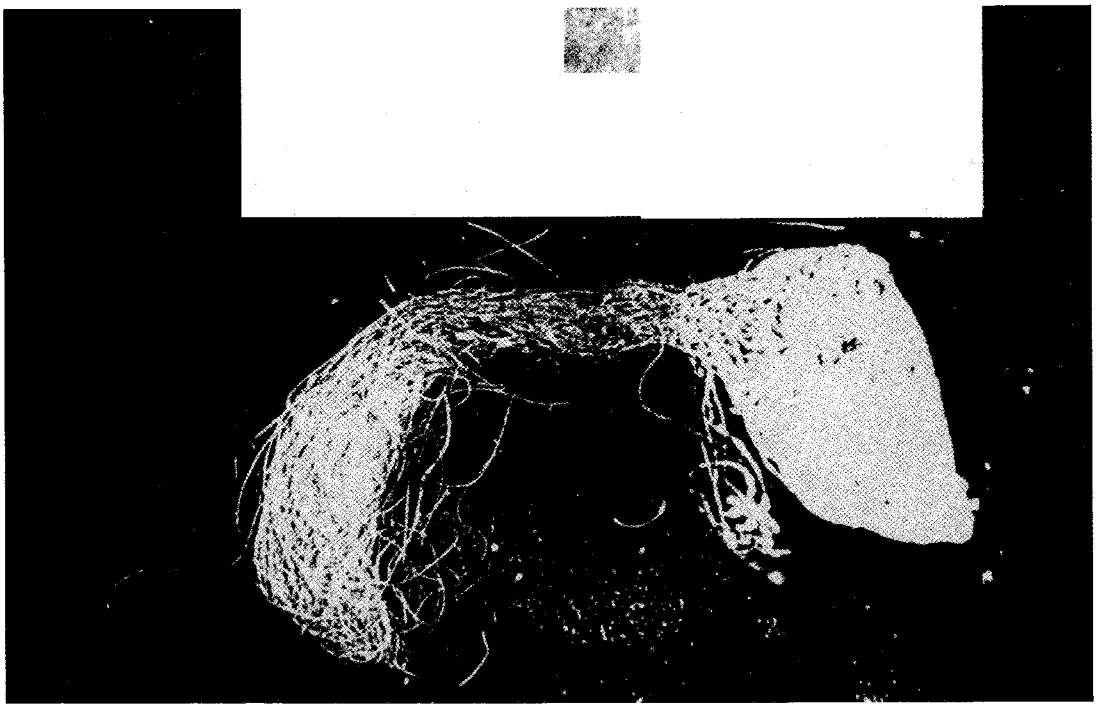

Fig. 4 A

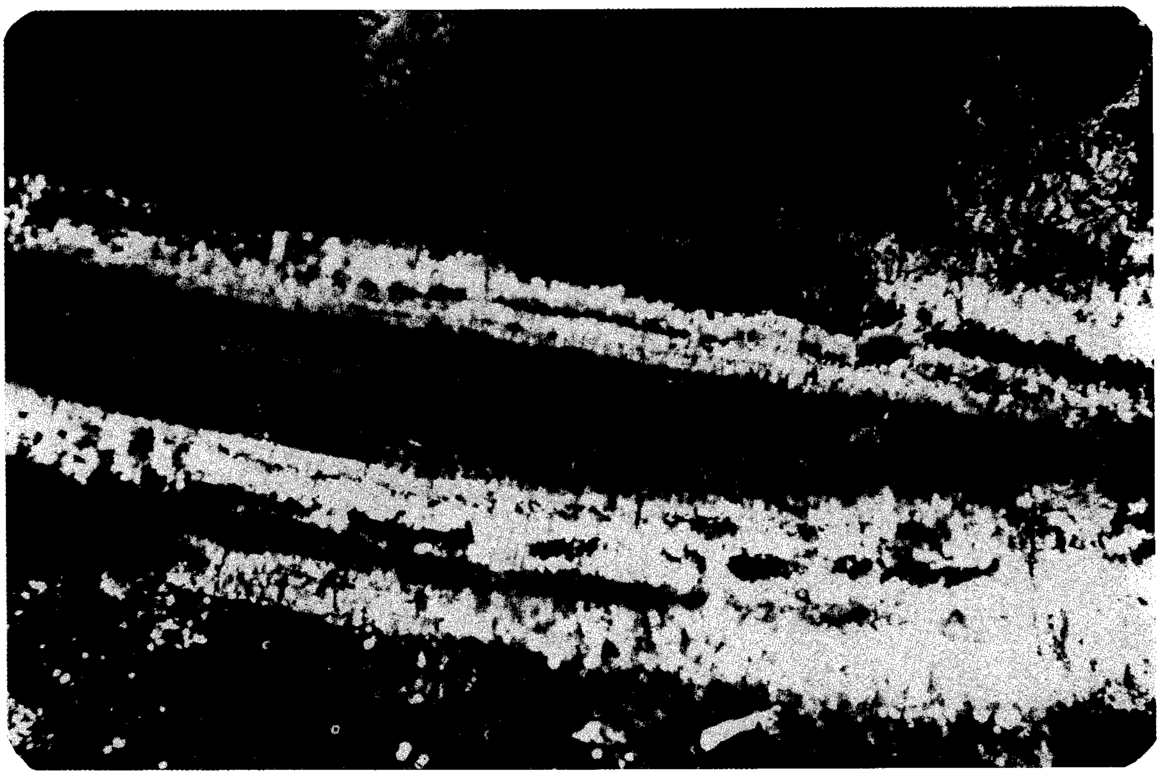

Fig. 4 B

Fig. 4. Mixed-type calculus. A, calculus grown on hair. B, photomicrograph of the same sample showing spindle shaped whewellite and microcrystalline podolite in the interspaces between the whewellite spindles (X 12.5)

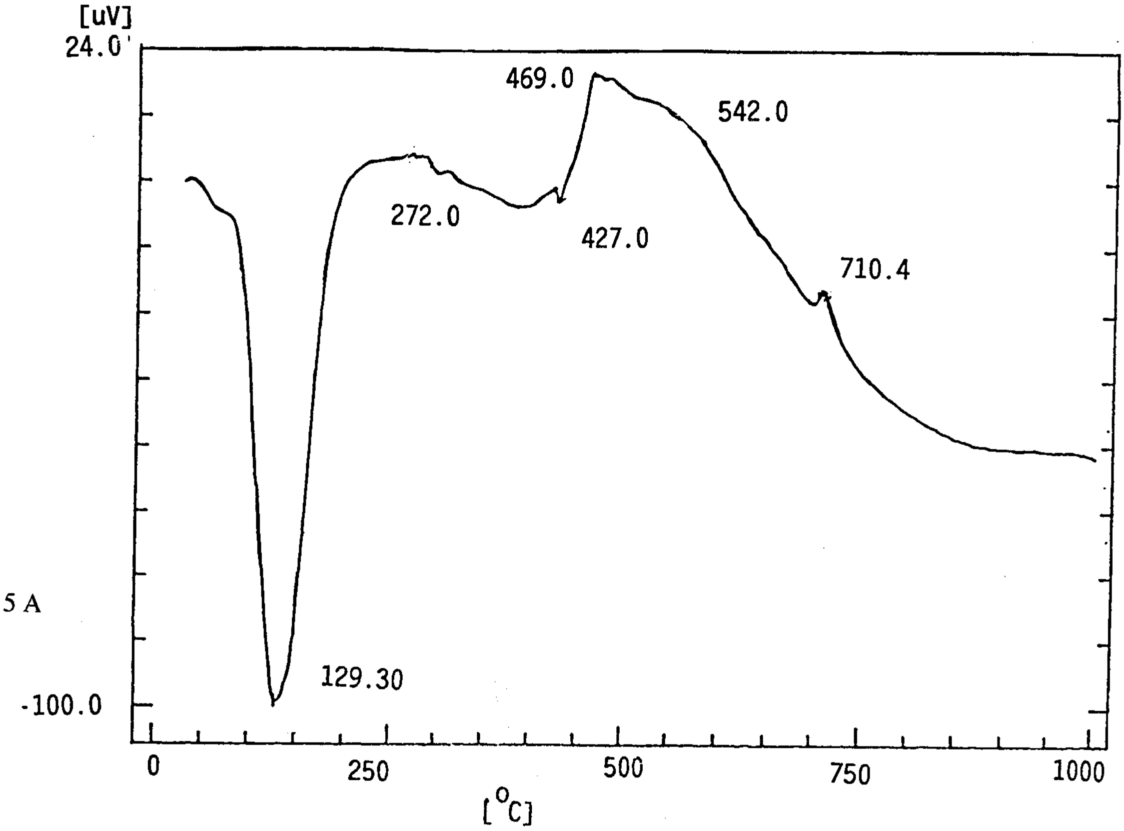

Fig. 5 A

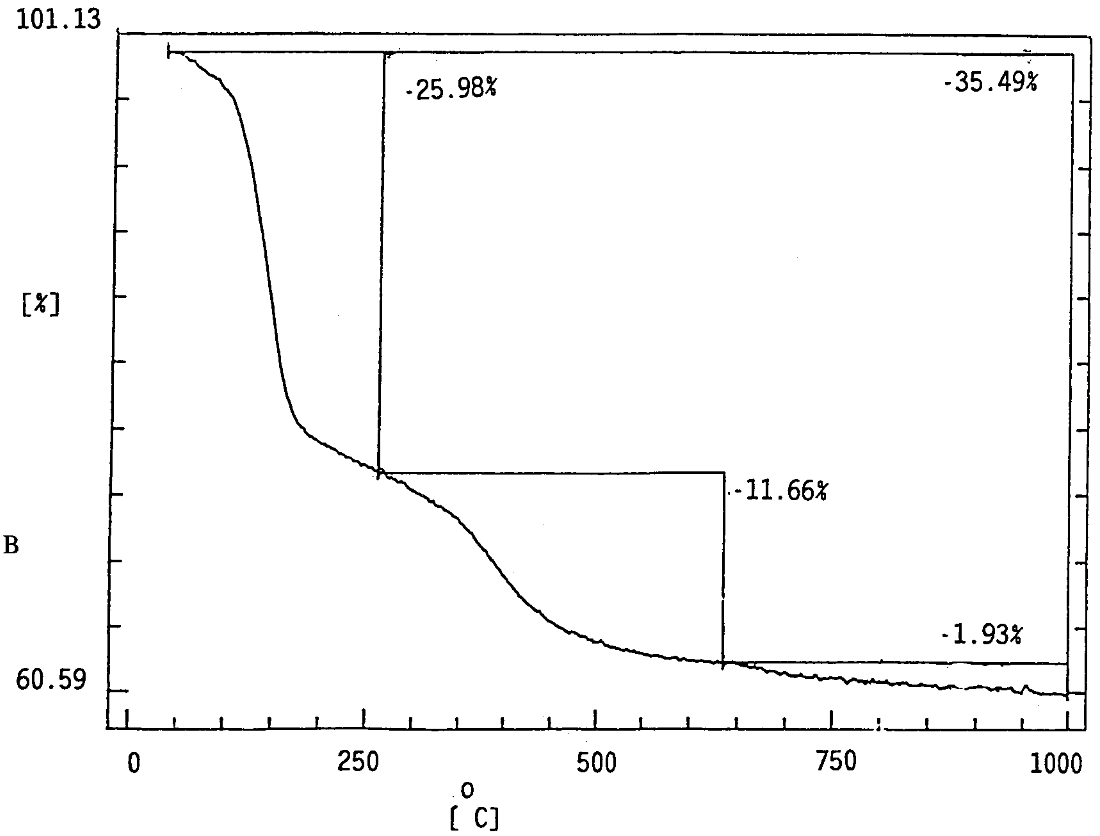

Fig. 5 B

Fig. 5. DTA diagram of phosphate calculus C-2 which consists mainly of struvite and minor podolite and ammonium calcium phosphate hydrate. B: TGA diagram of the same calculus.

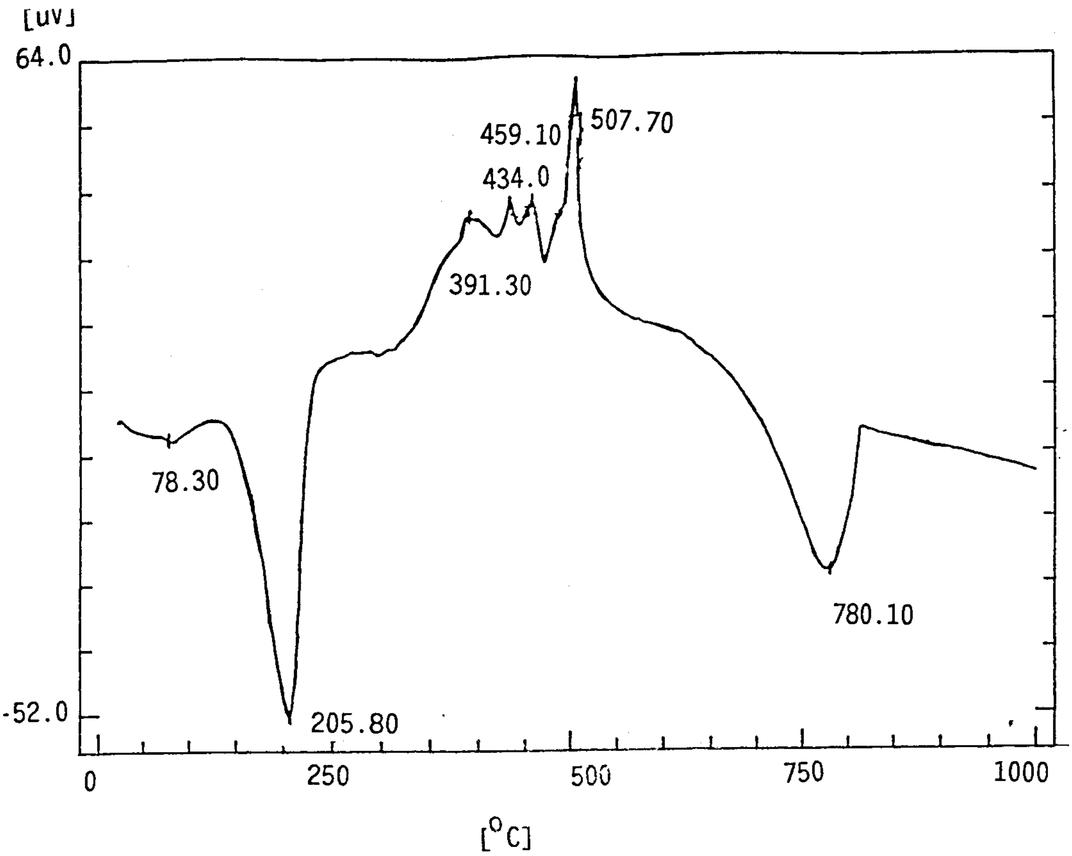

Fig. 6 A

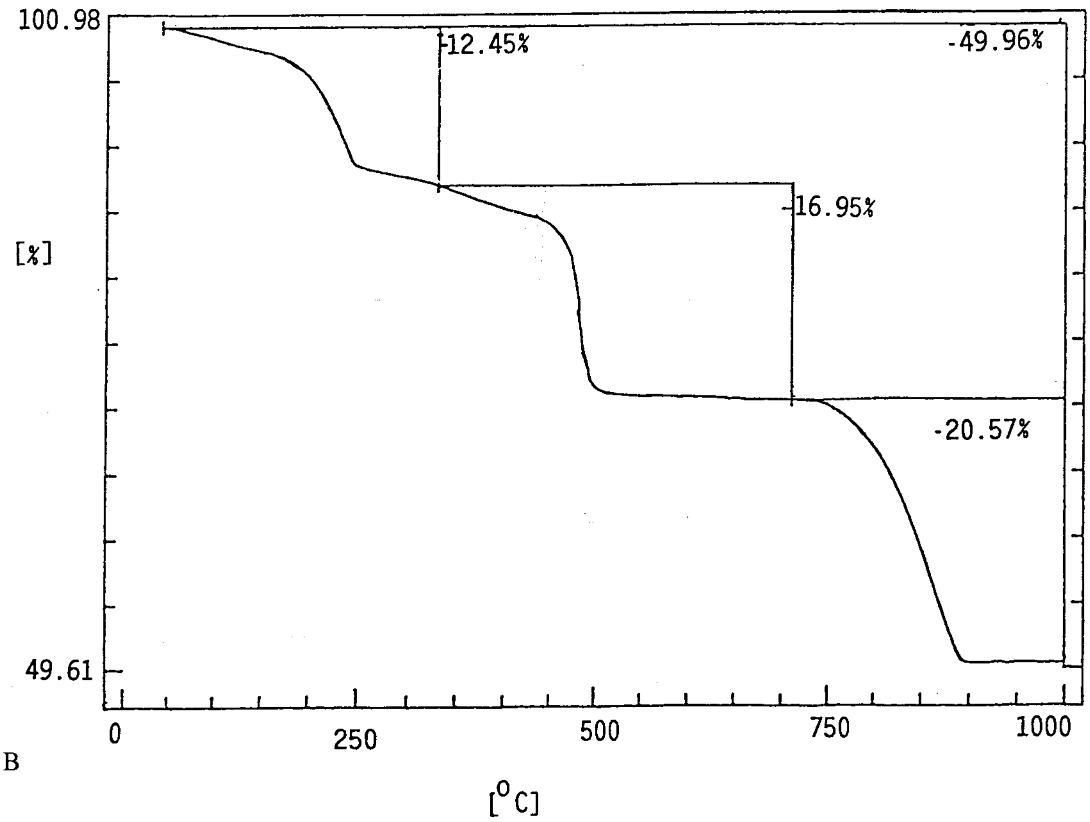

Fig. 6 B

Fig. 6. DTA diagram of oxalate calculus C-5 which consists only of whewellite. B: TGA diagram of the calculus C-5 showing gradual loss in weight.