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MINERALOGICAL AND CHEMICAL INVESTIGATIONS OF UROLITHIASIS

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More than 1250 urinary calculi were studied mineralogically and about 350 of these samples were analysed chemically. In general, Si, Al, Na, K, Mg and Sr analyses were carried out on the samples, and Fe and Zn analyses on some of them. Statistical analyses were made on the results of the chemical analyses of the kidney stones, and the regional distribution of the stones with different mineralogical compositions was also investigated. The distribution of the stones in the urinary system was investigated as regards their positions in kidney, ureter and bladder, and also their distribution among male and female patients.

Results of Mineralogical Analyses

1273 samples were used in the mineralogical analyses of the kidney stones. These samples were taken during the operations carried out on the patients in seven provinces, the most important of these sample groups being that obtained from the Hacettepe University Hospital. Since the samples obtained from Hacettepe were from patients coming from different regions, they should be regarded as a sampling of Turkey in general. X-ray diffraction analyses carried out on 946 samples of the Hacettepe group showed that 37.6% of the kidney stones were composed of only whewellite, 31.0% of them were composed of a mixture of whewellite + weddellite, 11.7% of struvite, and 5.0% of whewellite + ammonium acid urate. Thus, we see that more than 85% of the kidney stones were composed of these four mineralogical groups and that two-thirds of them were either whewellite or a whewellite + weddellite mixture. In the mineralogical analyses of 70 urinary system stones from the province of Eskişehir far more stones were found to be composed of only weddellite and of the mineralogical associations of struvite + ammonium acid urate, and of whewellite + weddellite + ammonium acid urate than was the case with the Hacettepe samples.

The mineralogical analyses of 53 urinary system stones from the province of Kayseri, have shown that in comparison with the Hacettepe sample group there is an obvious

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increase in the samples composed of pure whewellite and struvite and an obvious decrease in the samples composed of whewellite + weddellite mixtures.

In the mineralogical analyses carried out on 47 urinary system stones from the province of Sivas, the percentage of the samples containing pure whewellite and struvite is also very important. Furthermore, among the patients of this province, there is a notable increase in the number of mineralogical combinations of whewellite + ammonium acid urate and samples with cystine.

In the 72 urinary system stones obtained from the province of Samsun, the percentage of samples with whewellite - weddellite combination is higher than that of the Hacettepe sample group. It is interesting to note, however, that the frequency of the whewellite + ammonium acid urate combination is lower.

Of the 59 urinary system stones from the province of Erzurum, half of them are composed only of whewellite. In the other half whewellite + weddellite, whewellite + ammonium acid urate and struvite are frequently found.

The major mineral types and the mineralogical compositions in the urinary system stones of the patients in the province of Muğla are whewellite, whewellite + weddellite, and hydroxyapatite.

Existing Places of Stones in Urinary System

As a means of investigating the possible relation between the mineralogical compositions of the stones observed in the urinary system and the organs (kidneys, ureter, bladder) where they are found, the distribution of the stones with available status is given in Table II.

The point observed in this table is that about half of the ureteral system stones under investigation are in the kidneys and the rest of them are about equally distributed between the ureter and the bladder. The stone minerals and combinations most commonly found in the kidneys are whewellite, whewellite + weddellite and struvite. The stones with these mineralogical compositions can also be seen with approximately the same frequency in the ureter. Although the stones of whewellite, and with a combination of whewellite + weddellite, are common in the bladder, the big change here is in the quantity of stones composed of struvite, whewellite + uric acid and uric acid only. In particular, this last type of urinary organ stone shows a relatively big increase.

Distribution According to Sex of Urinary System Stones

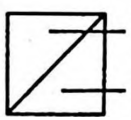
In Tables III a and b the distribution according to sex of urinary system stones is set down in actual figures and again as a percentage. From these tables it is apparent that:

TABLE I

Distribution According to Mineralogical Composition of the Urinary System Stones of Patients Coming from Different Regions

Origin of the sample	whew.	wed.	whew. + wed.	UA	Hap.	str.	AAU	whew. + UA	whew. + AAU	str. + AAU	whew. + wed. + AAU	whew. + wed. + UA	Cyst.	whew. + Hap.	whew. + UA	Total sample / %
Hacettepe	356 / 37.6	24 / 2.5	293 / 31.0	16 / 1.7	13 / 1.4	111 / 11.7	9 / 1.0	37 / 3.9	48 / 5.0	5 / 0.5	7 / 0.7	5 / 0.5	6 / 0.6	16 / 1.7	0 / 0	946 / 99.8
Eskişehir	25 / 39.0	5 / 7.8	18 / 28.0	0 / 0	1 / 1.5	7 / 10.9	0 / 0	3 / 4.7	1 / 1.5	2 / 3.1	2 / 3.1	0 / 0	0 / 0	0 / 0	0 / 0	64 / 99.6
Kayseri	23 / 43.0	1 / 1.9	9 / 17.0	0 / 0	1 / 1.9	8 / 15.0	0 / 0	3 / 5.7	4 / 7.5	1 / 1.9	0 / 0	0 / 0	0 / 0	0 / 0	3 / 5.7	53 / 99.6
Sivas	20 / 43.9	1 / 2.1	10 / 21.7	0 / 0	0 / 0	7 / 15.2	0 / 0	0 / 0	5 / 10.3	0 / 0	0 / 0	0 / 0	2 / 4.3	1 / 2.1	0 / 0	46 / 99.6
Samsun	27 / 37.5	0 / 0	28 / 38.9	2 / 2.8	0 / 0	7 / 9.7	0 / 0	3 / 4.2	1 / 1.4	1 / 1.4	1 / 1.4	1 / 1.4	0 / 0	1 / 1.4	0 / 0	72 / 100.1
Erzurum	30 / 50.0	1 / 1.7	12 / 20.3	0 / 0	0 / 0	5 / 8.4	0 / 0	3 / 5.0	6 / 10.2	0 / 0	2 / 3.4	0 / 0	0 / 0	0 / 0	0 / 0	59 / 99.7
Muğla	11 / 33.0	0 / 0	13 / 39.4	1 / 3.3	4 / 12.0	2 / 6.0	0 / 0	2 / 6.0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	33 / 99.7

whew: whewellite, wed: weddellite, UA: uric acid,
Hap: hydrocsiapatite, str: struvite, AAU: Ammonium acid urate, cyst: cystine



Number of samples in which the mineral is observed,
percentage of this observation

TABLE II

The Mineralogical Species of the Urinary System Stones and their Distribution in the Urinary System

	whew.	wed.	whew. + wed.	UA	Hap.	str.	AAU	whew. + UA	whew. + AAU	str. + AAU	whew. + wed. + AAU	whew. + wed. + UA	cyst.	whew. + Hap.	wed. + UA	Total observed
Kidneys	185	14	152	7	12	48	2	17	25	3	3	1	2	6	1	478
Ureter	81	3	62	0	1	14	2	4	12	1	2	1	2	3	0	188
Bladder	42	0	23	7	2	36	0	13	7	1	4	3	1	3	2	144

TABLE III

Distribution as to Sex of Stones with Different Mineralogical Composition

a) In actual numbers

Patients	whew.	wed.	whew. + wed.	UA	Hap.	str.	AAU	whew. + UA	whew. + AAU	str. + AAU	whew. + wed. + AAU	whew. + wed. + UA	cyst.	whew. + Hap.	wed. + UA	Total observed
Male	337	22	294	13	15	112	6	42	43	5	11	6	4	11	3	924
Female	151	10	86	6	4	22	3	9	22	2	0	0	4	7	0	326

b) As a percentage

Patients	whew.	wed.	whew. + wed.	UA	Hap.	str.	AAU	whew. + UA	whew. + AAU	str. + AAU	whew. + wed. + AAU	whew. + wed. + UA	cyst.	whew. + Hap.	wed. + UA	Total observed
Male	36.5	2.4	31.8	1.4	1.6	12.1	0.6	4.5	4.6	0.5	1.2	0.6	0.4	1.2	0.3	99.7
Female	46.3	3.0	26.4	1.8	1.2	6.7	0.9	2.8	6.7	0.6	0	0	1.2	2.1	0	99.7

a) The stones of whewellite, cystine and whewellite + hydroxyapatite composition are relatively more common in women than in men,

b) Stones composed of struvite, whewellite + weddellite, whewellite + weddellite + ammonium acid urate, and whewellite + uric acid are of higher frequency in men than in women.

According to the available data concerning stone formation in the urinary system it seems that 74% occurs in men and 26% in women.

Results of Chemical Analyses

Of the urinary system stones under investigation, 350 of them, from patients of different regions and with different mineralogical compositions, were analysed chemically. Wet chemical methods were applied to Si and Al analyses whereas atomic absorption methods were applied to Sr, Na, K, Mg, Fe and Zn analyses.

Silicium: Of the urinary system stones with this element struvites have the most, and stones with hydroxyapatite, weddellite and whewellite + weddellite compositions also have a considerable amount of Si tenor. Stones with organic composition such as cystine, ammonium acid urate and uric acid have very little Si.

Aluminum: There is about 150 ppm of this element in urinary system stones of organic origin and about 300 - 450 ppm in the others.

Zinc: The Zn content is high in urinary system stones with hyroxyapatite, but there is a very important standard deviation in the results of the analyses. Urinary system stones with weddellite and struvite also have an important quantity of zinc. Stones containing uric acid have the lowest zinc concentrations.

Strontium: This element is to be found in relatively large amounts in the urinary system stones containing Ca and Mg such as whitlockite, whewellite and weddellite; furthermore Sr concentration is high in the stones with whewellite, but very low in urinary system stones with ammonium acid urate and uric acid.

Iron: The distribution of this element in urinary system is very limited and, apart from samples with whewellite + weddellite + ammonium acid urate, the Fe concentration takes place between 143 - 206 ppm.

Sodium : Na is the most abundant element in the urinary system stones containing hydroxyapatite. Na concentration is very high (6000 ppm) in ammonium acid urate and uric acid and Na concentration is also high in struvite. Na concentrations of around 2900 - 3000 ppm are observed in whewellite, weddellite, and in their mixtures. Na concentration is rather low in the other samples under investigation.

Potassium: K concentrations are highest in urinary system stones with ammonium acid urate. A potassium content of over an average of 3000 ppm has been found among the urinary system stones with struvite, it averages around 2000 ppm in the stones with hydroxyapatite. Average potassium concentrations are around 800 - 1000 ppm in the other types which are pure mineralogical phases of the urinary system stones.

Magnesium: This is the major element in the urinary system stones with struvite and whitlockite, and is found in very high amounts. The mineral which has magnesium as a substitution element in the highest quantity is hydroxyapatite. Mg concentrations between 1000 - 2000 ppm are observed in whewellite, weddelite and in their

mixtures. Mg concentrations around 1600 ppm are determined in ammonium acid urate from the urinary system stones with organic components, and concentrations of this element are rather low in uric acid and cystine.

Results of Chemical Analyses of Kidney Stones with Different Mineralogical Compositions

We must not forget that the samples under investigation in this paragraph are the analytical results of kidney stones with similar mineralogical compositions of persons living in different places and under different conditions. For this reason, it is difficult to make valid comments on the results of the chemical analyses. However, in spite of this basic difficulty, it is possible to make some observations (Table IV).

It has been observed that:

a) Struvite and hydroxyapatite can be identified as Na-rich kidney stones,

b) Stones containing ammonium acid urate are K-rich,

c) Stones with struvite are Si-rich,

d) Cystine forms a very poor stone, compared with the others, by the elements being analysed,

e) Ammonium acid urate is poor in other elements apart from Na, K and Mg concentrations,

f) The existence of the minerals with organic components in kidney stones lowers the trace element concentrations, at least in case of those analyzed here.

Chemical Compositions in Kidneys, Ureter and Bladder of Some Kidney Stones

An attempt has been made to investigate this matter in kidney stones with whewellite mineralogy (Table V).

Samples of stones of bladder origin containing whewellite are richer in Na, K and Mg than those stones which are found in the two other organs, but poor in Al.

Furthermore, of the urinary system stones with whewellite, those found in the ureter are poorer in Zn, Sr and Mg than those found in the kidneys and the bladder.

Results and Suggestions

1. Of the minerals making up kidney stones, whewellite, a combination of whewellite + weddellite and struvite are the ones most frequently found. This triple association accounts for 80% of the samples analyzed.
2. It is obvious that whewellite and struvite minerals are frequently observed in the stones taken from patients of the Kayseri region.

TABLE IV

Average results of some trace elements in the kidney stones with different mineralogical compositions

	whewellite			weddellite			uric acid			hydroxy-apatite			struvite			whitlockite			AAU			whew. + wed.			whew. + UA			UA + AAU			whew. + AAU			whew. + wed. + AAU			cystine		
	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n		$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ
Sr	2149	26	1945	8293	4	5429	303	1	–	3017	5	2656	6475	51	5756	2171	1	–	–	–	–	3766	14	4877	1117	17	280	–	–	–	1406	2	560	1066	1	–	–	–	–
Al	377	66	300	220	5	140	140	14	76	430	10	466	300	50	397	250	1	–	185	2	26	290	37	241	352	15	536	301	3	223	461	11	513	828	2	722	165	–	–
Zn	129	64	146	303	3	117	43	4	26	726	3	676	260	34	217	–	–	–	–	–	–	208	30	187	51	10	31	179	2	121	81	11	44	173	1	–	–	–	–
Sr	1171	76	9130	130	7	42	52	9	19	178	11	104	137	50	98	180	1	–	30	3	0	121	48	64	77	14	54	80	1	–	102	9	42	151	2	60	30	–	–
Fe	185	65	152	201	3	98	105	9	60	170	3	24	143	35	71	–	–	–	–	–	–	166	33	49	208	10	128	170	2	60	166	11	65	110	1	–	–	–	–
Na	2907	87	2786	2975	8	2167	1506	15	1826	16362	11	9472	7036	61	7145	1415	1	–	3005	3	1891	2721	56	1809	1361	18	581	5875	3	3550	2701	12	881	2999	2	1026	175	–	–
K	839	87	705	963	8	666	1124	15	1131	1943	11	814	3222	61	1167	1826	1	–	8153	3	2041	793	55	586	1025	18	1483	14530	3	12536	15074	12	22530	7500	2	3208	165	–	–
Mg	1453	87	2242	1114	8	806	220	15	222	31043	11	30567	84677	61	35621	15600	1	–	1630	3	1366	2311	56	5687	397	17	240	1061	3	300	1766	12	880	6160	2	5185	78	–	–

n = Number of analyses

σ = Standard deviation

$\bar{m}$ = Average concentration (ppm)

TABLE V

Some trace element concentrations of whewellitic stones of the urinary tract, as to the organs in which they exist

	Kidneys			Ureter			Bladder		
	$\bar{m}$	n	σ	$\bar{m}$	n	σ	$\bar{m}$	n	σ
Si	2494	14	2446	2260	2	1408	1762	6	836
Al	409	39	369	380	5	109	290	9	198
Zn	136	38	149	95	5	53	147	10	193
Sr	127	46	70	95	4	23	116	10	58
Fe	174	39	69	386	5	458	136	10	36
Na	2892	52	2613	2121	5	730	3777	12	4020
K	726	52	639	546	5	252	1164	12	1164
Mg	1573	52	2191	510	5	148	2190	12	3626

3. It seems important that there should be a whewellite + ammonium acid urate mineralogical unity in addition to the whewellite and struvite stones in patients of the Sivas region.
4. As to the patients from the Samsun region, stones containing whewellite + ammonium acid urate are in a minority while those with a whewellite + weddellite mineralogical unity are in a majority.
5. Stones with weddellite and stones containing struvite + ammonium acid urate combinations are frequently found in patients of the Eskişehir region.
6. Stones containing whewellite and whewellite + weddellite combinations are frequently found in patients of the Erzurum region.
7. In patients of the Muğla region there are stones similar to those of Erzurum; however, in Muğla patients, there is also hydrocsiapatite.
8. Half of the urinary system stones are in the kidneys and the other half is approximately evenly distributed between the ureter and the bladder.
9. The composition of the stones in the bladder shows a difference from those of the kidneys and the ureter.

10. Three times as many men as women have urinary system stones. Further, stones with whewellite, cystine and whewellite + hydroxyapatite combinations are frequently found in women and stones with struvite, whewellite + weddellite combinations are more characteristic of men.
11. The probable relationship between the concentration of certain trace elements in the kidneys and the mineralogy of the stones is under investigation.
12. An attempt has been made to find out some chemical differences in the stones which are found in different organs and have the same mineralogical composition in the urinary system.

    The fresh water within the environment where the patients live should be analysed from the point fo view of both trace elements and oxygen isotopes in order to determine more definitely the relationship between the kidney stones and the patients' environment; afterwards more precise results could be obtained if these analyses were repeated on the kidney stones.