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MAJOR AND TRACE ELEMENTS IN MOROCCAN URINARY STONES

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ABSTRACT

The aim of this study, is to conduct an investigation on the variability of the composition of major elements and those in traces in 21 types of stones each corresponding to a particular pathological profile. The content of major and trace elements has been studied in 21 urinary stones of human kidney stones with a distribution in each types of stone to understand their contribution in urinary stone genesis. The ICP-EOS was used to determinate the content for 25 elements. Sulfur, magnesium followed by zinc were the most important elements in our samples, a high content of Zn and Sr in calcium lithiasis compared to other types of stones. An important content in lead in our samples compared with other studies was observed. More investigations and a higher number of samples must be conducted in order to determine etiological factors for this lithogenesis.

KEYWORDS: urinary stones, trace elements, urolithiasis.

1 INTRODUCTION

Urolithiasis or urinary stone diseases is a common pathology, which affects between 4 to 20% of the population, with a recurrence rate of around 50%.[1] Several epidemiological studies during the last 30 years have shown that the frequency of the lithiasis continues to increase.[2] This increase is economically significant expenses (hospitalization, additional examinations, work stoppages), which increases the management of this pathology, in the absence of adequate prevention.

From the bladder stones of the underprivileged populations, to the oxalocalcic renal lithiasis affecting the well-to-do populations, lithiasis disease is becoming more and more a socio-economic marker revealing our living conditions and our eating habits. This pathology has multiple origins; nutritional imbalances, urinary tract infection, anatomical malformations of the urinary system, pathologies of genetic or acquired metabolic origin, as well as environmental factors which constitute for some regions as an important factor in the prevalence of urolithiasis.[3-5]

Given the terrible consequences of urolithiasis (chronic renal failure), the management of this disease, especially in prevention, must take a more important place in public health programs.

Urinary stones are multifactorial origin, having a decisive influence on the excretion and saturation of urine in lithogenic environment. The role of trace elements in urinary lithiasis is still poorly defined. Experimental studies have shown that some elements have an effect on the crystallization of calcium oxalate and calcium phosphate.[6, 7]

Although some studies have been carried out on the chemical composition of lithiasis in Morocco, to our knowledge no study has focused on the presence of trace elements and their roles in these stones in our country.[4]

The objective of this study, is to conduct an investigation on the variability of the composition of major elements and those in traces in 21 types of stones each corresponding to a particular pathological profile.

2 MATERIALS AND METHODS

2.1 Sample collection

Our study was conducted on samples of kidney stones extracted from lithiasis patients followed by two urology departments of Avicenna hospital in Rabat. A total of 21 samples of pure urinary calculi representing 7 crystalline species (3 per species), was previously analyzed by infrared spectrophotometer.[8] These crystalline species are composed of calcium oxalate (monohydrate and dihydrate), phosphates (carbapatite and struvite), purines (anhydrous uric acid and various urate) and cystine.

2.2 Sample treatment

The stones were washed with distilled water to remove surface contamination for traces of blood and tissue debris, samples were subsequently dried at 60 °C. Each stone is then ground using an agate mortar. For the preparation and analysis of the samples; a nitric acid and reference materials of the trace elements to be analyzed were used.

For analysis, 500 mg of the homogenized powder stones were dissolved in 6 ml of nitric acid diluted to half, and left 15 minutes cold, then 6 ml of distillated water are added. The mixture is boiled for 30 minutes. Digested aliquots were transferred to a volume of 30 ml, then the analysis by ICP was conducted.

2.3 Apparatus

The kidney stones samples were analyzed using the Jasco Fourier transform infrared (FT-IR) spectrophotometer 460 Plus (Jasco Co, Hachioji, Tokyo, Japan) to determine mineralogical type.[8] Content of elements in urinary stones was determinate by using an inductively coupled plasma-atomic emission spectrometer with ULTIMA2 apparatus (Horiba Jobin Yvon, France) with spectral range between 120 and 800 nm. The calculi stones were weighted on a precision balance scale (BOSCH S 2000, Gebr Bosh Co, Freinwaagenfabric, Germany). For the drying stones, an Oven JOUAN was used. A block of wet mineralization and agate mortar and pestle was also used for sample preparation.

3 RESULTS AND DISCUSSION

3.1 Total content in major and trace elements

The determination of the levels of elements in the stones, five major elements (Cl, K, Mg, Na, and S) and 20 trace elements (B, Fe, Co, Mn, Mo, Cu, Zn, Cd, Cr, Ni, Pb, Mg, Cl, Se, Al, K, V, Na, Si, Sr, Ba, Sn, Li, Ti and S) were analyzed by ICP-EOS.

The distribution of the content of the major elements composing the 21 urinary stones illustrated in figure 1. A significant difference in the average metal content were observed as a function of the main crystalline phase of the urolithiasis.

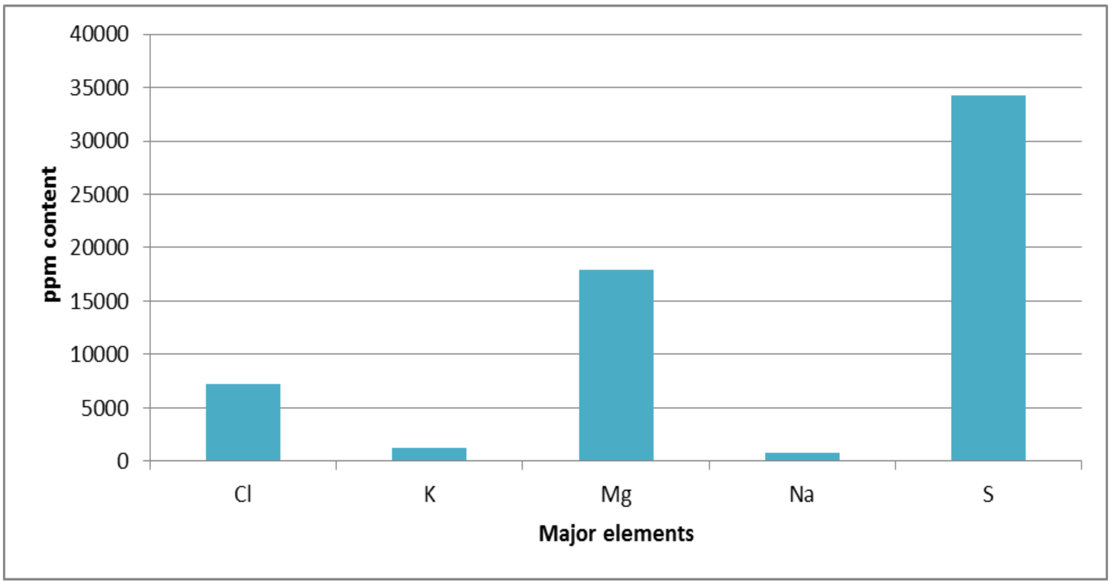

Figure 1: Content of major elements in 21 urinary stones.

The composition of trace elements in the 21 urinary stones analyzed is demonstrated in figure 2.

Five major elements (see Figure 1) and twenty trace elements (see Figure 2) were analyzed, the most abundant being sulfur, magnesium followed by zinc. Sulfur and magnesium were excluded from the elements studied because it is a major part of the crystalline composition of cystine and struvite urinary stones respectively. Zn represents 42.5% of all the trace elements studied which are Fe, Cu, Al, Pb, Sr and Se. the table 2 illustrate a content of elements in urinary stones of different studies.

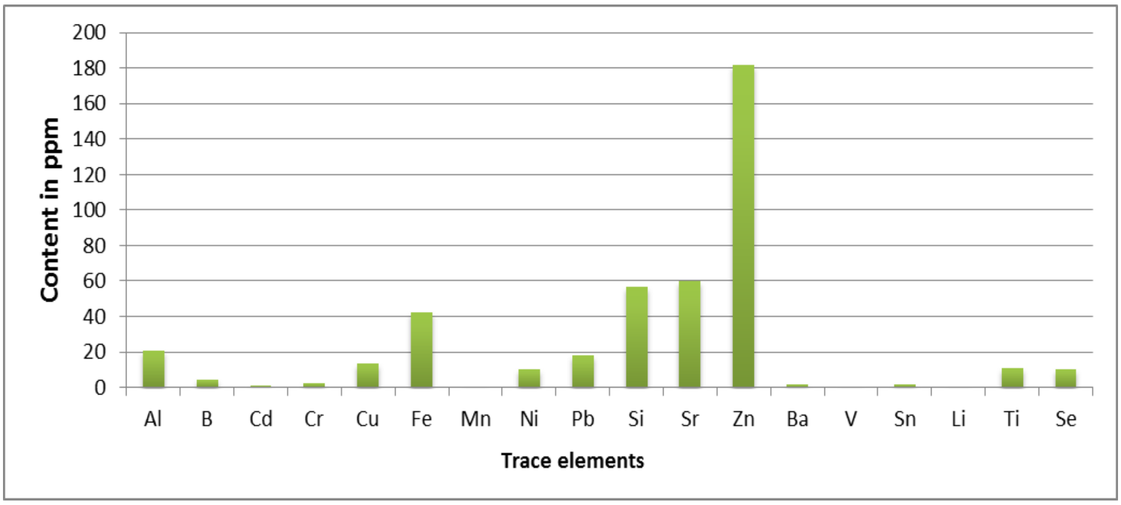

Figure 2: Content of trace elements in 21 urinary stones.

Table 1: Comparative table of elements' levels in urinary stones of principal studies in ppm (* en wt%).

Study	Our study	[9]	[10]	[6]	[11]	[12]	[13]	[14]
Country	Morocco	Sri-Lanka	Jordan	Italy	Iran	Czech	Poland	Iran
Al	20.83	-	1.42*	2	154	6	7.18	3
B	4.03	-	-	-	-	-	8.47	-
Ba	1.89	-	0.49*	-	2.8	1.02	1.74	11.15
Cd	0.86	-	-	-	0.34	0.14	0.15	-
Cl	7183.64	-	0.56*	-	-	-	-	544.55
Cr	2.36	-	0.17*	0.03*	7.3	0.05	1.15	-
Cu	13.31	67	1.04*	0.57*	5.1	1.1	3.79	39.8
Fe	42.17	258	1.33*	0.26*	82	48	19.75	-
K	1207.54	294	0.42*	0.90*	0.13*	307	408.44	-
Li	≤1.36	-	-	-	-	-	0.13	-
Mg	17915.06	1426	0.48*	1.63*	0.07*	0.041*	528.11	-
Mn	≤0.70	8.39	0.57*	0.12*	4.2	0.12	2.39	-
Na	741.35	1348	2.19*	-	0.17*	1220	592.42	-
Ni	10.03	-	0.11*	-	9.2	0.2	2.05	3
Pb	18.04	69	-	0.05*	12.1	4.41	4.32	5.17
S	34246.04	-	1.76*	-	1.88*	-	-	-
Se	10.09	-	-	-	1.85	0.3	3.16	-
Si	56.39	-	1.15*	-	-	-	8.46	-
Sn	1.81	-	-	-	-	0.82	0.16	-
Sr	59.89	-	0.16*	-	141	49.1	-	108.5
Ti	11.14	-	-	-	-	-	-	-
V	0.71	-	-	-	8.3	<LOD	0.24	4.75
Zn	181.97	675	0.16*	0.45*	83.0	67	187.23	36.95

3.2 Content of trace elements by kind of stones

Eight heavy metals were analyzed in urinary lithiasis (Mg, Fe, Zn, Cu, Sr, Al, Se and Pb). The content varied only from a few ppm for Sr to 51497 ± 17580 ppm for Mg. The results are summarized in table 1, for the study of the correlation between the trace elements and the crystalline phase, the figure 3 illustrates this distribution.

Table 2: Distribution of trace elements in urinary stones in ppm in urinary stones.

Chemical species	Fe	Cu	Al	Pb	Se	Sr	Zn	Mg
Oxalates	**35.2±11.9**	**13.2±1.7**	**38.7±67.3**	**16.6±6.9**	**9.3±1.4**	**59.3±27.5**	**219.1±274.5**	**1558±2207**
• *Whewellite**	33.1±15	13.7±1.9	12.1±2.7	14.1±2.8	9.8±1.7	46.9±23.6	21.1±11.4	444±197
• *Weddellite ***	37.2±10.8	12.7±1.6	65.3±95.8	19±9.7	9.3±1.4	71.7±29.5	417±266	2673±2901
Phosphates	**60.6±42.4**	**13.8±2.1**	**18.8±7.8**	**27.4±21.4**	**10.1±0.7**	**106.1±80.2**	**342±436**	**47203±25357**
• *Carbapatite*	81.9±50.2	13.9±1.4	14.8±9.7	33.7±24.7	10.4±0.7	99±82.0	340±488	42911±35259
• *Struvite*	**39,3**±34,6	13.7±3	22.8±1.9	21.1±20.5	9.7±0.6	113.2±96.0	345±493	51497±17580
Purines	**33,1**±8,8	**14.3±3.4**	**9.2±5.2**	**18.3±9.5**	**9.9±1**	**24.3±56.4**	**54.2±107**	**1172±2752**
• *Uric acid*	40.3±10.1	15.8±4.6	11.9±5.3	24.3±10.7	9.5±0.5	47.7±79.3	104±145	2316±3872
• *Various urates*	25.9 ±7.5	12.8±1.1	6.5±4.2	12.2±0.9	10.4±1	0.8±0.6	4.4±1.6	29.2±22.9
Cystine	**57.2±17.2**	**12.7±0.7**	**17.7±13.4**	**12.8±2.5**	**12.8±0.6**	**1.8±2.0**	**14.6±4.6**	**94.2±86.7**

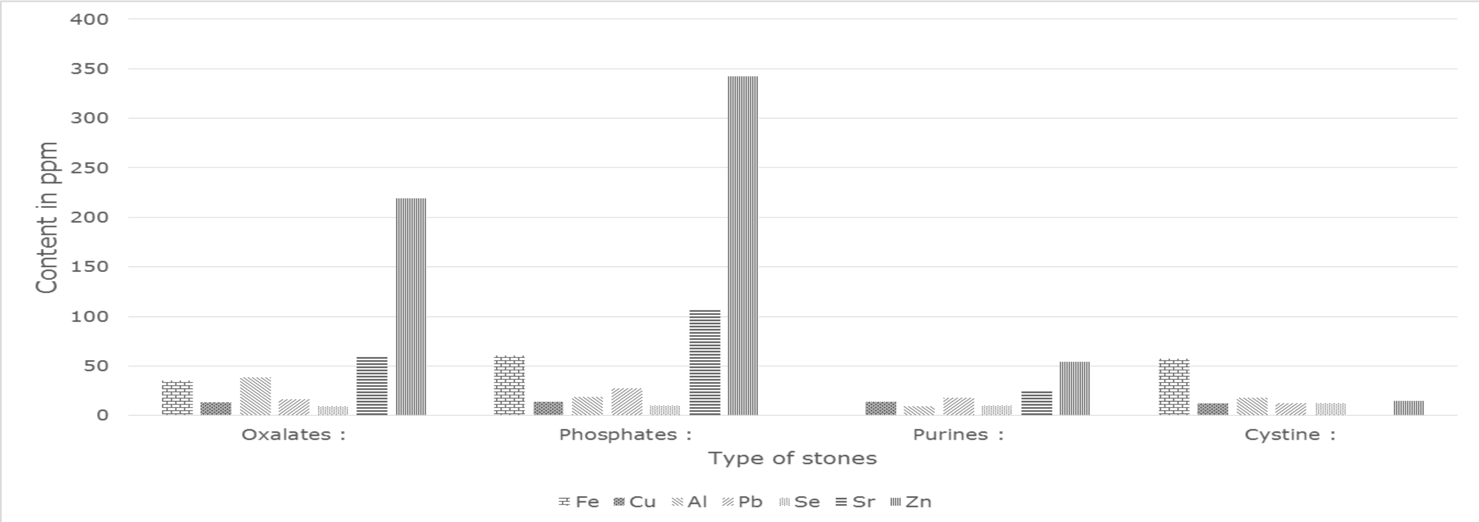

Figure 1: Distribution of trace elements in ppm in urinary stones.

As regards to the chemical composition of the stones, Zn and Sr were mainly present in calcium lithiasis (oxalocalcic and phosphocalcic), and only in trace amounts in urate and cystine stones (see Table.3). Moreover, for chemical species, these two elements are more abundant in calcium phosphate stones than in those of calcium oxalate, with a predominance in calcium oxalate dihydrate compared to calcium oxalate monohydrate. Other studies have reported this observation.[9, 10]

According to Goldschmidt's rules, the differences in the heavy metal content between calcium and non-calcium lithiasis can be explained by the similarity between the ion charge and the size of Zn, Sr and calcium, which allow these elements to substitute calcium in the crystal lattice.[10] Thus, divalent metal ions such as Zn and Sr are probably the most susceptible to incorporate in calcium lithiasis (calcium oxalate and calcium phosphate).[11, 12]

The content of Fe, Cu, Al and Pb are much less abundant, they were detected mainly in calcium stones. The Pb content (18.04 ppm) is particularly low in cystine stones but is appreciable in other stones. Unlike studies in industrialized countries where Pb levels are low(4.41 and 4.32 ppm).[13, 14] The presence of Pb in our current study compared to historical data, suggests environmental concentrations in Pb, due to the presence of lead in the water pipes not replaced by polyvinyl chloride pipes in our cities. In fact, lead pollution has decreased in industrialized populations in the recent decades.[15]

The appreciable quantities of Se found in sulfur-containing cystine stones, is in harmony with the similarity of Selenium and Sulfur in terms of atomic mass and biological properties. As a result, Selenium can be substituted for Sulfur to form Se-cystine.[16]

Many theories have been proposed to associate and explain the relationship between the concentration of certain trace elements and their role in the formation of urinary stones.[17, 18] However, no direct relationship has been found associated between the concentration of trace elements in urinary stones and the reasons for this.[9, 19] It can be said from the results of this study that the concentration of several trace elements in different lithiasis may be related to environmental and nutritional factors.[10, 17, 19]

Table 3: Comparative table of element levels in different types of urinary stones in ppm (* en wt%).

Chemical species	Concentration of trace elements in ppm (*en wt. %)								References
	Fe	**Cu**	**Al**	**Pb**	**Se**	**Sr**	**Zn**	**Mg**	
Whewellite	33.1±15	13.7±1.9	12.1±2.7	14.1±2.8	9.8±1.7	46.9±23.6	21.1±11.4	444±197	Our study
	33 ± 22	5 ±4	-	12 ± 10	1.5 ± 0.5	61 ± 41	42 ± 38	-	[16]
	0.222 ±0.111*	0.630±0.145*	-	0.066±0.012*	-	-	-	0.814± 0.984*	[6]
	-	-	-	13 ± 4	-	7 ± 8	66 ± 24	-	[15]
Weddellite	37.2±10.8	12.7±1.6	65.3±95.8	19±9.7	9.3±1.4	71.7±29.5	417±266	2673±2901	Our study
	29 ± 43	1 ±1	-	14 ± 4	0.7 ± 0.2	125 ± 82	290 ± 346	-	[16]
	-	-	-	31 ± 8	-	138 ± 18	440 ± 53	-	[15]
	200	-	-	-	-	-	180	1830	[23]
	0.269±0.072*	0.996±0.333*	-	0.082±0.013*	-	-	0.119±0.065*	0.611±0.389*	[6]
Carbapatite	81.9±50.2	13.9±1.4	14.8±9.7	33.7±24.7	10.4±0.7	99±82.0	340±488	42911±35259	Our study
	44 ± 60	7 ± 11	-	31 ± 39	1 ± 0.5	455 ± 364	1059 ± 934	-	[16]
Struvite	-	13.7±3	22.8±1.9	21.1±20.5	9.7±0.6	113.2±96.0	345±493	51497±17580	Our study
	0.421±0.349*	0.338±0.117*	-	0.039±0.016*	-	-	0.953±0.364*	9.629±1.272*	[6]
	-	13	-	3	-	774	96	-	[14]
Uric acid	40.3±10.1	15.8±4.6	11.9±5.3	24.3±10.7	9.5±0.5	47.7±79.3	104±145	2316±3872	Our study
	6 ±5	1.5 ±1	-	0.8 ± 0.7	0.3 ± 0.1	4 ±5	4±3		[16]
	0.216±0.104*	0.635±0.102*	-	0.005±0.002*	-	-	0.201±0.051*	0.051±0.023*	[6]
Various urates	25.9 ±7.5	12.8±1.1	6.5±4.2	12.2±0.9	10.4±1	0.8±0.6	4.4±1.6	29.2±22.9	Our study
Cystine	57.2±17.2	12.7±0.7	17.7±13.4	12.8±2.5	12.8±0.6	1.8±2.0	14.6±4.6	94.2±86.7	Our study
	6 ±6	3±2	-	1± 0.7	4± 1.3	5 ±5	11 ±4	-	[16]
	0.197*	0.220*	-	0.008*	-	-	1.405*	0.218*	[6]

4 CONCLUSION

In conclusion, this study shows a high content of Zn and Sr in calcium lithiasis compared to other types of stones. Additional studies must be carried out to define the exact role of these two elements in calcium lithogenesis which is the main cause of stone formation in the lithiasis population.

Levels of lead are high compared to industrialized countries due probably to the use of metal water pipes in most Moroccan households.

An analysis of a larger number of samples is necessary to have a clearer information on the composition of urinary stones in metals in the Moroccan population, and to evaluate a probable correlation between a content of metal level in urinary stones to lithogenesis of calculi.

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