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Phase and Microelement Composition of the Kidney Stones of Ob' River Watershed Residents

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Abstract

Phase composition of 2567 patient's kidney stones, who were residing on the territory of the Ob' River (Russian Federation) watershed was investigated. It is shown that 73 % kidney stones are oxalates, 18 % – uric acid and its salts, 8 % – phosphates. In studying the trace element composition of the 36 kidney stones, the ICP-AES method was applied. Phosphorus was found in the kidney stones containing no P according to powder XRD. Comparison of statistical data on the composition of patient's kidney stones from the Novosibirsk, Omsk and Chelyabinsk regions with data 10-15 years ago, published in the literature was carried out. In the Novosibirsk and Omsk regions, phosphates stones were found more often – 10-12%, in Chelyabinsk region uric acid and its salts stones, were found more often – 21 %.

Keywords: atomic emission spectroscopy, kidney stones/urolites, X-ray phase analysis.

INTRODUCTION

Kidney stone disease, also known as urolithiasis, occupies one of the first place among urological diseases in the World [1]. Russia is no exception (an average of 34.2%) [2]. Though the causes of urolithiasis are not fully understood [3, 4, 5, 6] wherein urolithiasis depends on the individual characteristics of the patient and adverse environmental factors (ecology, food [7], etc.). For the treatment of urolithiasis, the following methods are traditionally used: surgery, ultrasonic chipping stones, drug dissolution uralites [8], etc. It should be noted that in more than half the cases, simple removal of the uralite leads to relapse of urolithiasis without further correction of the patient's diet [9]. The stones composition is a long-term characteristic of the existing pathology of the patient's urinary system. To designate an appropriate diet information about the mineral composition of stones is required. To identify the patterns of their formation processes, as well as the methods of preventing both primary and re-development of urolithiasis, this work is devoted to the urological stones study by various physicochemical methods. As objects for the study, the patients' uroliths living on the territory of the Ob River watershed were chosen. For the inhabited localities in this area, a high anthropogenic load is common. The literature describes research of the phase and elemental composition of kidney stones from Novosibirsk region [10, 11], Omsk Region [12, 13, 14] and Chelyabinsk region [15, 16]. However, in this work, the number of objects is small, about 100-150 samples. It seems interesting to study the change in the phase and trace element composition for 10-15 years for these subjects of the Russian Federation.

MATERIALS AND METHODS

Powder X-ray analysis of polycrystals was performed on Shimadzu XRD-7000 and DRON 3M diffractometers (CuK-alpha radiation, Ni-filter, 5-60° 2 theta range). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the polished side of a standard quartz sample holder, and a smooth thin layer being formed after drying. Indexing of the diffraction patterns was carried out using data for compounds reported in the PDF database. [17]. Quantitative XRD analysis was made by RIR (reference intensity ratio) method.

The element composition of uralites was determined by ICP-AES method iCAP-6500 Duo (Thermo Scientific) with a pneumatic solution injection system (nebulizer – SeaSpray). We studied 36 samples of urinary stones by ICP-AES method, 17 of them monomineralic composition were had (3 – oxalate stones, 3 – phosphate stones, 9 – uric acid and its salts, 2_stones completely of cystine consisted). The remaining 19 stones are polymineralic.

RESULT AND DISCUSSION

Table 1 shows the statistical data about the kidney stones mineral composition of patients who lives on the territory of the Ob River over the period 2011-2017. The results from the powder X-ray diffraction analysis were obtained. It should be noted that various quantity of kidney stones were analyzed from different regions, as the only possible way of selecting stones that are related and it does not represent the risk of disease. Type of stone "oxalate", "phosphate" or "uric acid and its salts" to the uralites was appropriated if it contains more than 50% of the relevant compound.

The most common of the uralite:

- oxalate: whewellite $CaC_2O_4 \cdot (1+x)\ H_2O$ ($x \approx 0.00$-0.07) and weddellite $CaC_2O_4 \cdot (2+x)H_2O$ ($x \approx 0.30$-0.37), it is confirmed by literary data [18];

- phosphate: struvite $MgNH_4PO_4 \cdot 6H_2O$, hydroxylapatite $Ca_5(PO_4)_3(OH)$, brushite $CaHPO_4 \cdot 2H_2O$;
- uric acid and its salts: uric acid $C_5H_4N_4O_3$, uric acid dihydrate $C_5H_4N_4O_3 \cdot 2H_2O$, ammonium urate $(NH_4)_2C_5H_2N_4O_3$.

Other phases, for example, cystine $C_6H_{12}N_2O_4S_2$, quartz SiO_2 or calcite $CaCO_3$ are detected rarely. On average, throughout the territory of the Ob River 72.79 % are oxalates, 18.01 % – uric acid and its salts, 8.19 % – phosphate from all urological stones. There are stones that consist of an equal number of these phases and rare stones (cystine, quartz, calcite), their total content is 1.01 % from all urological stones.

In the three most represented (by the quantity of samples) areas – Novosibirsk region, Omsk region and Chelyabinsk region oxalates are most often found (69.5-72.7%), uric acid and its salts are prevailing over phosphate (in 1,4-3,4 times). In the Novosibirsk and Omsk regions, phosphates are found in ~ 2 times more often than in the Chelyabinsk region and in the Russian Federation as a whole.

Earlier in the monograph OA. Golovanova [14], it was published in 2004, describes a study of a sample of 155 kidney stones of Novosibirsk region patients and 129 stones of Omsk region patients. As this monograph shows oxalates of Omsk region patients are found in 57.7% of cases, phosphate – in 23.7% of cases, uric acid and its salts – in 18.6% of cases. In the Novosibirsk region: oxalates – 65,7 %, phosphate – in 23.5% of cases, uric acid and its salts – in 10.8% of cases. Thus, over the past 10 years, the composition of the kidney stones has changed significantly (see table 2). In the Omsk region, the quantity of oxalates increased more than 10% while phosphates and uric acid decreased. In the Novosibirsk region, oxalates and uric acid increased by 5-7%. The number of phosphates decreased by 13%.

The literature published the data on the composition of 112 uralites of patients from the Southern and Middle Urals [19]. Part of these territories belongs to the Ob basin, so does the Chelyabinsk region. Literature [19] shows that oxalates were found in 61.0% of cases, uric acid and its salts – in 23.6% of cases, phosphates – 14.7% of cases. In this study, 669 stones from Chelyabinsk were investigated. It was established that oxalates are found in 73.0% of cases, uric acid and its salts – in 21.0% of cases, phosphates – 6.0% of cases. As in the case of the Novosibirsk and Omsk regions quantity of oxalates more than 10% was increased (see table 2). Perhaps, these changes are related to global consumption of the products. For example, the policy of import substitution, conducted in the Russian Federation from 2014 [https://ria.ru/spravka/20151125/1328470681.html].

It seems interesting to trace the change in the ratio of types of kidney stones depending on the age of the patient. The largest number of samples is presented for patients from 21 to 70 years (see table 3.). Figure 1 shows that with age, the quantity of patients with uralytes from uric acid and its salts increases: from 1% in 21-25 years to 65% at 71-75 years. The number of patients with oxalate stones is decreasing, for example, 21-25 years old – 81 %, 71-75 years old – 65 %. The number of patients with phosphate stones also decreases: from 16% in 21-25 years to 9% at 71-75 years.

The dynamics of the samples number containing any quantity of phosphates in the composition (triangle down) is presented. It can be seen that the maximum content of phosphates corresponds to the age of 25 to 40 years. The maximum proportion of phosphate stones from the total number of uralites (ie, containing more than 50% by weight of phosphates) also corresponds to the period of 20-35 years, this period is characterized by active sex life. Probably, the maximum proportion of phosphate stones in this period is due to genitourinary infections. There is an opinion that the genesis of phosphate stones is associated with infectious diseases [20].

The results of ICP-AES analysis have shown that the composition of the stone includes both macro elements (Ca, P, Mg, Na, K > 0.1 % by wt.) and microelements – Al, Ba, Bi, Cd, Cr, Cu, Co, Fe, Mn, Mo, Ni, Re, Rb, Si, Sr, Ta, Zn, Pb, W (0.001 – 0.1 % by wt.).

In 9 samples consisting only of oxalate minerals – № 1, 5, 6, 7, 8, 9, 11, 12 and 13 (see table 4) phosphorus by ICP-AES analysis was detected. The phosphorus of these stones varies from 0.71 to 4.5% by wt. [21, 22, 23]. This gives grounds to consider that X-ray amorphous phosphate minerals are present in these stones, this is confirmed by literary data [21-23]. The authors of the article indicated that the products of vital activity lead to the amorphous phosphates formation or accelerated the concernments growth if the crystallization nuclei is present in the system. In all oxalate stones the content of Na (0.13 – 1.8 % wt.), Mg (0.02 – 0.52 % wt.), K (0.021 – 0.12 % wt.) were found, at a concentration level of 0.001 to 0.1% wt. Zn, Sr, and Fe often were found, microelements Pb, Mo, W were found less often.

As in the case of oxalate stones in phosphate minerals Na (0.17 – 3.0 % wt.), and K (0.022 – 0.57 % wt.) were found, at a concentration level of 0.001 to 0.1% wt. Zn and Sr were found in all samples, microelements Fe, Mo, Ba were found less often.

When analyzing uric acid stone elements, a content of more than 1% was detected to be extremely rare. 15 uric acid stones were analyzed wherein only one stone contained 15.0 % wt. Ca. Probably phases with these elements X-ray amorphous are present. At a concentration level of 0.1 to 1.0% wt. Na, Ca, K, P were found. In one sample 0.62 % wt. Si was found, in another uralite 0.22 % wt. Mo was found. Generally, in urate stones, an amount of all microelements was found. At a concentration level of 0.001 to 0.1 % wt. Al, Bi, Cd, Cu, Fe, Mo, Pb, Rb, Ta, W, Zn were found.

Today researchers do not have a common opinion about the factors influencing the urates trace element composition. Some researchers relate these factors to patient's region of residence [24] while others relate it to the samples phase composition [25]. Generally, due to the differences in the methods used in studying the composition and list of the microelements analyzed, the comparison of literature data is difficult to make.

Table 1. Statistical data on the mineral composition of kidney stones of the Ob basin patients for the period 2011-2017.

Basin/river	City	Number of samples	Mineral composition, %			
			Oxalates	Phosphates	Uric acid	Other
Ob (cities in the mainstream of river)	Barnaul	170	75.88	6.47	15.30	2.35
	Berdsk	27	81.48	0.00	18.52	0.00
	Biysk	11	63.64	9.09	27.27	0.00
	Nefteyugansk	8	75.00	12.50	12.5	0.00
	Nizhnevartovsk	119	75.63	6.72	17.65	0.00
	Novosibirsk	569	71.53	10.37	16.70	1.40
	Nyagan'	14	85.71	0.00	14.29	0.00
	Surgut	28	77.78	7.41	14.81	0.00
	Total:	**946**	**73.44**	**8.68**	**16.61**	**1.27**
Berd'	Iskitim	7	71.43	0.00	28.57	0.00
Irtysh	Ekaterinberg	149	72.48	10.74	15.44	1.34
	Kurgan	57	77.20	1.75	21.05	0.00
	Nizhny Tagil	30	66.67	13.33	20.00	0.00
	Omsk	302	69.54	12.25	17.22	0.99
	Tyumen'	109	67.89	11.01	19.27	1.83
	Chelyabinsk	669	72.65	5.98	20.63	0.74
	Total:	**1316**	**71.58**	**8.36**	**19.15**	**0.91**
Tom'	Belovo	7	57.14	0.00	42.86	0.00
	Kemerovo	116	78.45	5.17	16.38	0.00
	Mezhdurechensk	5	40.00	20.00	40.00	0.00
	Novokuznetsk	33	63.64	24.24	12.12	0.00
	Prokopyevsk	7	100.00	0.00	0.00	0.00
	Yurga	8	75.00	0.00	25.00	0.00
	Tomsk	95	78.95	3.16	17.89	0.00
	Total:	**271**	**76.02**	**6.64**	**17.34**	**0.00**
Tromyogan	Kogalym	7	71.43	0.00	0.00	28.57
Chulym	Achinsk	9	77.78	0.00	22.22	0.00
Yaya	Anzhero-Sudzhensk	11	81.82	0.00	18.18	0.00
Throughout the Ob' basin		**2567**	**72.79**	**8.19**	**18.01**	**1.01**
Throughout the Russian Federation on 30.01.18		**14935**	**73.93**	**7.41**	**17.59**	**1.07**

Table 2. Change the composition of uroliths patients Novosibirsk and Omsk regions, %.

Type of the stone	Chelyabinsk region		Omsk region		Novosibirsk region	
	2004 [19] 112 stone	2011-2017 669 stone	2004 [14] 155 stone	2011-2017 302 stone	2004 [14] 129 stone	2011-2017 603 stone
Oxalates	61.0	73.0	57.7	69.5	65.7	70.8
Phosphates	23.6	21.0	23.7	12.2	23.5	11.8
Uric acid and its salts	14.7	6.0	18.6	17.2	10.8	16.7
Rare phase	a	0.7	b	1.0	b	0.7

a – the author of the paper [19] does not give data on the presence of rare phases in the investigated uralites, the content of rare phases was 0.7%.
b – the author of the paper [14] does not give data on the presence of rare phases in the investigated uralites, but the sum of the main phases is 100%, therefore the content of rare phases was zero.

Table 3. Statistical data on the distribution of the mineral composition of kidney stones, depending on age in the Ob basin for 2011-2017 period.

Full age, years	Number of samples	The proportion of men, %	Oxalates, %	Phosphates, %	Uric acid and its salts, %	Others, %
11-15	7	71.43	85.71	0.00	14.29	0.00
16-20	37	35.13	97.30	2.70	0.00	0.00
21-25	114	43.86	80.70	15.79	0.88	2.63
26-30	268	56.72	82.84	13.43	2.61	1.12
31-35	321	63.55	81.00	11.53	6.85	0.62
36-40	263	62.74	82.82	8.02	8.78	0.38
41-45	292	71.92	82.53	4.11	11.99	1.37
46-50	249	73.49	78.31	4.82	15.66	1.21
51-55	327	59.81	72.78	4.89	21.41	0.92
56-60	292	56.16	56.85	8.56	32.88	1.71
61-65	210	53.81	53.33	6.67	40.00	0.00
66-70	85	58.82	48.24	7.06	42.35	2.35
71-75	34	41.18	26.47	8.82	64.71	0.00
76-80	35	45.71	37.14	8.57	54.29	0.00

Table 4. Sample code number, type of stone and composition of stones for 36 uralits analyzing by ICP-AES method.

№	Sample code number	Type of stone	Composition of stones			
			Oxalates	Uric acid and its salts	Phosphates	Other
1	128305478	Oxalate	Whewellite 11% weddelit 89%	-	-	-
2	600443554	Oxalate	Whewellite 17% Weddelit 62%	-	Hydroxylapatite 21%	-
3	216500628	Oxalate	Whewellite 89% Weddelit 7%	-	Hydroxylapatite 4%	-
4	114031250	Oxalate	Whewellite 39% Weddelit 55%	-	Hydroxylapatite 6%	-
5	127260576	Oxalate	Whewellite 29% Weddelit 71%	-	-	-
6	216820294	Oxalate	Whewellite 100%	-	-	-
7	600570811	Oxalate	Whewellite 65% Weddelit 35%	-	-	-
8	600462675	Oxalate	Whewellite 96% Weddelit 4%	-	-	-
9	600527762	Oxalate	Whewellite 91% Weddelit 9%	-	-	-
10	600182190	Oxalate	Whewellite 85%	-	Hydroxylapatite 15%	-
11	600410250	Oxalate	Whewellite 100%	-	-	-
12	600476364	Oxalate	Whewellite 100%	-	-	-
13	127714265	Oxalate	Whewellite 80% Weddelit 20%	-	-	-
14	127623719	Urate/ Oxalate	Whewellite 11% Weddelit 37%	Dihydrate 14% Uric acid 38%	-	-
15	600448158	Urate	-	Urat 100%	-	-
16	125339402	Urate	-	Urat 100%	-	-
17	600420069	Urate	-	Dihydrate 40% Uric acid 60%	-	-
18	127276326	Urate	Whewellite 11%	Urat 85% Dihydrate 4%	-	-
19	119633771	Urate	-	Uric acid 100%	-	-
20	128169399	Urate	-	Urat 100%		
21	126841437	Urate	-	Uric acid 100%	-	-
22	127285960	Urate	-	Urat 100%	-	-
23	600462533	Urate	-	Uric acid 100%	-	-
24	216216707	Urate	Whewellite 23%	Uric acid 77%	-	-
25	216116717	Urate	-	Dihydrate 62% Uric acid 38%	-	-
26	218736694	Urate	Whewellite 10% Weddelit 4%	Dihydrate 8% Uric acid 78%	-	-
27	124983311	Urate	-	Uric acid 100%	-	-
28	600439673	Urate	-	Urat 100%	-	-
29	600470420	Phosphate	-	-	Brushit 100%	-
30	119174781	Phosphate	-	Ammonium Urate 7%	Hydroxylapatite 24% Struvite 69%	-
31	125465322	Phosphate	-	-	Struvite 100%	-
32	215524145	Phosphate	-	-	Struvite 100%	-
33	216455122	Phosphate	-	-	Hydroxylapatite 5% Struvite 95%	-
34	601342494	Phosphate	Weddelit 5%	-	Brushit 95%	-
35	129124426	Organic	-	-	-	Cystine 100%
36	216394739	Organic	-	-	-	Cystine 100%

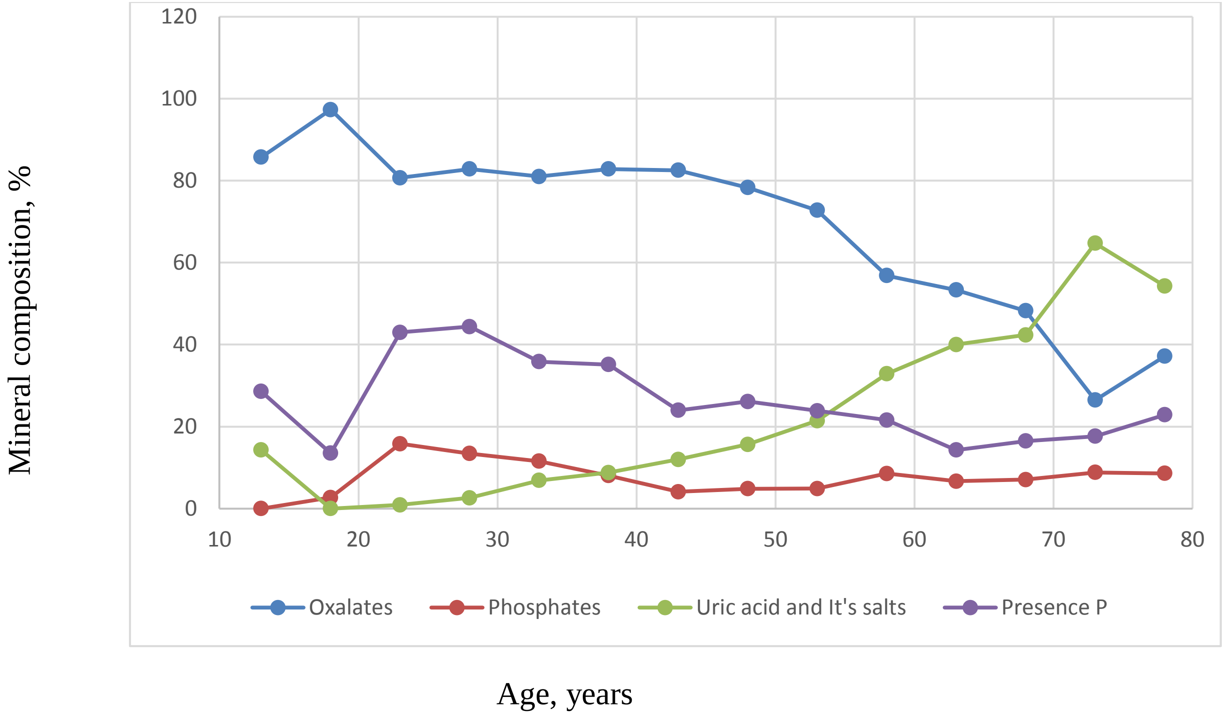

Figure 1. Change in the composition of kidney stones, depending on the age of the patient, %.

CONCLUSIONS

The example of the Novosibirsk, Omsk and Chelyabinsk regions in the last 10-15 years has presented significant changes in the phase composition of kidney stones. The number of oxalate stones was increased at 10% wt. and the number of phosphate stones at 5-10%. were decreased. In the Novosibirsk and Omsk regions, phosphates stones were found more often – 10-12%, in Chelyabinsk region uric acid and its salts stones, were found more often – 21 %.

We studied 36 samples of urinary stones by ICP-AES method. The presence of phosphorus in oxalate type stones was determined. The phosphorus content of these stones varies from 0.71 to 4.5% wt. The results of ICP-AES analysis have shown that the composition of the stone includes both macro elements (Ca, P, Mg, Na, K > 0.1 % by wt.) and 19 microelements – Al, Ba, Bi, Cd, Cr, Cu, Co, Fe, Mn, Mo, Ni, Re, Rb, Si, Sr, Ta, Zn, Pb, W (0.001 – 0.1 % by wt.).

Oxalates stones are characterized by the presence of K, Mg, Na, at lower concentrations, Zn, Sr, and Fe are encountered. Phosphate stones are characterized by the presence of K, Na, Sr, Zn. Uric acid stones are characterized by the presence of Ca, K, Na, P. In one sample 0.62 % wt. Si was found, in another uralite 0.22 % wt. Mo was found. Generally, in urate stones an amount of all microelements were found, for example Al, Bi, Cd, Cu, Ta, Rb.

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