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Chemistry of Major and Trace Elements of Kidney Stones in Fallujah City/Iraq

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Abstract
The current paper aims to identify the concentrations of major and trace elements in 20 sample kidney stones in Fallujah, Iraq. These elements were estimated using ICP-MS method and X-ray diffraction were used for mineral structures. The study showed that there are six mineral groups (Calcium Oxalate, Cholesten, Phosphate, Uricite, Uricite and Calcium and Mixed stone). Ca is the main constituent of kidney stone because Calcium is the highest concentrations of other the elements (6.75%). and it is Concentrated in the stones of Calcium Oxalate and Calcium Phosphate. P is the main component of Phosphate with a concentration of all kidney stones (0.715%). The groups of calcium oxalate and Phosphate contain large amounts of trace elements, especially Zn and Sr, .There are high quantities of Mn in Cholesten because the manganese plays an important role in the metabolic pathway of amino acids, fats, proteins and carbohydrates. The results indicated that concentrations of these elements in kidney stones depend on the type of mineral aggregates that form the kidney stones.
Keywords Kidney stone.Cholesten. Trace element. Fallujah .Iraq

1.Introduction

The kidney liquidates the blood from body waste in the form of urine. Acid salts and minerals adheres together in the urine to form small stones in kidney called kidney stones. It is known as a solid mass of sediments made up of organic and inorganic substances, ranging in size from the size of small sand to the size of the golf ball (Encyclopaedia Britannica Articale, 2005). It is the main cause of ureteral obstruction, In the narrow canal leading to the bladder causing renal failure that threatens human life (Lin et al., 2014). The process of urinary stones in the kidney, bladder and urethra is a complex and understood phenomenon clearly and one factor cannot contribute to in their composition. This could be due to disorders in metabolism, infections, hormonal effects, dietary habits and reduction of fluid intake that focuses and reduces the amount Urine (Durgawale et al., 2010). Moreover, genetics, drugs, lifestyle factors and some medical conditions cause urinary changes forming kidney stones (Evan, 2010). Other important factors play a major role in their composition such as depression, nutrition, gender, climate, region geography, fluid intake and associated diseases (Golovanova et al., 2006; Safarnejad, 2007; Pourmand and Pourmand, 2012; Pearle and Loan, 2012) Taking proteins and decrease having potassium are the most important dietary factors in their composition (Tur et al., 1991) and intake of milk or salts that increase the amount of calcium in the urine (Sobhi, 2006), but genetic factors and food effects outweigh the climatic effects (Pearle and Loton, 2012).

Urine stones are formed when the concentration of certain substances, especially, Oxalate, Uric Acid, Cysteine, Calcium, Citrate deficiency in the urine, or insufficient water in the kidneys for the purpose of disposal of the waste. Therefore the urine usually contains chemicals such as pyrophosphate, magnesium, Citrate, which prevents the formation of crystals, so the urine becomes very concentrated and acidic or alkaline (Encyclopedia Britannica Article, 2005). The lower concentrations of these chemicals contribute to the formation of kidney stones. Citrate is believed to be the most important factor in the formation of urinary stones, which are present in the kidneys but sometimes in the bladder and ureter. The genetic effects are also taken. Vitamin C plays an important role in the formation of stones (Finlayson, 1974; Robertson, 1980).

The presence of some chemical elements naturally in the human body is necessary for health because more than 40 elements have different biological functions on the human body and health, if they have been taken during eating and drinking and its concentrations may be variable either very low or very high (Fell, 1984). These elements, which are usually low concentrations, are trace elements which are toxic at the height of their concentrations (Pousanpayne, 2006).

These elements have different levels and functions and that few of them can adversely affect biological processes in the human body (Wandt and Underhill, 1988).

The prevalence of kidney stones in both sexes increased from 2 to 3 times and was more common in males than in females (Dajani et al., 1988). Those who have a family history were more likely to be infected (Eboud, 2008) (Dajani et al., 1988). The statistical studied indicated that the men between 20-40 years are the most infectious compared with children. The disease in hot and dry areas is more common than in temperate regions (Andrew and Chandil, 2001). Those who are living in arid environments have the highest rates of infection provided that meals shared in these poor areas are limited to some vegetables and tea (Sobhi, 2006).

Environmental factors play an important role in human health and can increase urinary stones prevalence.These factors include the number of hot days in the summer (Baker, 1993) Moreover, exposure to sunlight leads to the addition of vitamin D which could increase the absorption of calcium in the blood (Gunes et al., 2006), hard water (Sierakawski,1979), fluoride in groundwater (Singh et al., 2001), the arid environment (Pendse and Singh, 1980) and the dry season (Bond et al., 2008).

Several epidemiological studies have documented that the geographical variation has had a significant impact on the prevalence of urinary incontinence (Komatin, 2004). Evidences have proved, to be the most convincing yet, that high temperature and exposure to sunlight play an important role in the geographical variation of the disease with kidney stones.Individuals living in hot climates have been confirmed to have increased their lifetime prevalence (Curhan and Curhan, 1994). The main chemical components of the gravel are Calcium Oxalates, Phosphate and Uarates. About 70% of all kidney stones are made up of calcium oxalates either individually or mixed with Phosphate (Nasir et al., 2004). Other non-organic phases such as Struvite, Brushite and Rarely Whitlockite (Bichler et al., 2002) are currently being investigated. The current paper aims to assess the major and trace elements of kidney stones in patients with renal failure in Falluja, and determining the aggregates and mineral structures which bear kidney stone.

2.Materials and methods

In 2017, 20 samples were collected for patients in Fallujah city hospitals. The samples were placed in Polyethylene dry bottles. These samples placed in medical plastic containers and sorted according to sex and age. Hydrogen peroxide and distilled water have been added to each sample was placed in a glass baker and left for 24 hours for the purpose of eliminating of all organic materials. After that washed again with distilled water and then placed in a ceramic pot, then dried at 100 ° C for 24 hours according to the method proposed by Lin et al. (1985).These samples were analyzed at the University of Wollongong, Australia using X-ray diffraction (XRD) .The major and trace elements have been analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) in Acme labs, Canada.

3.Results and discussion

Table 1 shows the mineral composition of 20 samples in Al-Fallujah city. Accordingly, the samples can be classified into four mineral groups depending on the age and gender categories. The first comprises 30-40 years (6 samples), the second 40-50 years (8 samples) 60 years (4 samples) and fourth from 60-62 years (two samples). They are more common in males than in females.

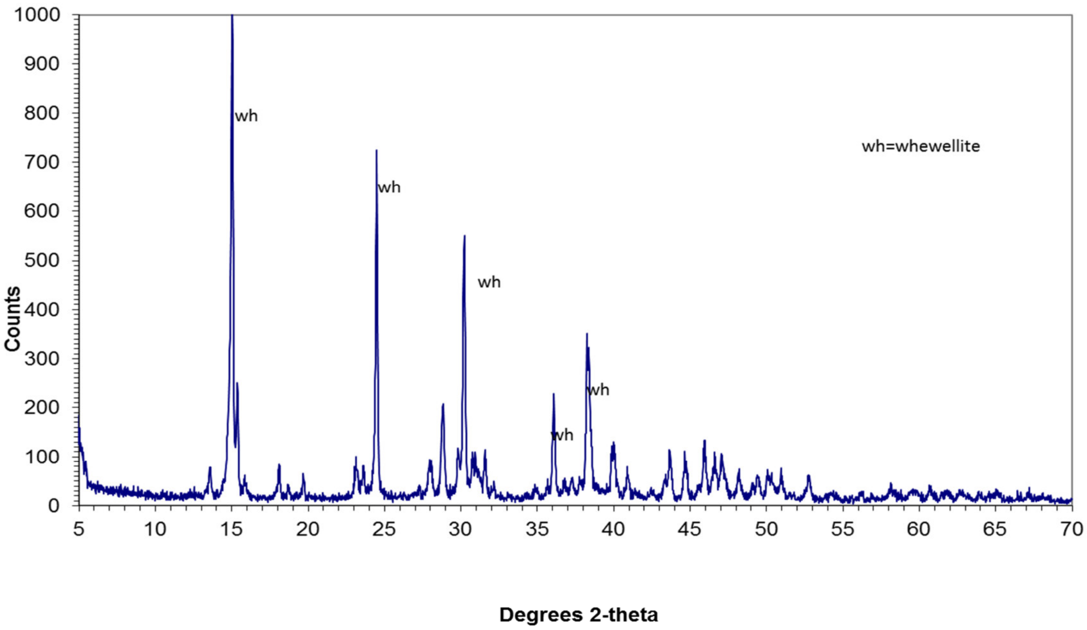
Table(1):mineral structure of kidney stone depending on age and gender in study area.

Sample No.	Gender	Age (year)	Major Phase	Minor Phase
F1	Male	57	Whewellite	-
F2	Male	55	Struvite	Newberyite
F3	Male	52	Uricite	Whewellite
F4	Female	38	Uricite	-
F5	Male	42	Uricite	Whewellite
F6	Female	35	Struvite	Newberyite
F7	Female	37	Whewellite	-
F8	Male	61	Uricite	Weddellite
F9	Male	40	Uricite	Weddellite
F10	Female	37	Cholesten	-
F11	Female	42	Whewellite	Weddellite
F12	Male	43	Uricite	Whewellite
F13	Male	62	Uricite	Whewellite
F14	Male	44	Uricite	Whewellite
F15	Male	45	Whewellite	Uricite
F16	Male	46	Uricite	Weddellite
F17	Male	39	Whewellite	Uricite and Whitlockite
F18	Female	50	Uricite	Whewellite
F19	Female	44	Cholesten	-
F20	Female	33	Uricite	Whewellite

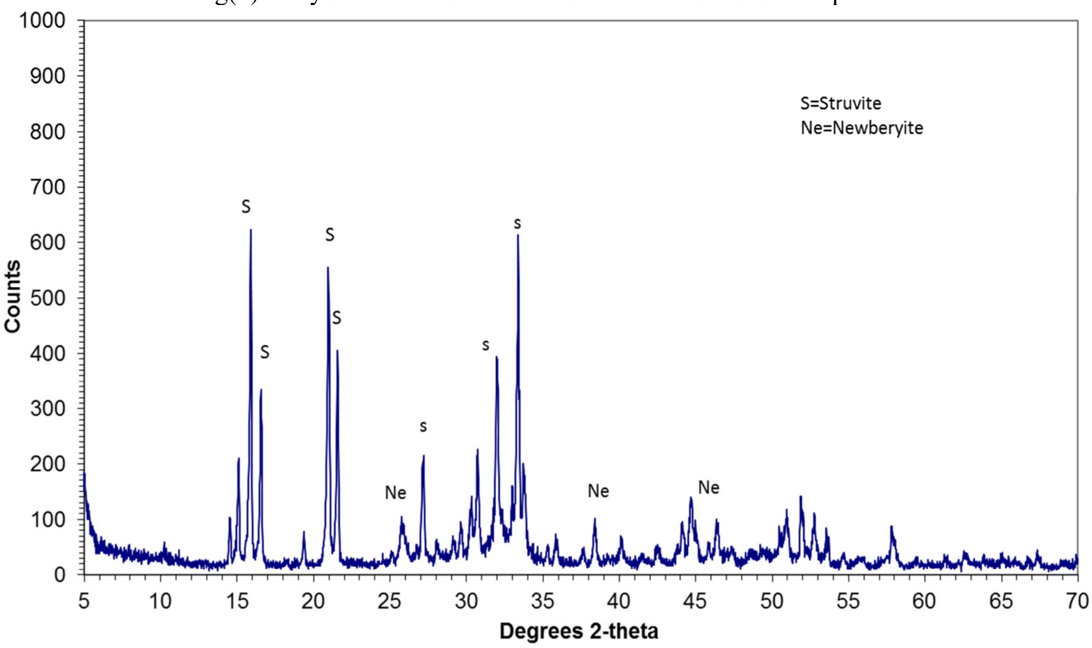
Table 2 shows the classification of mineral groups according to their mineral composition, classified into six groups, The first common group is Mixed stone, which is made up of Uricite / Whewellite / Whitlokite minerals (55%) figure (1), and the second group is calcium oxalate (15%),The third is the Cholesten group and the fourth is the Phosphate group of Struvite / Newberyite and 10% respectively, as shown in Figure (2), The fifth group is the Uric Acid group and the sixth group is the combination of Uric acid and Calcium oxalate (5%).

Table (2):classification of minerals group of kidney stone in study area.

	Group minerals	Mineral	Number of stone	%
1	Calcium Oxalate	Whewellite/Weddellite	3	15
2	Cholesten Calculi	Cholesten	2	10
3	Phosphate Calculi	Struvite/Newberyite	2	10
4	Uric Acid	Uricite	1	5
5	Uric Acid and Calcium Oxalate	Uricite and Whewellite	1	5
6	Mixed Stone	Uricite/Whewellite/Whitlokite	11	55



Fig(1):x-ray diffraction of calcium oxalate minerals for sample F1



Fig(2):x-ray diffraction of magnesium phosphate minerals for sample F2

Table (3) represents the results of the chemical analysis and the concentration of the major and trace components of all types of kidney stones. The concentration of the calcium component in the ranges (0.03-

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22.68%) and average (6.75%) and it is the predominant element in kidney stones compared to the other elements . This is belongs to the increasing Ca levels in the body, including increasing the activity of the neighboring glands to the thyroid which increase the proportion of calcium in the blood and urine as well as taking Calcium-rich foods, which include milk, low-fat milk, sapang and various types of fish and beans. Therefore, Ca plays an important role in the process of lithogenesis (Schubert, 2006; Chaudhri et al., 2007).

The phosphorus component is the main component of phosphate stones, the second most abundant element in the human body after calcium, which helps build teeth and bones and eliminates waste in the kidneys (Bassavaraj et al., 2005). The percentage of its concentration in all samples of kidney stones between (0.02-5%) and average(0.715%). The food sources of P are milk and meat as the lack of phosphorus is rare. The most important reasons that lead to the disease of kidney are the loss of its ability to absorb vitamin D necessary for phosphorus absorption, the dysfunction of thyroid gland secretions adjacent to the thyroid, as well as the use of certain drugs and drugs (Kuta et al., 2012). The Mg and Fe concentrations in all samples of kidney stones ranges between (0.01-8.2%)(0.01-0.04%) and average (0.76%(0.020%))respectively. The K and Na concentrations were found in all kidney stones range (0.01-0.43%) and (0.02-0.46%) and average (0.067%) (0.119%) respectively. The potassium component has several functions within the human body and its concentration has an important role to maintain the proportion of calcium Ca in the body because it controls the urinary loss of Ca (Lemann et al., 1991; Curhan et al., 1993), while the element of sodium is necessary to maintain balance Fluids within the human body. Iron is an inhibitor in the growth of calcium oxalate crystals (Lieu et al., 2001).

Table (4) presents the binary correlation coefficients of the major and trace components of kidney stones. Phosphorus (P) has a positive correlated with both K and Na for (r = 0.95) (r = 0.87) respectively. This may be due to the effect of liquids and foods containing potassium phosphate and sodium phosphate (Nriago and Moor, 1984). Magnesium (Mg) with phosphorus has positively correlated with the of(r = 0.97), which may indicate the magnesium is found in the phosphate minerals to be one of the major components of them(Atakan et al., 2007).

Cadmium concentrations ranges between (0.01-0.44 ppm) at an average of(0.108ppm) and correlated with calcium with a positive correlation (r = 0.61), suggesting that cadmium increases the crystallization of calcium oxalate (Ferraro e al.,2011), The average of Zn and Sr concentrations in kidney samples reached (50.4 ppm) (59.83ppm) respectively (Table 3). These elements are correlated with a strong positive (r = 0.89), suggesting that there are found in phosphate minerals (Zarasvandr et al.,2013). zinc (Zn) is correlated with a significant positive correlation with lead (Pb) (r = 0.45), which may be due to the geochemical associated between them (Angelovicova and Fazekasova, 2014).

Table (3):concentration of major and trace elements of kidney stone in study area.

Element	Group1(n=3)			Group2(n=2)			Group3(n=2)			Group4(n=1)			Group5(n=1)			Group6(n=11)			Total(n=20)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Ca(%)	14.87	22.68	18.90	0.36	1.98	1.17	4.08	8.57	6.32	14.62	14.62	14.62	0.03	0.03	0.03	0.43	14.81	4.906	0.03	22.68	6.758
Mg(%)	0.03	0.19	0.1	0.02	0.04	0.03	6.43	8.2	7.315	0.03	0.03	0.03	0.01	0.01	0.01	0.01	0.07	0.020	0.01	8.2	0.76
Fe(%)	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.03	0.025	0.01	0.01	0.01	0.04	0.04	0.04	0.01	0.04	0.020	0.01	0.04	0.020
P(%)	0.32	1.22	0.76	0.03	0.14	0.09	5	5	5	0.33	0.33	0.33	0.03	0.03	0.03	0.027	0.768	0.173	0.02	5	0.715
K(%)	0.04	0.1	0.068	0.01	0.02	0.01	0.18	0.43	0.305	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.07	0.040	0.01	0.43	0.067
Na(%)	0.12	0.23	0.18	0.05	0.10	0.08	0.39	0.46	0.425	0.1	0.1	0.1	0.02	0.02	0.02	0.029	0.146	0.067	0.02	0.46	0.119
Zn(ppm)	44.4	215.2	118.9	4.7	19.9	12.3	45.3	308.8	177.0	41.1	41.1	41.1	38.5	38.5	38.5	5.1	106.2	25.07	4.7	308.8	50.4
Pb(ppm)	4.63	8.05	6.08	1.01	2.39	1.7	3.91	6.22	5.065	2.89	2.89	2.89	2.31	2.31	2.31	0.32	4.49	1.611	0.32	8.05	2.630
Cu(ppm)	2.83	8.73	5.82	20.81	48.37	34.59	1.78	9.27	5.52	3.46	3.46	3.46	47.96	47.96	47.96	2.94	30.28	12.23	1.78	48.37	13.75
Ni(ppm)	0.4	0.9	0.64	0.1	0.5	0.3	0.3	0.4	0.35	0.6	0.6	0.6	0.6	0.6	0.6	0.1	0.5	0.21	0.1	0.9	0.33
Mn(ppm)	2	3	2.4	16	63	39.5	3	4	3.5	1	1	1	0.6	0.6	0.6	1	4	1.846	1	63	5.85
Cr(ppm)	1	1.7	1.36	0.5	1	0.75	0.7	0.8	0.75	1.1	1.1	1.1	4	4	4	0.8	1.9	1.369	0.5	2.2	1.275
Se(ppm)	0.5	0.8	0.66	0.1	0.2	0.15	0.1	0.1	0.1	0.9	0.9	0.9	0.2	0.2	0.2	0.4	1.8	0.938	0.1	1.8	0.68
Sr(ppm)	80.2	122.4	99.74	2.9	9.3	6.1	136.6	473.7	305.1	51	51	51	0.6	0.6	0.6	2.4	84.9	24.13	0.6	473.7	59.83
Cd(ppm)	0.12	0.44	0.029	0.1	0.1	0.1	0.2	0.9	0.055	0.05	0.05	0.05	0.01	0.01	0.01	0.01	0.42	0.115	0.01	0.44	0.108
Hg(ppb)	0.11	1.35	0.64	0.011	0.084	0.047	0.017	2.104	1.06	0.151	0.151	0.151	0.018	0.018	0.018	0.033	0.766	0.239	0.01	2.10	0.321

n=number of stone
Group 1: Calcium oxalate calculi :Whewellite(Whe)/Weddellite(wed).
Group 2: Cholesten(Cho).
Group 3: Phosphate calculi minerals: struvite (Str)/Newberyite(New).
Group 4: Mixed uric acid/calculi calcium oxalate/calcium Phosphate: uricite/ Whewellite(Whe)/Whitlockite(Whit).
Group 5: Uric Acid calculi minerals:Uricite(U).
)Group 6: Mixed uric acid/calculi calcium oxalate minerals:Uricite (U)/ Whewellite(Whe

Table (4):correlation matrix between major and trace elements of kidney stone in study area.

	Ca	Mg	Fe	p	K	Na	Zn	Pb	Cu	Ni	Mn	Cr	Se	Sr	Cd	Hg	Whe	Wed	Uri	Str	New	Whi	Ch
Ca	1																						
Mg	-0.02	1																					
Fe	-0.06	0.17	1																				
P	0.13	0.97**	0.14	1																			
K	0.06	0.92**	0.24	0.87**	1																		
Na	0.37	0.87**	0.06	0.95**	0.77**	1																	
Zn	0.43	0.48*	0.01	0.66**	0.27	0.77**	1																
Pb	0.74**	0.42	0.15	0.51*	0.51*	0.62**	0.45*	1															
Cu	-0.51*	-0.22	0.12	-0.28	-0.28	-0.38	-0.22	-0.25	1														
Ni	0.51*	0.05	0.22	0.13	0.17	0.23	0.25	0.47*	0.12	1													
Mn	-0.21	-0.05	-0.18	-0.09	-0.13	-0.02	-0.13	-0.15	0.26	-0.16	1												
Cr	-.009	-0.33	0.31	-0.43	-0.24	-0.48*	-0.35	-0.11	0.28	0.29	-0.41	1											
Se	-0.03	-0.46*	-0.01	-0.49*	-0.36	-0.50*	-0.41	-0.39	-0.38	-0.19	-0.36	0.33	1										
Sr	0.33	0.72**	0.02	0.83**	0.49*	0.88**	0.89**	0.47*	-0.28	0.13	-0.11	-0.38	-0.40	1									
Cd	0.61**	-0.13	-0.19	-0.03	-0.02	0.10	0.14	0.42	-0.32	0.26	-0.22	0.18	0.02	0.10	1								
Hg	0.09	-054*	0.19	0.53*	0.69**	0.50*	0.16	0.41	-0.32	0.14	-0.12	-0.28	-0.23	0.15	-0.13	1							
Whe	0.90**	-0.31	-0.03	-015	-0.17	0.06	0.22	0.57**	-0.46*	0.38	-0.28	-0.01	0.18	0.03	0.53*	0.06	1						
Wed	-0.20	-0.13	-0.40	-0.15	-0.13	-0.19	-0.16	-0.25	-0.05	-0.26	-0.12	0.24	0.14	-0.17	0.32	-0.51	-0.22	1					
Uri	-0.51*	-0.34	0.34	-044	-0.31	-0.58**	-0.44	-0.60**	0.23	-0.28	-0.28	0.53*	0.46*	-0.44	-0.40	-0.20	-0.31	-0.18	1				
Str	-0.01	0.98**	0.14	0.97**	0.85**	0.88**	0.57**	0.38	-0.20	0.02	-0.05	-0.39	-0.46*	0.81**	-0.12	0.43	-0.32	-0.13	-0.34	1			
New	-0.04	0.99**	0.17	0.96**	0.93**	0.85**	0.45*	0.41	-0.22	0.04	-0.05	-0.38	-0.45*	0.69**	-0.14	0.56**	-0.31	-0.12	-0.37	0.99**	1		
Whi	0.27	-0.07	-0.24	-0.06	-0.09	-0.04	-002	0.02	-0.17	0.28	-0.08	-0.09	0.12	-0.02	-0.09	-0.07	0.23	-0.09	-0.13	-0.07	-0.07	1	
Cho	-0.28	-0.11	-0.18	-0.14	-0.19	-0.11	-0.16	-0.15	0.52*	-0.04	0.83**	-0.39	-0.42	-0.17	-0.24	-0.17	-0.32	-0.13	-034	-0.11	-0.11	-0.07	1

**.Correlation at 0.01(2-tailed) | *.Correlationat at 0.05(2-taild)

*Whe=Whewellite, Wed=Wedditite, Uri=Uricite,Str=Struvite,New=Newberyit,Whi=Whitlocite, Cho=Cholesten

4. Conclusion

The present study shows that different types of kidney stones contain many major and Trace elements such as (Ca, Mg, Fe, P, K, Na, Zn, Pb, Cu, Ni, Mn, Cr, Se, Sr, Cd, and Hg).This gives great importance in knowing the type of kidney stone. The results showed that the content of these elements differs for the same type of kidney stone, as they form low soluble salts with phosphates and oxalate ions, suggesting a clear role in the process of Lithogenesis .Calcium oxalates contain Cd and Pb elements because they increase the crystallization of oxalic oxides, while Cu acts as an inhibitor for the formation of stone .Cholesten stones contains Mn and Cu because they play an important role in the formation of the protein and fat that make up the cholesterol. The element of copper regulates the metabolism of cholesterol. Sr and Zn accumulate in phosphate stone, indicating that they tend to be in phosphate minerals. Uricite stones contain Cr and Se elements because they tend to enter Uricite minerals and are necessary to maintain metabolism and in the process of Lithogenesis. Human beings take these elements through food. Any deficiency or increase of these major and trace elements in the rocks, soil, water, plant and foods leads to the reduction or increase in the human body and exposure the kidney to kidney diseases.

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