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Mineralogy and elemental composition of urinary stones: a preliminary study in northwest of Iran

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ABSTRACT

The Formation of Urinary Calculi [or Kidney stones (renal lithiasis, nephrolithiasis)] is a serious disease among Iran's population, inasmuch as renal stone prevalence rate is annually about 145 cases per 100,000 men and women. In this study, the mineralogy and elemental composition of urinary stones were studied in East Azerbaijan province, located in northwest of Iran. X-ray diffraction (XRD), X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) analyses were used to investigate the mineralogy of different types of Urinary Calculi. The results showed that the collected Urinary Calculi samples can be divided into four groups, based on their mineralogical aspect: mono-hydrated calcium oxalate, di-hydrated calcium oxalate, uric acid and urate/calcium oxalate/cystine, in which whewellite and uricite were the most abundant mineral phases. The oxalate stone types were characterized by the high concentrations of zinc, phosphorus and magnesium. Common minerals in the studied renal stones indicated that calcium oxalate urinary stones have a similar prevalence ratio as in Middle East countries. However, urate compounds were significantly higher in Iran compared to other countries; The niahite mineral was not found in studied samples. In the cities having very hard and hard drinking water, uric acid and oxalate type stone were the main phases in East Azerbaijan province with Mediterranean climate, urate urinary stones were dominant. XRF results indicated that the frequency of Ca was from 0.11 to 25.63%, which has the highest concentration among other elements. The strong positive correlation between Ca and P indicated that calcium tends to be participated in the structure of phosphorus-bearing urinary stones.

Keywords: Mineralogy; Environmental geology; Urinary stones; Calcium oxalate; Water quality.

INTRODUCTION

Urinary Calculi found in any part of the urinary tract are named based on their original location, including pelvic, ureteral, kidney and bladder stones. Kidney stones vary from painless to extremely painful, which require treatment (Geraghty et al., 2017). Up to 20% of world's population are affected by urinary stones (Singh, 2008). After urinary tract infections and prostate disorders, urinary stone formation is the third most common urinary tract problem. Some researchers believe that the geological and hydrological conditions of the environment are directly related to the formation of these stones (Atan et al., 2005; Golovanova et al., 2006; A Zarasvandi et al., 2014; Atabey, 2005). As a result, many researchers from different fields, e.g., medicine, environmental geology and medical geology, have studied them (Lindh, 2013). Although the prevalence of stones in children of both sexes is equal, the age of 30-50 is the period of maximum incidence (Kustov et al., 2018), while prevalence in men is three times higher than in women (Lindh, 2013). However, recent publications stated undoubtedly that modern life style, obesity and dietary habits seem to be in fact the promoters in the development of stone disease.

From mineralogical point of view, different compositions have been recognized for Urinary Calculi, including calcium oxalate, phosphate, uricite (uric acid), cystine, struvite (infectious) and ammonium urate (Abboud, 2008; Kuta et al., 2013). A scientific study by Schubert (2006) on kidney stones has shown that calcium oxalate is the major component of them (70-75%). This substance forms sedimentary particles with a central core and concentric rings. Urinary stones are mainly composed of crystalline and an organic phase which up to 98% of the weight belongs to the crystalline components. Calcium oxalate (>90%) and calcium phosphate (3-5%) are the two major calcium containing crystals present in the urinary stones. Gypsum, calcium acid urate, calcium sodium urate, and various forms of calcium carbonate (e.g. vaterite, aragonite and calcite) are some of other calcium salts found in human stones (Khan, 1992). Calcium is the main ion in urinary stones. Several factors such as age, sex, diet, geology, climate, water quality and minerals can affect the formation of urinary stones (Bellizzi et al., 1999; Kohri et al., 1989; Kuta et al., 2013; Tracy et al., 2012). Moreover, several risk factors associated with the formation of calcium oxalate stones have been identified by Kustov et al., 2018, including obesity, acid-base balance of urine abnormality, and low fluid intake. Urinary stones can provide complementary information on the human exposure to elements, which can be possibly used to study the involved environmental risks (Keshavarzi et al., 2014). The analysis of the kidney stones identifies risk factors leading to stone disease and this information can be utilized to direct therapy (Smith, 1998).

Iran is located in the kidney stone belt region of the world, showing an increasing trend for this disease (Abboud, 2008; Zarasvandi et al., 2014). In this regard, kidney stones have become a serious disease and the most common reason for emergency department visits in hospitals. The prevalence and incidence rate of kidney stone in Iran is equal to 5.7% and 145 per 100,000, respectively, with a gender (male:female) ratio of 1.15-1.38:1 (Pourmand and Pourmand, 2012).

East Azerbaijan province is located in northwest of Iran, where the drinking water is mostly hard water (Hosseinpour Feizi et al., 2012). To the best of authors' knowledge, there is no published data about the relationship between geology, environmental factors and urinary stones, and very limited studies have been conducted on the medical geology in this province. This contribution pursuits the following objectives: (i) analyzing the mineral and microelemental compositions of the urinary stones collected from patients in various localities of East Azerbaijan province, and (ii) determining the possible geochemical relationships between the mineralogy of the stones and the influence of climatic conditions on them.

GEOLOGY AND DESCRIPTION OF STUDY AREA

East Azerbaijan province covers an area of approximately 47,830 km² in northwest of Iran. The latitude and longitude are 45° to 47°30' E and 37° to 38°30' N, respectively. It has a cool to temperate climate with fairly abundant rainfall due to the mountainous area, high altitude and the effects of the Caspian Sea, Black Sea, Mediterranean Sea and Urmia Lake. However, East Azerbaijan's low-lying areas in the northern parts are warm. Given the sharp differences in altitude and the effects of both Mediterranean and Siberian weather streams, different climatic conditions can be observed in this province. Accordingly, the province can be placed in the range of warm Mediterranean climate (in Bonab, Malekan and Maragheh counties), temperate mountain climate (in Tabriz, Marand, Shabestar and Sufian counties) and cold mountain climate (in Sarab, Ahar and Kaleybar counties) (Figure 1).

The western and southwestern parts of the province are actually the Paleozoic platform sequences of the central Iran and the western Alborz mountain range. This area encompasses the Sahand-Bozghush Mountains and the northern highlands of Tabriz, such as Misho and Moro mountains, and the western highlands of Jolfa. The northern part of the province (Ahar, Kaleybar and Kharvanagh counties), apparently without Paleozoic platform facies, is similar to other parts of Iran, where Mesozoic flysch-facies are widespread and Tertiary sedimentary facies have special features (Aghanabati, 2004). This part includes Mugan sedimentary basin, as well as the Ahar and surrounding mountains.

Drinking water supply in East Azerbaijan province relies mostly on groundwater resources; however, in some cities, surface waters collected in dam reservoirs are used. The average hardness of drinking water in the area is about 228±100 mg/l (as $CaCO_3$) (Hosseinpour Feizi et al., 2012).

METHODS AND MATERIALS

In this study, 25 renal stones were collected from the people who were undergoing surgery in Amir Al-momenin and Imam Reza hospitals of Tabriz (Table 1). The first hospital covers kidney diseases and the second one has a full set of urinary stones with recorded patient information. Eighteen samples, including kidney (16 samples) and bladder (2 samples), were selected from the

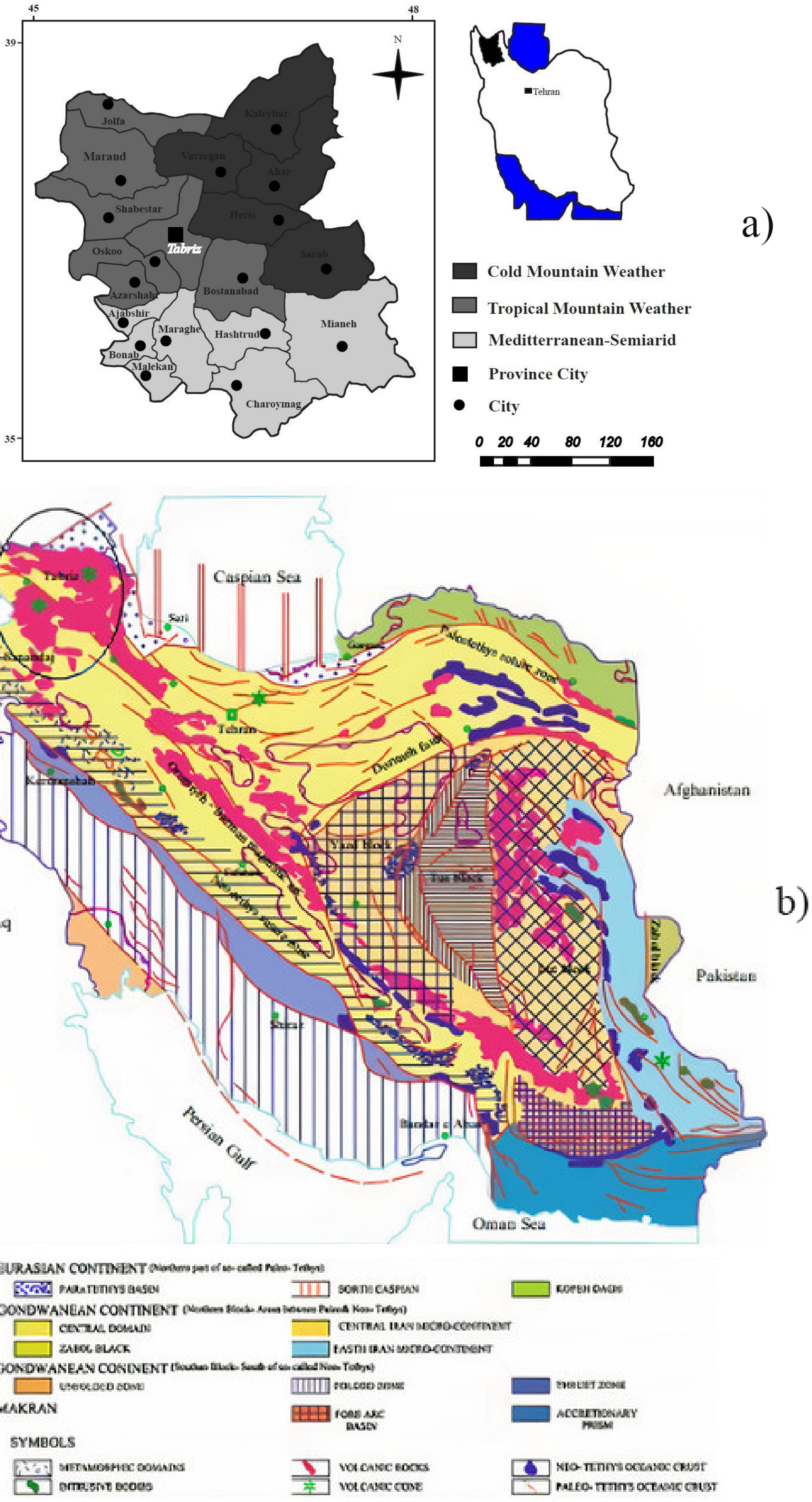

Figure 1. Locations from which the urinary stones samples are collected, classified by climate(a), and tectono-sedimentary areas map (Ghorbani, 2013) (b).

Table 1. Characteristics of the cases selected for stone analysis.

Color and Surface appearance	City	Age	Mineral (pathological report sheet)
Female			
White and Yellow-Rough(5×4×3mm)	Ahar	59	Cystine(50), Calcium Oxalate (20)phosphate Calcium(10), Others(20)
Brown-Rough and Smooth (18×20×3mm)	Tabriz	41	Calcium Oxalate
Brown-Rough (7×5×2mm)	Shabestar	-	Calcium Oxalate
Male			
Brown-Rough (3×4×5mm)	Marand	46	Uric acid (70)-Calcium Oxalate (30)
Brown-Rough (7×5×2mm)	Tabriz	50	Calcium Oxalate
White and Brown-Rough (18×15×3mm)	Sarab	49	Calcium Oxalate (70)-Calcium phosphate (30)
Brown-Rough (5×4×3mm)	Tabriz	-	Calcium Oxalate
Brown-Rough (2×6×8mm)	Tabriz	-	Calcium Oxalate
Brown-Rough (5×3×3mm)	Tabriz	-	Calcium Oxalate
Brown-Rough (10×8mm)	Sofian	51	Calcium Oxalate
Yellow Brown-Rough (10×8×3mm)	Sofian	53	Uric acid (60)–Calcium Oxalate (40)
Yellow Brown-Rough (8×6×3mm)	Bonab	54	Uric acid (70) -Calcium Oxalate (30)
Yellow Brown-Rough* (8×5×3mm)	Bonab*	48	Uric acid (60) -Calcium Oxalate (40)
-	Marand	57	Calcium Oxalate-Calcium phosphate
Brown-Rough (5×3×3mm)	-	42	Calcium Oxalate
Brown-Rough	-	-	Calcium Oxalate
Brown-Rough (2×6×8mm)	Tabriz	52	Calcium Oxalate
Brown-Rough (5×3×3mm)	Tabriz	38	Calcium Oxalate

*In urine analysis of this patient, it was found that there was a relationship between uric acid stone formation, hypertension, blood glucose and acidic urine (pH=5).

samples, based on the availability of required recorded data of patients and having enough weight to carry out the planned analyses. Also, a gallbladder stone sample was selected to compare its composition with urinary stones. Researchers tried to collect the samples from different parts of the province to provide good coverage and reduce probable errors. Age of patients ranged from 38 to 59 years in which 15 of them belonged to males' samples (samples from Tabriz, Marand, Sarab, Shabestar, Bonab and Ahar) and 3 samples were from females (from Tabriz and Shabestar). All of our study's patients were ethnically Azeri (Turk) and had lived all their life in the abovementioned towns. Although prevalent ratio of urinary stones in men is 2-3:1 in comparison with women in the world, moreover the ratio is 1.15-1.38:1 in Iran (Reza Safarinejad, 2007; Abboud, 2008), this ratio was 5:1 in the samples collected in this study. This considered as a limitation for the study. Researchers tried to collect the samples from different parts of the province in order to provide good coverage and to reduce the probable errors. Ages of the patients ranged from 38 to 59 years, 15 of which, belonged to male samples (from Tabriz, Marand, Sarab, Shabestar, Bonab and Ahar) and 3 samples belonged to females (from Tabriz and Shabestar). All of the patients were ethnically Azeri (Turk) and had lived all their life in the abovementioned towns. Although global prevalent ratio of urinary stones in men is 2-3:1 in comparison with women and moreover, the ratio is 1.15-1.38:1 in Iran (Reza Safarinejad, 2007; Abboud, 2008), this ratio was 5:1 in the samples collected in this study. This considered as a limitation for the study.

To prepare the samples for mineralogical study, the residual urine, blood and organic materials were removed from the sample surface. Each sample was rinsed repeatedly with distilled water and then dried. After preparation of the samples and performing gravimetric measurements, at least two different methods were used for providing a detailed analysis in order to identify crystalline and amorphous phases. Generally, the accepted standard methods for stone analysis are infrared spectroscopy and X-ray diffraction. Both methods are precise enough to detect stone components in the range of 5-10% (Straub et al., 2005). At the mesoscopic scale, the morphology and the size of crystallites are determined by scanning electron microscopy (SEM) (Daudon et al., 2009). Several authors have used this method to study the morphology of different types of Urinary Calculi in different areas (Kustov et al., 2009; Daudon et al., 2009; Kustov et al., 2012).

X-ray diffraction (XRD) device (Phillips, model 3040) at Kansaran-Binalud laboratory in the Pardis Science and Technology Park (Tehran) was used to determine the minerals of 10 out of 18 urinary stones, as the remaining stones had similar structures. X-ray diffraction patterns were recorded on a DRON-3M diffractometer using CuKα radiation. X-ray fluorescence (XRF) measurements (model Philips Magix PW 1480) were performed at the Kansaran Binalud Lab in Tehran, in order to determine the chemical compositions of elements in all 18 stones, the mineralogy of which was already determined. Moreover, the atomic absorption spectroscopy (AAS) method was used to measure the consentrations of Pb, Cu, Mn, Ni, Cr, Fe and Zn in the samples, which was carried out in the central laboratory of Islamic Azad University, Tabriz, after sample digestion with HNO_3+HCl (35 mg sample +HNO_3 4 mL+HCl 0.2 mL) in a beaker on a hot plate. Several researchers in different countries (Joost and Tessadri, 1982; Abboud, 2008; Sobhi, 2006) have used this method to study the mineralogy of urinary stones. The Pearson correlation coefficient was calculated using the statistical package for the social sciences (SPSS) version 16.0 and Microsoft Excel, in order to determine the probable correlation between elements.

RESULTS AND DISCUSSION

Determining the morphological characteristics of urinary stones such as shape, size and color is a preliminary stage for the mineralogical studies. Morphological studies normally involve studying the formation location (organ) and the morphological characteristics influenced by the chemistry of urinary stones. As reported by Prasongwatana et al. (1983), in addition to the composition, the shape of stones are also different in adults and children.

The kidney is the most common site for the formation of urinary stones. However, the stones can also form outside the kidney. According to Evan (2010), there are three common pathways for kidney stone formation including stones fixed to the surface of a renal papilla at sites of interstitial apatite plaque (as observed in idiopathic calcium oxalate stone formers); stones attached to plugs protruding from the openings of ducts of Bellini, (as observed in hyperoxaluria and distal tubular acidosis); and finally, stones forming in free solution in the renal collection system, (as in cystinuria). Morphology and formation location of urinary stones can also provide useful information about effective environmental and human factors in the studied regions. For example, it has been shown that incidence of kidney stones at surficial and inner parts of the kidney is directly related to the presence of various industries in the residential areas (Kerr and Laing, 1992). The location of urinary stone formation affects the shape of the stones. For example, urinary stones formed in kidneys can have various forms, such as cruciform, staghorn or spherical (Hesse, 2009). The most striking example in this regard is related to phosphate. Typically, these stones are deposits in the cross-section of kidneys and are in staghorn form (Kerr and Laing, 1992) (Figure 2a). In contrast, the small spherical kidney stones collected from the patients in different regions of East Azerbaijan province are found frequently (Figure 2b).

The location of urinary stone formation, in addition to its appearance, is the most important factor in determining stone size as well. Stone size can range from a sand grain to a golf ball. The biggest stones are always formed in the bladder (Abboud, 2008). In the samples from East Azerbaijan province, the biggest stones were bladder stones, which may have formed due to the presence of enough space for the accumulation of urine and consequently, high levels of dissolved materials. Course, bladder stones are initially appeared into a kidney. Then, if their size does not exceed 6-7 mm, they are able to migrate down to the bladder and increase in size. Kidney stone samples with monohydrate are mainly seen in the form of cubes (Figure 2c). Urates are either hydrated (uric acid) or dehydrated (uricite). Both of them are rare and formed in very acidic urine. Uric acid is found as pure acid in the samples studied. Urate group stones, usually called uric acid stones, are mostly yellow to red in color (Figure 2f) and are usually observed in soft spherical agglomerates with smooth surfaces. The uric acid stones collected from the patients in different cities of East Azerbaijan province range from yellow to red, which are similar to the color reported from other parts of the world. However, the studied stones were mostly reddish-brown (Figure 2h). The special morphology of the urate samples was likely related to the elemental composition and mechanism of formation.

Mineralogy of the samples

Table 2 shows the results of X-ray diffraction analysis. XRD analysis revealed the presence of 7 various crystalline phases in the samples, identified using PDF-4

Figure 2. a) Staghorn kidney stone sample (male 50, Tabriz); b) Round kidney stone sample; c) crystals of calcium oxalate (monohydrated type; brown whewellite and some yellow weddellite can be seen among the samples (male 52); d) Whewellite (COM) + uric acid stone sample; e) Cystine hexagonal crystalline microscopic thin section image; f) The samples and crystals of uric acid stones (yellow to reddish-brown color); g) Calcium oxalate microscopic thin section image (quadrilateral crystal); and h) Microscopic image of uric acid crystals.

Table 2. Mineralogical composition of the urinary stones collected from East Azerbaijan province.

Residence patient	Sample type	Gender-Age	Major Mineral Phases	Minor Mineral Phases
Marand	Renal	Male-57	Whewellite ($CaC_2O_4H_2O$)	Weddellite (CaC_2O_4, $2H_2O$)
Sarab	Bladder	Male-49	Whewellite ($CaC_2O_4H_2O$)	Uric acid ($C_5H_4N_4O_3$ Weddellite (CaC_2O_4, $2H_2O$)
Bonab	Renal	Male-54	Uric acid ($C_5H_4N_4O_3$)	-
Bonab	Renal	Male-48	Uric acid ($C_5H_4N_4O_3$)	-
Tabriz	Renal	Female-41	Whewellite ($CaC_2O_4H_2O$)	-
Sufian	Renal	Male-53	Uric acid ($C_5H_4N_4O_3$)	Whewellite ($CaC_2O_4H_2O$)
Tabriz	Renal	Male-51	Whewellite ($CaC_2O_4H_2O$)	-
Ahar	Bladder	Female-59	Uric acid ($C_5H_4N_4O_3$) Whewellite ($CaC_2O_4H_2O$)	Cystine ($C_6H_{12}N_2O_4S_2$)
Marand	Renal	Male-46	Uric acid ($C_5H_4N_4O_3$)	Calcium Urate
Shabestar	Gallbladder	Male-55	Silica (SiO_2)	Calcite ($CaCO_3$)

database (International Centre for Diffraction Data 2017). The obtained data suggest that whewellite biominerals and uric acid are the major mineral phases in the kidney stones, while weddellite minerals, urate-calcium and calcite are the minor mineral phases. The whewellite and weddellite groups (calcium oxalate monohydrate COM and calcium oxalate di-hydrate COD), have the highest frequency compared to other minerals, and account for about 40% of mineral diversity of urinary stones (Figure 3a). These minerals, known to occur with calcium at a high frequency (Abboud, 2008), sometimes co-exist with urate compounds. In our study area, whewellite was the dominant mineral among the calcium oxalate types (Figure 3a) and the presence of calcium oxalate compounds in ureter and bladder stones was limited to those containing whewellite. However, weddellite was observed both in kidney and bladder stones.

According to the results, urate compounds in the studied samples mostly formed the main mineralogical phases. Uric acid was the only hydrated urate mineral in the urinary stones, and calcium urate was observed in the analyzed samples (Figure 3c). During the sample preparation, one sample was dissolved very hard. XRD analysis showed that the minerals of this sample were different from the others; cristobalite (SiO_2) was the main phase and calcite was the minor mineral phase (Figure 3b). This was the same instance of gallstone and might be attributed to the probable silica contamination in the patient's workplace or living area, which requires further research (Table 2). Silica stones present in the gallbladder and are rare. A review of the literatures discloses that the occurrence of silicon dioxide in human urinary calculi is more common than generally believed. For example, Alpaugh and Johnson (1983) analyzed about 750 human urinary stones during a 3-year study using the scanning electron microscope and X-ray crystallographic methods. Silicon dioxide of the alpha quartz variety was found to be the principal constituent in the calculi from 5 male patients. In none of the 5 cases was there any history of gastric disorders or of any ingestion of antacids in the form of magnesium trisilicate.

Also, Leusmann and et al. (1985) reported a patient who repeatedly produced urinary stones. Investigations using scanning electron microscopy revealed minute particles containing silicon in the core of the stone as well as in urine sediment. The patient had consumed about 3 grams of cristobalite (SiO_2) per day for years. According to themes research, a mechanism similar to that proposed for the effect of silicone-containing drugs against gastric ulcers may play a role in this formation of silicon-containing urinary stones. Drug-induced stones currently account for about 1% of urinary stones (Daudon et al., 2011). Magnesium trisilicate, component of a number of antacid preparations, when administered for long periods, has been reported to cause the formation of stones made of pure amorphous silicon dioxide, with about 30 cases reported worldwide. Several cases of calculi have been observed in babies receiving colloid silica (Gelopectose®) in their feeding bottle as a milk thickener to prevent esophageal regurgitation. In Japan, silicate calculi observed in adult subjects, as well as in an infant, were attributed to the consumption of silicate-rich

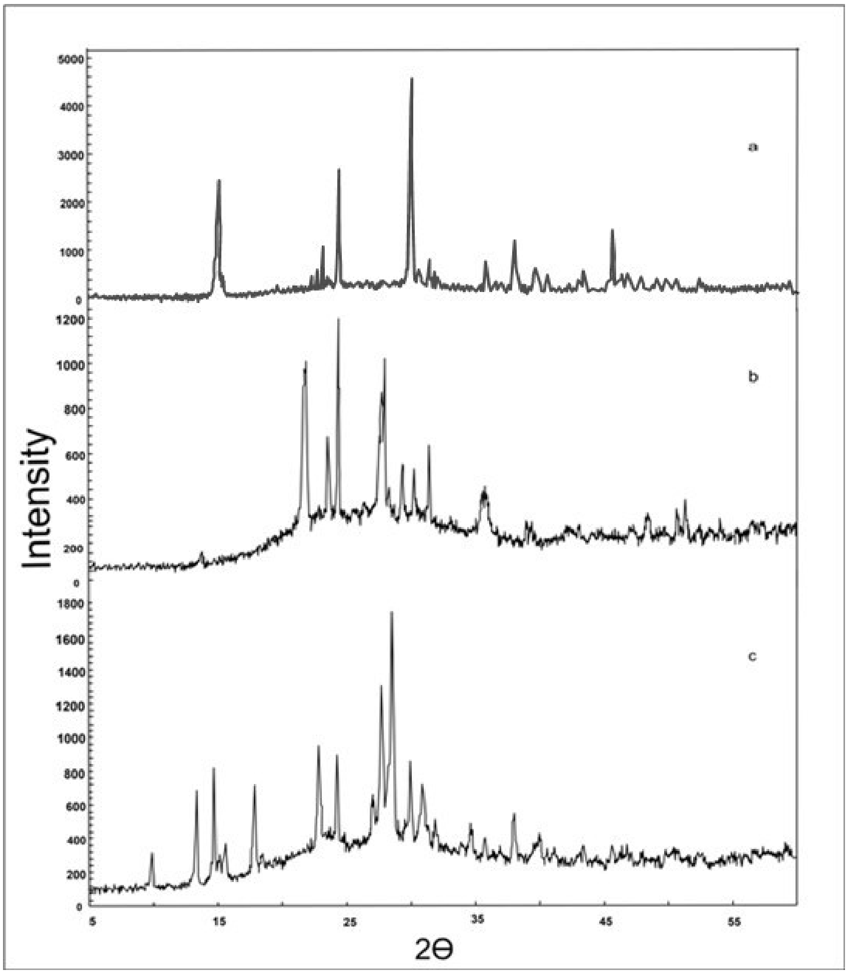

Figure 3. a) X-ray diffraction pattern of whewellite and weddellite (minor phase) minerals; b) X-ray diffraction pattern of crystobalite -calcite mineral and c) X-ray diffraction pattern of uric acid (main phase) and cystine compounds (minor phase).

water. However, Yamamoto and et al. (1990) report a case of silicate calculi with no history of taking magnesium trisilicate. Analysis by infrared spectrophotometry demonstrated the composition to be over 98% of silicate.

Despite the presence of calcium phosphate (30%) in the pathological report sheet for sample No. 2, hydroxyl apatite was not observed in the XRD result. Similarly, the niahite minerals with (NH_4) (Mn, Mg) (PO_4) H_2O composition, which have been reported as secondary phases from tropical areas of the Middle East (e.g., in Jordan and also the Khuzestan province in southwest Iran), were not observed in the current study.

Figure 4 compares the mineralogical results of the present study with other studies conducted in other parts of the world, especially focusing on regions in the Asian-African kidney stone belt, such as Baghdad in Iraq (Qaader et al., 2006), northern Jordan (Abboud, 2008), Natal in South Africa (Kerr and Laing, 1992), Calgary in Canada, Quito and Honolulu in the United States of America (Levinson et al., 1985). Based on the results of these studies and from mineralogical point of view, four groups of renal stones can be considered in East Azerbaijan province: calcium oxalate whewellite (COM), calcium oxalate weddellite (COD), uric acid (UA) and urate/calcium oxalate/cystine (U/CO/Cs) (Table 2). These results are in a good agreement with the list of the most important stone types and stone constituents for Germany reported by Straub et al. (2005).

Wu et al. (2014) have reported the major stone constituents of their analyzed renal stones as: calcium oxalate (78.3%), infection stone components (14.6%), uric acid (3.6%) and calcium phosphate (3.4%), while only 1 stone was composed of cystine (0.2%). According to Figure 4, the frequency of calcium oxalate urinary stones in East Azerbaijan province is relatively similar to the samples from Iraq (Qaader et al., 2006), Jordan (Abboud, 2008) and Khuzestan (southwest of Iran) (Zarasvandi et al., 2013; Zarasvandi et al., 2014), but is less similar to the

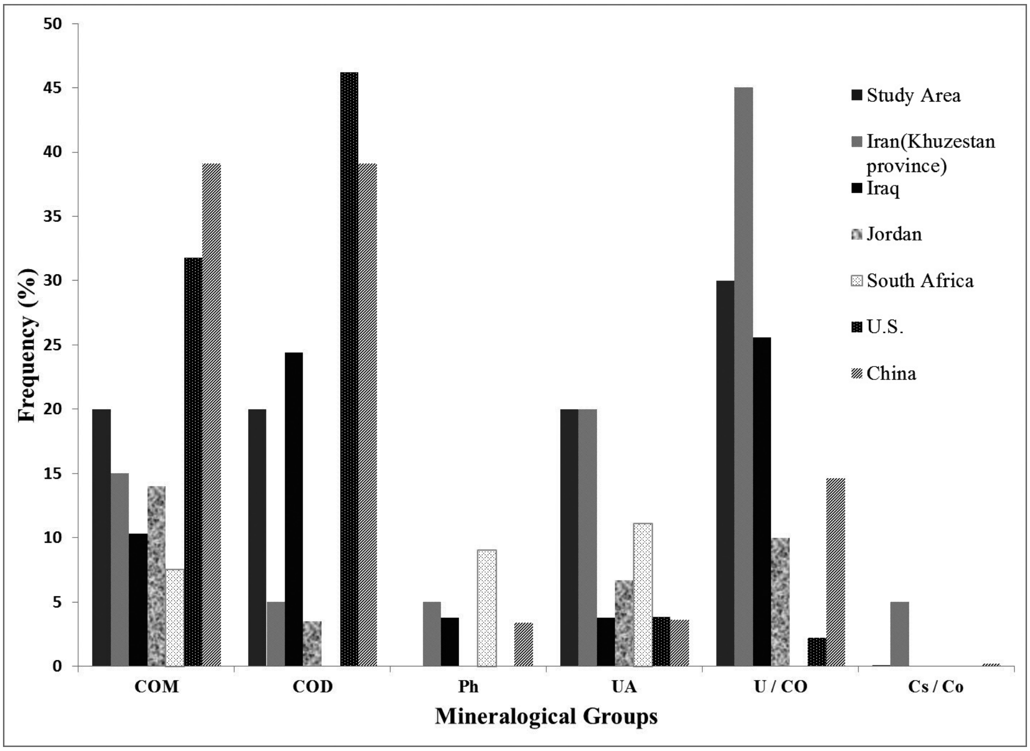

Figure 4. Comparison of the samples from East Azerbaijan province with the samples from other parts of the world in terms of the frequency of urinary minerals.

samples analyzed in South Africa (Kerr and Laing 1992). In Calgary (Canada), Quito and Honolulu in the USA, the very high frequency of calcium oxalate can be attributed to the level of calcium in the diet and drinking water consumed by people (Levinson et al., 1985). Kustov et al. (2018) have reported that about 44% of calculi were composed of pure calcium oxalate monohydrate.

Figure 4 also illustrates the mineral frequency of the urate group in East Azerbaijan province. Similar to the study carried out in Khuzestan, Iran, the frequency of this group is significantly higher than other countries. This may be related to the high distribution of uric acid minerals in the diet of the people, in addition to the semi-arid conditions in the area. However, a more detailed study is required to prove the authenticity of this finding. Considering the dissimilation of climate and diet, it seems that the geo-environmental conditions at the local scale may be the reason for high distribution of urate stones in East Azerbaijan province. Unlike the urate types, phosphate minerals such as struvite were not observed in the samples collected in this province. The small number of analyzed samples can be considered as an important limitation in this study. High levels of urate group minerals and the absence of niahite minerals are distinctions of urinary stone mineralogy in East Azerbaijan province, when it is compared with other provinces of Iran. Niahite was first reported in Malaysia and also in the study conducted in Khuzestan province, Iran (Zarasvandi et al., 2014; Zarasvandi et al., 2013).

Elemental composition of the samples

Urinary stones are usually composed of organic and inorganic materials that may threaten the health of biological organs. Determining elemental composition of urinary stones can provide useful information for taking mitigation measures in the treatment of patients (Khan, 1995; Vergauwe et al., 1994; Levinson et al., 1978). On the other hand, urinary stones may contain diverse chemical compounds (Yagisawa et al., 1999). Therefore, knowing the chemistry of urinary stones enables the researchers to determine the most common elements in the biological system of inhabitants, thereby estimating the effect of environmental conditions, particularly the geological situation on the living organisms and humans. Since urinary stones are formed inside the organs, the deposition of organic and inorganic substances in the body requires certain effective conditions.

In the present study, XRF and AAS methods were used to determine the chemical composition of the samples. Interesting results were achieved regarding the presence of some elements in particular mineral groups. In this context, the elemental distribution of urinary stones was

Table 3. Concentration of main elements in mineral urinary stones from East Azerbaijan province.

	Groups 1 and 2 N=4	Group 3 N=2	Group 4 N=3	Group 5 N=1	Total N=10
Ca	0.23-25.63	0.11-0.8	0.13-5.83	5.06	0.11-25.63
Na	0.015-0.17	0.022-0.04	0.007-0.022	3.68	0.007-3.68
K	0.04-0.05	0.05-0.066	0.058-0.157	1.54	0.04-1.54
Mg	0.066-0.11	0.011-0.012	0.006-0.01	0.42	0.006-0.42
P	0.127-0.725	0.006-0.020	0.008-0.073	0.038	0.006-0.725
Al	0.05-0.17	0.056-0.063	0.06-0.09	7.54	0.05-7.54
Ti	0.006-0.008	0.0006-0.001	0.0006-0.002	0.14	0.0006-0.14
S	0.27-0.3	0.04-0.06	0.11-0.31	0.0004	0.0004-0.31
Si	0.16-0.78	0.014-0.098	0.0046-0.009	30.55	0.0046-30.55
LOI	58.95-94.2	99.25-98.4	90.4-98.31	3.9	3.9-99.25

Groups 1 and 2: The calcium oxalate minerals: calcium oxalate mono-hydrated whewellite (COM), calcium oxalate di-hydrated weddellite (COD); Group 3: uric acid minerals (UA); Group 4: urate /calcium oxalate/cystine minerals (U/CO/Cs); Group 5: silica/calcite minerals (Si), Gallbladder stone. LOI: Loss or Ignition.

investigated in five mineral groups (Table 3). It can be seen that the contents of ten main constituents of Al, Fe, Ca, Na, K, Mg, Ti, Mn and P are different. Most of the samples had low levels of major elements except one sample (silica type group 5, Figure 3c). Moreover, this sample (gallbladder stone) had the lowest LOI (loss on ignition) and S concentration in comparison with others. The results reveal that Ca had the highest concentration in the calcium oxalate urinary stones with a frequency range of 0.23 to 25.63%. In terms of calcium frequency, urate/calcium oxalate stones were in second place. The mentioned urinary stones with the highest level of calcium were mainly formed within the kidney. Calcium oxalate stones had higher P levels than other urinary stones. K and Na had low levels. Mg and S levels were higher in calcium oxalate stone types in comparison with urate and urate/calcium oxalate. The Al levels were very low in the urinary stones.

Table 4 shows the correlation coefficients between the major elements in order to assess the element controllers determining the chemistry of urinary stones (element dispersion). It should be mentioned that in addition to the determination of chemical composition and the elements in the urinary stones and their possible role in the formation of these aggregates, evaluation of the correlation between different elements in the stones can also be used as an important tool to identify the processes involved in the formation of urinary stones. In other words, the correlation between major and trace elements within the structure of urinary stones indicates that in addition to environmental parameters, such as environmental concentration of elements, pH of the urinary system during the stone formation and so on, the elements themselves could be effective in absorption of other elements within the urinary stones. According to Table 4, Ca correlates well with P and S correlates with P (r=0.9, 0.48). During the formation of urinary stones, calcium oxalate is precipitated in the urinary tract while other alkali elements (sodium, potassium) and earth alkaline elements (magnesium) are precipitated in the presence of aluminum. The strong positive correlation between these elements and aluminum (respectively, r=0.99, r=0.99 and r=0.97) emphasizes this phenomenon. Furthermore, a strong correlation was observed between Ca and Zn in urinary stones, which was confirmed by the existence of calcium oxalate stones. This is consistent with the results of a study on urinary stones in Sri Lanka (Chandrajith et al., 2006). Table 5 compares the concentrations of different elements of urinary stones in East Azerbaijan province with those in other parts of the world. It also compares the average concentrations of elements in the present study with the previous studies carried out in Khuzestan and Fars provinces and other geological regions in Iran (Heidari, 2011; Al-Maliki, 1998; Chandrajith et al., 2006; Abboud et al., 2008; Keshavarzi et al., 2014). It can be seen that elemental contents of renal stones in East Azerbaijan province are similar to those in Khuzestan and Fars provinces. The

Table 4. Correlation among the major elements in the analyzed urinary stones.

	Si	Al	Fe	Ca	Na	K	Mg	Mn	P	S	L.O.I
Si	1										
Al	0.99	1									
Fe	0.99	0.99	1								
Ca	0.01	-0.01	0.05	1							
Na	0.99	0.99	0.99	0.01	1						
K	0.99	0.99	0.99	-0.06	0.99	1					
Mg	0.98	0.97	0.99	0.21	0.98	0.96	1				
Mn	0.57	0.99	0.99	-0.05	0.99	0.99	0.96	1			
P	-0.13	-0.14	-0.07	0.98	-0.11	-0.18	0.09	-0.17	1		
S	-0.50	-0.51	-0.48	0.46	-0.50	-0.49	-0.42	-0.55	0.48	1	
L.O.I	-0.92	-0.92	-0.94	-0.38	-0.93	-0.90	-0.98	-0.90	-0.26	0.28	1
Ca.Mg	-0.25	-0.25	-0.25	0.21	-0.25	-0.27	-0.25	-0.27	0.11	0.56	0.15

Table 5. Comparison of the concentration of different elements in the urinary stones in East Azerbaijan province and in other regions.

Element	Present study*	Khouzestan Heidari, 2011	Fars Keshavarzi et al., 2014	Jordan Abboud[a]et al., 2008	Iraq Al-Maliki[b], 1998	Sri Lanka Chandrajith et al., 2006
Major element	(%)	(%)	(%)	(%)	(%)	(%)
Na	0.5	0.09	0.15	1.56	-	0.13
K	0.29	0.06	0.13	0.9	0.098	0.03
Ca	4.98	10.79	14.76	20.33	16.71	31.92
Mg	0.07	0.31	0.06	3.08	2.92	0.14
P	0.14	1.81	0.95	10.35	-	1.93
S	0.2	0.45	1.85	1.88	-	-
Trace element	ppm	ppm	ppm	%	%	ppm
Zn	50.2	36.95	83	0.7	0.432	675
Cu	3.7	39.8	5.1	0.19	0.155	67
Pb	10.89	108.5	12.1	0.306	-	69
Cr	17.7	-	7.3	0.15	-	-
Mn	4.1	8.39	4.2	0.029	0.045	-
Ni	1.74	3	9.2	0.014	0.03	-
Al	198.4	0.04	154	0.49	-	-
Fe	55.06	-	82	3.08	1.094	258

concentrations of Pb, Mn, Ni, Al, Fe and Cr in the present study were very close to the concentrations of samples from Fars province. The differences among the contents of elements in the urinary stone samples collected from different regions can be influenced by geology, fluid intake, diet, climate and ambient temperature, genetics, etc. (Ferraro et al., 2017). Meanwhile, the role of nutrition is very prominent in urinary stone formation, especially in calcium oxalate, uric acid, calcium phosphate, and cystine urolithiasis. The process of crystallization and stone formation can be affected by dietary factors that alter urinary composition and supersaturation. Based on the current knowledge, dietary factors which affect stone formation include fluid, protein, carbohydrates, fat, oxalate, calcium, magnesium, sodium, ascorbic acid, phytate, and purines intake. Overweight and associated dietary patterns are proposed to be significant risk factors for stone formation as well (Siener, 2011). Accordingly, elemental composition of the urinary stones can vary when comparing two populations. Therefore, the differences between the elemental composition of the urinary stones collected from East Azerbaijan province with those from other parts of the world such as Jordan, Iraq and Sri Lanka can be justified.

Table 6 presents some information about urinary stone mineralogy, water hardness (Hosseinpour Feizi et al., 2012) and climate of East Azerbaijan province. As mentioned above, the risk factors affecting urinary stone formation are basically diverse (Turney et al., 2014). Oversaturated urine can lead to the formation of urinary stones, which depends on urine pH, ionic strength, concentration of dissolved solids, etc. (Skolarikos et al., 2015). Urine pH changes physiologically during different times of a day (Torricelli et al., 2014). For example, morning urine is relatively acidic and often becomes alkaline after meals. Increasing in the concentration of dissolved substances and reducting urine output increase the risk of material deposition. Various theories have been proposed about stone formation and none of them are fully confirmed. Calcium oxalate stones are often induced by hypercalciuria or excess excretion of calcium ions. Moreover, urate stones are usually associated with excess uric acid excretion or acidic arrest of urine (Sakhaee, 2011).

Relationship between drinking water hardness and urinary stone disease is not clear yet. In a study conducted in the USA, no significant correlation was found between drinking water hardness and urinary stone disease (Siener, 2011). Alkalinity of water due to the presence of bicarbonate ions can have a positive effect on treatment of calcium oxalate, uric acid, and cystine stones excluding calcium phosphate stones. It is expected that drinking water as a neutral fluid dilutes urine without affecting its composition and lowers the risk of urinary stone formation.

Based on the drinking water quality data (Mohebbi et al., 2013), 90% of the consumed drinking water in Iran is hard or very hard water (hardness 150-300 mg/l as $CaCO_3$ and >300 mg/l, respectively) and only 4% of it can be classified as soft water (hardness <75 ppm as $CaCO_3$). Basiri et al. (2012) applied the stone risk index (as the ratio of calcium to magnesium-bicarbonate) to assess the risk of calculus formation. They observed a marginally significant nonlinear inverse relationship between the incidence of the disease in the capitals with magnesium and concluded that stone risk index was associated nonlinearly with the calculus incidence (Basiri et al., 2011). According to Table 6, drinking water in East Azerbaijan is generally hard or very hard. In Sufian and Bonab counties with very hard water (more than 300 mg/l as $CaCO_3$), uric acid was the main phase of urinary stones, but in Tabriz and Sarab with hard water (150-300 mg/l as $CaCO_3$), kidney stones were mainly of oxalate type. Urate urinary stones were dominant in the warm Mediterranean climate of the province. Whether there is a relationship between the hardness of drinking water and the formation of kidney stones in the study area is not clearly known. More comprehensive study is required to better understand the effect of drinking water quality on urinary stone formation.

Principally, urinary stones are more common in warm seasons. The amount of daily water consumption by a person has a significant role in the formation of urinary stones, so that consumption of less drinking water will led to increased risk of stone formation. The most important inhibitors of renal stone formation in urine are citrates and glucosamine glycans (Hess, 2011). Higher phytate in women's urine is an effective factor in reducing the incidence of urinary stones. Phytate, of course, decreases absorption of oxalate, calcium or purines from a gastrointestinal tract. However, the role of citrate seems to be much more important (Caudarella et al., 2003). Poor diet can be considered as an underlying cause of stone formation in the people prone to kidney stones. Also, excessive consumption of food containing calcium oxalate and uric acid rises the risk of stone formation in kidney. Sedentary lifestyle and warm working environments also contribute to increase the urinary stones forming (Torricelli et al., 2014; Ferraro et al., 2017). According to the studies, the salt content in the urine of Iran's population is higher than the standard levels, indicating less consumption of liquids (drinking water) and high consumption of salt (He and MacGregor, 2009; Mazloomy Mahmoodabad et al., 2016). It should be noted that the risk of calcium stone formation is increased with higher sodium consumption. This is due to the propensity of sodium to increase urinary calcium excretion. The annual prevalence of kidney stones in Iran is in the range of 3 to 5%, and the rate in men is higher than in women (Zarasvandi et al., 2014). The major risk factors of renal stone formation in the study area may be in very low diuresis, life style (low physical activity) and dietary preferences (for example high salt intake). All these factors lead to the increasing of calcium and uric acid concentration in urine. More comprehensive study will help to clarify the reasons of kidney stone formation.

Table 6. Climate, water hardness and alkalinity of the studied cities versus mineralogical group.

City	Total hardness (mg/L as $CaCO_3$)	Alkalinity (mg/L as $CaCO_3$)	Climate type	Mineralogical Group
Ahar	298	235	Cold Mountain	Calcium Oxalate / Urate
Sarab	221	208	Cold Mountain	Calcium Oxalate / Urate
Shabestar	270	268	Tropical Mountain	Calcium Oxalate / Urate
Tabriz	255	190	Tropical Mountain	Calcium Oxalate
Marand	258	209	Tropical Mountain	Calcium Oxalate
Sufian	480	235	Tropical	Urate/ Calcium Oxalate
Bonab	349	230	Meditterranean-Semiarid	Urate

CONCLUSIONS

Studying the mineralogy of 18 urinary stones from patients living in different parts of East Azarbaijan province (NW Iran) showed that whewellite and uricite (uric acid) are the major mineral phases, whereas weddellite, calcium urate and calcite are the minor mineral phases. Calcium oxalate and urate compounds are the most abundant compounds in the analyzed samples. According to the XRD data, urinary stones in East Azerbaijan province can be divided into four groups in terms of mineralogy: calcium oxalate mono-hydrated, calcium oxalate di-hydrated, urate and urate/calcium oxalate/cystine. The mineralogy of gallstone sample was different from others. Comparing the common minerals indicated that calcium oxalate urinary stones in this province had the same prevalence ratio as in Khuzestan province and Middle East countries. However, the urate compounds were significantly higher in this province in comparison with other cities of the world. Niahite, which was observed in Malaysia and Khuzestan province, was not found in East Azerbaijan province. XRF results indicated that Ca, with a frequency range of 0.11 to 25.63%, had the highest concentration compared to other elements within the urinary stones. Obviously, the highest level of calcium was seen in the calcium oxalate stones. Furthermore, P had higher values in calcium oxalate stones compared to other urinary stones. K and Na alkali metals had lower values. One exception was the higher Mg and S contents in calcium oxalate stones than the urate and urate/calcium oxalate stones. A strong positive correlation between Ca and P indicated the tendency of calcium to participate in the structure of the phosphorus-bearing urinary stones. Also, strong positive correlation among Na, K and Ca with Al indicated the strong tendency of alkali metals to accumulate in the calcic stones containing aluminum. The kidney stone formation process is similar to the crystallization process of sedimentary particles such as pisoids and oncoids. This process starts by material deposition around one or more initial cores. However, studying the diet and chemistry of drinking water in the kidney patients is necessary to identify the potential causative agents for biomineralization of kidney stones. In the cities with very hard drinking water, uric acid was the main phase of urinary stones and in the cities with hard drinking water, the kidney stones were mainly of oxalate type. In the warm Mediterranean climate of East Azerbaijan province, urate urinary stones were dominant.

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