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Rare Earth Elements: In Silicon Water and Features of the Ecological Status

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ABSTRACT

The qualitative and quantitative composition of the natural surface and groundwater of the artesian basin is formed on the basis of the metallogenetic indicators of the catchment areas. In the chemical indicators of waters, in addition to ions of bicarbonate, sulfate, fluorine and chlorine, there are SiO_2 (H_4SiO_4), cations Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and noble, colored, rare and rare earth elements.

KEY WORDS:surface natural and ground waters, chemical composition, silicon, carnelian, rare element

INTRODUCTION

The development of civilization is impossible without the constant expansion of the use of mineral resources, involving more and more new types of mineral raw materials in the technological process. According to V.A. Mikhailov (2010) one of the examples of such raw materials can be rare earth elements (REE), which include lanthanides and similar yttrium in terms of properties, sometimes scandium.

For a long time, they did not find wide practical application, although already at the end of the 19th century. their practical use began, and in 1885 - the development of monazite placers in Brazil with the aim of obtaining thorium and cerium from monazite, which are used in small quantities to increase the brightness of the glow in hot gas nets, caps of burners of gas lamps, kerosene and alcohol lamps.

Research of rare earth elements in mineral waters is of great importance for the national economy. Since the qualitative and quantitative composition of macro- and microelements of natural surface and ground waters is formed depending on the mineral composition, lithology and metal content of the catchment area [6].

MATERIALS AND METHODS

In the Pritashkent mining area, coastal-marine (littoral) sediments of chert rocks (Yusuptash, Apartak-Angren brown coal quarry, Sukok, Mayskoye, Tavaksay, Azatbash, Krasny waterfall, etc.) Upper Essecene - Lower Oligocene (P23 - P31) quartzites from quartz horizons (fractions from less than 5-20 to 20-70 mm and more) consists of a set of minerals of the family of quartz, chalcedony, opal in combination with silicon, jasper, etc. The matrix of detrital flint and carnelian is composed of micro-fibrous chalcedony on an opal substrate and in the presence of

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organic inclusions from the remains of sponges, echinoderms, etc., contains inclusions of Fe - Si-Au (oxides and hydroxides of Fe, Mn), microdispersed clayey (montmorillonite) components and organic residues (cluster dimensions).

To assess the state of rare earth elements, the study of the chemical composition and geochemical properties of condensed siliceous waters is used.

Natural waters washing the Upper Paleozoic volcano-plutonic associations (Pritashkent region, Chatkalo-Kuraminskaya active continental margin) are extracted from them and enriched with ions of hydrocarbonate, sulfate, chlorine, fluorine, etc. [5]. The share of the transferred hydrocarbonate of them accounts for up to 30-150 mg / l, sulfate ion - about 15-20 mg / l, chlorine ion - up to 20-50 mg / l. The reactions of hydrolysis of rock-forming and other nonmetallic minerals, as well as ores, affect the carbon dioxide, sulfate and chlorinated content of waters, against the background of deeper weathering of bedrock rocks. Biological factors of weathering of rocks and ores [6,15] are the most important events in the weathering of rocks and ores, the subsequent mineralization of surface and ground waters.

RESULTS AND DISCUSSION

In natural surface and underground waters, silica is present in the form of monosilicon MnSiO4 and other (water pH less than 9) compounds; silicic acid [17] dissociates (-) into ions only at pH above 9. In most natural waters, the presence of colloidal fractions of silica (gels, etc.) is practically not established. The weathering of rocks enriches the washing waters with a small amount of silica. Silica dissolves at 18-250 C of water (up to 0.012 -0.014% [5]) with the formation of a molecular (dispersed) form (true solution). The crystalline form of silica and quartz itself dissolve in comparison with its amorphous form; at ordinary water temperatures, the scattered metals are ten times less [14] (up to 2.5 - 10 mg / l). In waters, in addition to true solutions, they form suspensions (very thin clusters - for example, Au, etc.).

The results of the analysis of the water extraction of flints and carnelian serve as indicators of the presence of ionic-cationic components, as well as the values of hardness, oxidizability, pH, and other properties. Therapeutic and prophylactic indicators of natural flints [5] inherit the so-called. "Silicon waters" (distilled water extract on silicones, or chalcedony, or carnelian). (Table 4).

Small (scattered) elements (Table 1) are borrowed by distilled water from minerals (samples of silicon and carnelian from the Upper Eocene - Lower Oligocene littoral deposits, Yusuptash on the Angren plateau) consist of noble metal sets, elements of the iron family, rare metal and rare earth elements (Table 6) and etc.

Table 1. Content of impurity elements in water extraction on natural flints and carnelian, μg / l

Elements	*Sample numbers: coefficient of extraction of elements - "impurities"*						$\overline{x}_r$[4] (amount 100%)	$K_к$ – *water extraction concentration factor*	
	Water extraction of Silicon			*Water extraction of carnelian*				FromSilicon	From carnelian
	170-1	170-3	Xк	170-2	170-4	$\overline{x}_c$ average			

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Fe	**35,80**	**15,70**	**25,75**	**29,10**	**51,50**	**40,30**	**0,01**	**3,60**	**4,00**
Mn	**3,76**	**0,62**	**2,19**	**1,7**	**5,34**	**3,37**	**0,002**	**1,1**	**1,7**
Co	**0,03**	**0,03**	**0,03**	**0,05**	**0,10**	**0,08**	**0,0005**	**0,06**	**0,16**
Ni	**0,26**	**0,08**	**0,17**	**0,83**	**0.19**	**0,51**	**0,002**	**0,10**	**0,30**
Ca	**13870**	**13304**	**13587**	**11433**	**26321**	**18877**	**408**	**0,03**	**0,05**
Mg	**675**	**3438**	**2057**	**730**	**4208**	**2469**	**1297**	**0,002**	**0,002**
K	**392**	**668**	**530**	**579**	**1091**	**835**	**387**	**0,001**	**0,002**
Na	**403**	**1609**	**1006**	**1493**	**1679**	**1586**	**10354**	**-**	**-**
P	**25,6**	**10.6**	**18,1**	**14.1**	**48,4**	**31,25**	**0,07**	**0,30**	**0,50**
Cu	**1,09**	**0,74**	**0,92**	**1,61**	**2,10**	**1,86**	**0,003**	**0,30**	**0,60**
Mo	**1,34**	**2,90**	**2,12**	**0,16**	**2,83**	**1,50**	**0,01**	**0,20**	**0,20**
Re	**-**	**0,01**	**0,01**	**-**	**0,01**	**0,01**	**-**	**-**	**-**
Zn	**0,31**	**0,45**	**0,38**	**0,36**	**2,69**	**1,53**	**0,01**	**0,04**	**0,20**
V	**1,84**	**1,80**	**1,82**	**1,23**	**1,32**	**1,28**	**0,003**	**0,60**	**0,40**
Cr	**6,34**	**8,26**	**7,30**	**4,88**	**3,57**	**4,23**	**0,0002**	**365**	**212**
Ti	**0,19**	**0,24**	**0,22**	**0,10**	**0,70**	**0,4**	**0,001**	**0,1**	**0,40**
Au	**0,03**	**0,01**	**0,02**	**0,03**	**0,01**	**0,02**	**0.000004**	**5,0**	**2,5**
Ag	**0,02**	**0,002**	**0,011**	**0,04**	**0,07**	**0,06**	**0,0003**	**0,04**	**0,02**
J	**3,09**	**2,51**	**2,80**	**3,01**	**6,96**	**5,00**	**0,05**	**0,06**	**0,10**
Br	**5,87**	**11,9**	**8,89**	**4,48**	**12,20**	**8,34**	**65,0**	**-**	**-**
Li	**0,48**	**2,34**	**1,41**	**1,22**	**2,02**	**1,62**	**0,15**	**0,01**	**0,01**
Rb	**0,46**	**0,81**	**0,64**	**0,44**	**1,21**	**0,83**	**0,2**	**0,003**	**0,004**
Cs	**0.03**	**0,04**	**0,04**	**0,04**	**0,04**	**0,04**	**0,00037**	**0,12**	**0,12**
Ba	**18,4**	**40,9**	**29,65**	**9,69**	**47,20**	**28,45**	**0,02**	**1,50**	**1,42**
Sr	**52,5**	**124,0**	**88,25**	**73,4**	**135,0**	**104,0**	**8,0**	**0,01**	**0,01**
Zr	**0,01**	**0,01**	**0,01**	**0,04**	**0,06**	**0,05**	**0,00005**	**0,20**	**1,00**
W	**16,20**	**9,20**	**12,70**	**5,26**	**5,23**	**5,24**	**0,1**	**0,13**	**0,05**
Nb	**0,01**	**0,01**	**0,01**	**0,003**	**0,01**	**0,01**	**0,00001**	**1,00**	**1,00**
Ta	**0,002**	**0,008**	**0,005**	**-**	**0,003**	**0,002**	**-**	**-**	**-**
Sn	**0,03**	**0,03**	**0,03**	**0,02**	**0,27**	**0,15**	**0,003**	**0,01**	**0,05**

Note: ICP-analysis in the SE SPC "Geology of Hydromineral Resources" of the State Committee for Geology of the Republic of Uzbekistan. Water extraction of flint (sample 170-1, 170-3), carnelian (170-2,170-4). Extraction from samples 170-3 and 170-4 was carried out with boiling in distilled water; Xk, Xc, Xr are the average values in aqueous extracts on flints (Xk), carnelian (Xc) and the average value of the hydrosphere [7] (Xr).

Table 2. Rare earth elements, yttrium (total REE + Y, 100%), scandium, uranium and thorium (µg / L) in condensed water extraction on flints and carnelians.

Elemenrs	*Extraction on silicon*	*Carnelian extraction*	$\overline{x}_r$[4] *(amount*	$K_к$– *coeff. concentration of aqueous extraction*

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							100%)		
	170-1	**170-3**	**$X_к$**	**170-2**	**170-4**	**$\overline{x}_c$** average		From silicon	From carnelian
Ground-Ce									
La	**22,72**	**4,41**	**13,57**	**21,62**	**7,77**	**14,7**	**0,93**	**14,6**	**15,8**
Ce	**36,36**	**8,09**	**22,23**	**21,62**	**27,79**	**24,71**	**0,42**	**52,9**	**58,8**
Pr	**5,56**	**1,47**	**3,01**	**5,41**	**3,33**	**4,37**	**0,19**	**15,8**	**23,0**
Nd	-	**72,79**	**36,4**	**29,73**	**25,55**	**27,01**	**0,07**	**520,0**	**385,9**
Sm	-	-	-	-	-	-	**0,14**	-	-
Ground-Tb									
Eu	**3,20**	**3,68**	**3,44**	-	**5,56**	**2,78**	**0,35**	**9,8**	**7,9**
Gd	**1,35**	-	**0,68**	-	**4,44**	**2,22**	**0,20**	**3,4**	**11,1**
Tb	-	**0,73**	**0,37**	**2,70**	**1,10**	**1,90**	-	-	-
Ground-Er									
Dy	**4,55**	**2,95**	**3,75**	-	**3,35**	**1,68**	**0,24**	**15,6**	**7,0**
Ho	-	-	-	-	**1,10**	**0,55**	**0,07**	-	**7,9**
Er	**13,63**	-	**6,82**	-	-	-	**0,19**	**35,9**	-
Tm	-	**0,73**	**0,36**	-	-	-	**0,05**	**7,2**	-
Ground-Yb									
Yb	**3,00**	-	**1,50**	-	-	-	**0,17**	**8,8**	-
Sc	**0,084**	**0,323**	**0,204**	**0,128**	**0,253**	**0,191**	**0,040**	**5,1**	**4,8**
Th	**0,012**	**0,005**	**0,009**	**0,011**	**0,011**	**0,011**	**0,700**	**1,4**	**1,4**
U	**0,133**	**0,316**	**0,225**	**0,134**	**1,860**	**0,997**	**3,000**	**0,1**	**0,3**
REE,μg / L	**0,021**	**0,126**	**0,074**	**0,037**	**0,090**	**0,061**			
REE_{Ce}	**0,014**	**0,109**	**0,062**	**0,029**	**0,058**	**0,044**			
REE_y	**0,007**	**0,017**	**0,012**	**0,008**	**0,032**	**0,020**			

The mineralogical and geochemical connections of carnelian proper [7, 10, 11, 12] with the component composition of waters and their origin (mechanisms of sedimentation and adsorption of silica, the phenomenon of diagenesis with the formation of silica organic residues, etc.) are of particular interest. The mineral compositions of flint (carnelian) contain inclusions of Fe-Si-Au (Ag) (oxides, hydroxides, Fe, Mn) [11, 12], microdispersed (cluster nature, from less than 100 nm and more) inclusions of clay (montmorillonites) and organic matter (carriers of noble metal - Au, Ag, Pt, Pd, Rh), rare metal - and rare earth components).

Experimental studies (Table 1) made it possible to calculate the coefficient Кк - distilled water extraction. High values are typical for Cr (212-365), Fe (3.6-4.0), Mn (1.10-1.70), Au (2.5-5.0). These are the main elements of the chemical compositions of the aqueous extraction of natural flint and carnelian. In this regard, conclusions arise about their biochemical, medical and ecological-physiological status and positive effects on the body [6,8].

Based on the results of the chemical compositions of the aqueous extractions of flint and carnelian, associated with the intensity of accumulation of small (scattered) elements in the

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waters, the calculated coefficients (Kk) for each element and the series of their accumulation were obtained: [8]

I. *Silicon*$_4Cr^-$ - ($_1Au^+$ $_{14}Fe^+$) – $_3Si^-$ - $_7Ba^+$ - ($_1Mn^-$, $_1Nb^+$) – $_2V^-$ - $_3Zr^-$ $_2Cu^+$ - $_7Mo^-$ - $_5Ti^-$ ($_5Ni^+$, $_1Co^+$) - $_1J^+$ - $_5Zn^+$, $_2Ag^+$ - ($_6Ca^+$ - $_4Sr^+$) – ($_{10}Sn^-$, $_2Li^-$) – ($_3K^-$, $_2Rb^-$) - ….

II. *Cornelian*$_4Cr^-$ - ($_4Fe^+$, $_1Au^+$) – $_3Si^-$ - $_1Mn^-$ - $_7Ba^+$ - ($_5Zn^-$, $_1Nb^-$) – $_2Cu^+$ - ($_5Ti^-$, $_{12}V^-$) – $_5Ni^+$- $_5Zn^+$, $_1Co^+$ - $_7Mo^-$ - $_1Cs^-$ - $_1J^+$ - $_6Ca^+$ - ($_{10}Sn$, W^-) – $_2Ag^+$- $_4Sr^+$ - ($_2Li^-$, $_2Rb^-$) – $_3Mg^+$ - $_3K^-$ - ….

Note: the number of stable isotopes of the element is at the bottom, (+) - right-handed, (-) - left-handed rotation [10,13].

In natural waters, the Fe family is closely associated with Au and Cr ions with the accompanying Ba. The lowest contents belong to Ca, Mg, Sr, K, Rb; their water extraction from flint (I) and carnelian (II), compared with high values of extraction of Cr, Fe, Mn, Ba, serve as indicators of their saturation in the experimental water extract.

In the water extraction of flint (I) and carnelian (II), rare earth elements are constantly present in combination with sodium, scandium, uranium and thorium and their series of Кк - water extraction:

I. *Silicon* - [Nd – (Ce,Er] –(Pr, Dy, La) – (Eu, Yb,Tm) – Sc, Cd, Lu – Th – (Y,U)- …

II. *Cornelian* - Nd - [Ce –Pr – (La, Gd)] – (Eu,Ho, Dy) - Sc - Lu – Th – $_3U^-$ - $_6Y^-$ …

All REE - elements, sodium, scandium, uranium and thorium belong to levorotatory, with Sc and Th - monoisotones, U- triisatone, Y- hexaizatone, Ce and other REE elements - tetraisotones.

BI Kogan [7] REE considers “very important elements” (III), of which La, Ce, Pr and Nd are glass components (La and other optical drains, heat-resistant, resistant to radiation and UV transmission), compounds for radio electronics, Ce144 - in isotopic current sources for spacecraft, Er - absorption of neutrons in portable nuclear reactors; luminaphores for television. In nature, REE - elements are ubiquitous [7], they are not indifferent to plants, animals, humans. It should be noted that the very low concentration of La in bone tissue plays an important role in the development and growth of bones.

Experimental studies have shown that "silicon water" [8] with a complex of REE - elements, sodium, scandium, uranium and thorium (see Table 6) helps to suppress opportunistic microorganisms of the genus Micrococcacea, causing fermentation, removes the dead disease-causing microflora and microorganisms ... Silicon in the body precipitates "heavy" (Pb, Mg, Sr, Cd, Zn, Fe, Cs) metals, neutralizes chlorine, removes phenolic and nitrate compounds, sorbs radionuclides, suppresses fungi, bacteria, algae, parasites, protozoa.

Silicon water for the body is the most physiological, improves metabolism, promotes calcium absorption, stimulates bone growth; strengthens blood vessels, cartilage, tendons, improves the condition of the skin, nails and hair, reduces the risk of developing cardiovascular diseases.

The large isotonic series of the REE set [10] consists of 30 elements (Sm, Eu, Gd, Tb, Dy, (-) Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, (-) Jr, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Rd, Ac, Th, Pa). "Torsion portrait" of isotonicity of REE - elements is formed on internuclear (neutron) bonds and

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the number of neutrons in the nuclei of each element). In the theory of physical vacuum [13], solid bodies (minerals) have high relative information content, energeticity with their primary torsion fields, created by the rotation of particles (REE - elements, Y, Sc, Th, U - levorotatory with a minus sign).

CONCLUSION

1. Components of natural surface and groundwater are products of physical, biological and chemical weathering of rocks and minerals, which significantly change the chemical composition (natural vertical landscape - chemical stratification) of waters based on:

a) chemical weathering of rocks and minerals, the waters are enriched with a monosilicon form of silica (H_4SiO_4);

b) mechanical weathering, maintaining the presence of molecularly dispersed - cluster-mineral (quartz, field lipates, zirconium, gold, etc.) forms in water compositions;

c) biological processing of silicon minerals of rocks by microorganisms, including phytolitaria, enriches the presence of amorphous (colloidal) forms in waters.

2. Experimental studies on the enrichment of surface and ground waters with silica and a complex of accompanying elements were carried out by water extraction (condensation) on flints and carnelians (see Tables 5 and 6), the results of which are consistent with the materials [5,6,17] in terms of solubility amorphous silica in a similar artificially created natural geological setting. Extracted from flint, carnelian and other REE - elements, Y, etc., take part in certain quantities in the development and growth of crop yields [7]. "Silicon waters" from flint and carnelian are characterized by high values of Кк - water extraction of REE - elements:

I. Silicon. [Nd - (Ce, Er)] - (Pr, Dy, La) - (Eu, Yb, Tm) - Sc - Gd, Lu - Th- (Y, U) - ...

II. Cornelian. Nd - Ce - [Pr - (La, Gd)] - (Eu, Ho, Dy) - Sc –Lu - Th - (Y, U) -…

In nature, REE - elements are ubiquitous [7], their indifference is absent for plants, through them - for animals, through sea water - for fish, worms, plants, animals and drinking water - for mankind.

3. Analysis of the results obtained shows that artificially prepared waters based on natural minerals - flint and carnelian for therapeutic and prophylactic purposes have broad prospects and are of scientific and practical interest. Also, everywhere it will promote the transition to the use of the method of biodynamic production of agricultural products, "upgrading" of sown lands based on the wider use of natural agromineral rocks and ores (phosphorites, celadonites, glauconites, bentonites, etc.) without their preliminary chemical processing.

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