

Trace and Rare-Earth Elements in Natural Ground Waters: Weathering Effect of Water-Rock Interaction

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ABSTRACT: The distributions of Ca, Cr, Fe, Co, Zn, Ga, Se, Rb, Ba, Tl, Bi, Th, U and rare-earth elements (REEs), measured by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) in ground natural waters characterized by near-acidic to alkaline pH (5.7 – 9.0), were evaluated to examine the major processes of water-rock interaction. Cluster analysis of ground water quality parameters resulted in three clusters: 1) transition elements (Cr, Co and Zn); 2) REEs; and 3) geogenic elements (Rb, Ga, Ba and Th) with 55%, 60% and 75% similarity levels, respectively. Also, natural ground waters with relatively high salinity (5.3 – 6.8 g/L) were found to be significantly enriched with Ca, Cr, Co, Zn, Ga, Rb and Ba compared to lower-salinity waters (0.5 – 3.7 g/L). Negative Ce (from 0.4 to 0.9) and positive Eu (from 1.2 to 17.5) anomalies were found in the investigated waters and most of them were associated with heavy rare-earth elements (HREEs) enrichments. It was established that the relative proportion of total REE concentration (range 75 – 470 ng/L) to Ca abundance (from 1 to 180 mg/L) could be a useful indicator of weathering processes in studied ground waters. This observation is attributed to the increase in the calcite dissolution during the weathering process, as well as to REEs leaching due to the complex formation of bicarbonate. The reliability of the ICP-SFMS method was checked by using certified reference materials (SLEW-3, SLRS-4 and TMRAIN-04). The relative standard deviation (RSD) was < 10%.

Key words: Transition and non-transition elements, heavy and light rare-earth enrichments, Ce and Eu anomalies, Inductively Coupled Plasma Sector Field Mass Spectrometry

INTRODUCTION

Awareness of the interaction between rocks and waters during the weathering process is important for investigations not only of water quality but also of the greenhouse effect caused by CO₂ (Gaillardet et al., 1999, Millot et al., 2002, White and Blum, 1995). As noted by White et al. (1999), atmospheric CO₂ is affected by weathering processes, and calcite (CaCO₃) in rocks is one of the main components that carry CO₂. According to authors (Garrels, 1967, Garrels and Mackenzie, 1967), the weathering of rocks is associated with dissolution reactions, including: $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$. CaCO₃ is the second most common mineral in nature and, together with metals, readily precipitates in liquids (Munemoto et al., 2014). As ground water moves through calcite rocks, its chemical composition depends on the specifics of water-rock interaction processes

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(Johannesson et al., 1999, Mapoma et al., 2014, Mapoma et al., 2016, Sharaf, 2013). These processes include the precipitation and dissolution of minerals, adsorption and desorption reactions with colloidal particles, and oxidation and reduction reactions (Alam and Umar, 2013, Mas-Pla et al., 2016). Thus, in ground waters, metals are present as colloids, dissolved ions, in suspension and solid forms, and their state significantly depends on pH, redox condition, ionic strengths as well as on weathering processes (Nesbitt and Markovics, 1997, Thuyet et al., 2016).

The non-transition elements could be subdivided into scavenging (e.g., Ga and Ba), conservative (e.g., Rb) and other anthropogenic elements (Lalraj and Nair, 2009). Transition metals such as Cr, Co and Zn, with a lower valency in oxic conditions, could form

insoluble oxides (Calvert and Pedersen, 1993). In turn, Cr, Fe, Co and Zn change their oxidation states in anoxic conditions, which is associated with sufficient changes in their solubility (Laluraj and Nair, 2009).

The actinides U and Th are commonly distributed in the environment (Kringel et al., 2010). Normally, Th abundances in soils and rocks are three times as high as U, and Th isotopes are products of the decay of U. In oxic aquatic systems U is prone to form a stable complex $UO_2CO_3^{4-}$ (Garrels and Christ, 1965). Nevertheless, in anoxic conditions U^{4+} mostly exists in the hydroxide or oxide forms.

Rare-earth elements (REEs) belong to the third group in the periodic table: they have similar chemical properties and are very sensitive to environmental changes. This group of elements is mobilized during weathering and could be used as one of the most effective tools in geochemical studies (Bwire et al., 2003, Fiket et al., 2015, Johannesson et al., 2006, Li et al., 2016, Migaszewski et al., 2014, Tweed et al., 2006, Willis, 2010). The mobility of REEs from minerals is complex due to the emergence of accessory phases that are resistant to acidic weathering (Johannesson and Lyons, 1995, Johannesson et al., 1994, Johannesson et al., 1996). Nevertheless, the release of REEs from minerals may be due to the reactions with complexing ions that are widely present in natural waters (Alakangas et al., 2014, Minarik et al., 1998). The steady decrease of ionic radius from La to Lu significantly affects the strength of complexation (De Baar et al., 1991, Hemberger et al., 2004). Thus, on the one hand, heavier lanthanides could form stronger and more stable complexes in liquid form (Michael, 1999); on the other hand, significant removal of light REEs could be observed due to their salt-induced coagulation of colloids (Feely et al., 1981, Sholkovitz, 1992). A study (Dobashi and Shikazono, 2008) found that carbonate minerals in sedimentary rocks are enriched with light rare-earth elements (LREEs) rather than HREEs. As a result, we can observe a predominance of HREEs over LREEs in liquid forms (Sholkovitz, 1995, Yuan et al., 2014, Zhan et al., 2013). Also, it was noted (Möller, 2003) that LREEs were less leachable from rocks than the heavy ones, and Eu was more leachable compared to other light REEs.

Ce and Eu could be present in different oxidation states, e.g., in enriched oxygen conditions, the oxidation of Ce^{3+} to Ce^{4+} is observed and further removal of less soluble Ce^{4+} from liquid occurs (DeCarlo et al., 1998, Moffett, 1994, Otsuka and Terakado, 2003). Studies have shown (Jianfei et al., 2014, Kurian et al., 2008, Marmolejo et al., 2007, Michael and Kamber, 2006) that REE abundances are basically linked with pH, and that feldspars could cause a Eu anomaly. It was also

found (Sverjensky, 1984, Yuan et al., 2014) that the concentrations of redox sensitive ions such as Fe^{2+} / Fe^{3+} correlate with Ce and Eu anomalies in groundwaters. Therefore, Ce and Eu anomalies (4+ and 2+ valence) relative to other REEs may be used to probe redox conditions in the environment (Guo et al., 2010, Olias et al., 2005).

Other authors (Nakajima and Terakado, 2003) found that REE abundances in waters tend to be higher in strongly weathered areas and lower in weakly weathered ones. Moreover, waters from weakly weathered areas presented higher Ca contents, associated with abundant calcite in those rocks. By contrast, low Ca abundances were found in strongly weathered areas, due to the calcite being consumed by previous weathering processes. Thus, considering the above-mentioned calcite weathering reaction ($CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$) and the predisposition of REE to complexate with HCO_3^- (Johannesson et al., 1999, Millero, 1992), it can be assumed that REE enrichments in liquids could be caused by water-rock interactions due to chemical weathering – an assumption which correlates with the results obtained by Nakajima and Terakado (2003).

Ukrainian groundwater resources are generated in Pre-Cambrian crystalline rocks and overlain by Neogene fluvio-glacial sands and limestone ($CaCO_3$) (Zektser and Everett, 2004). These waters are mainly used as sources of potable water and for medicinal purposes. The available literature on Ukrainian groundwaters includes only a limited number of studies dedicated to the distribution of some trace elements (Alpatova et al., 2004, Kurochkin et al., 2014, Polumbryk et al., 2014, Vystavna et al., 2012, Vystavna et al., 2015, Zhuravlev et al., 2016). So far, the distribution of REE elements in natural ground waters in different regions of the Ukrainian territory has not been widely reported.

In order to fill this gap, the present research work focuses on the distribution of REEs, transition and non-transition elements, including U and Th, in natural ground waters collected from the Ukrainian territory. For the present study, Ca, Cr, Fe, Co, Zn, Ga, Se, Rb, Ba, Tl, Bi, Th, U and 14 REEs were selected on the basis of their environmental interactions and natural abundances. The main goal of this work is to understand the major processes of water-rock interaction by controlling the relationship between REEs and trace elements, including Ca, in ground waters.

MATERIALS & METHODS

ICP-SFMS measurements were performed with an Element 2 (Thermo Fisher Scientific, Bremen, Germany) with the high-efficiency introduction system Apex

(Elemental Scientific, USA) in a laboratory at the Department of Environmental Sciences, Informatics and Statistics (DAIS) of Ca' Foscari University of Venice, Italy, under a class-100 clean bench. Three different resolution settings (m²/m), namely low-resolution (300), medium-resolution (4000) and high-resolution modes (10000), were used throughout this work. Daily-optimized parameters for the instrument are presented in Table 1.

Table 1. Operating parameters for Inductively Coupled Plasma Sector Field Mass Spectrometry

ICP-SFMS - "Element 2"	
RF power -	1150 W
Cooling gas -	11.0 L/min
Sample gas -	0.9 L/min
Auxiliary gas -	1.3 L/min
Dwell time -	10 ms
Sample uptake -	0.1 mL/min
Acquisition mode -	E-scan: over a small mass range
APEX spray chamber temperature -	140 °C
APEX cooler temperature -	2 °C
Ion lens settings:	
Extraction	-2000 V; Focus - 952 V
X-Deflection	4.15 V; Shape 133 V
Y-Deflection	- 1.72 V

High-purity water from a Purelab-Ultra system (ELGA-Vivendi Water Systems, Bucks, UK) was used for all the preparations. All reagents and chemicals were

by Merck (Darmstadt, Germany) and Romil (Cambridge, UK) of suprapure quality.

Multi-element chemical standards IV-STOCK-6 (Inorganic Ventures, Christiansburg, USA) and IMS-101 (LGC) were used to prepare calibration solutions. Internal standard of In (1.0 µg/L) acidified with suprapure HNO₃ (5%) was obtained from a 1000 mg/L standard stock solution.

All materials and vials used for sampling, treatment and analysis were acid-cleaned with HNO₃ and finally rinsed with MilliQ water.

The Certified reference materials (CRM) Estuarine Water (SLEW-3), River Water (SLRS-4) and Rain Water (TMRAIN-04), produced by the National Research Council of Canada, were used to check the accuracy of the method.

The natural ground water samples (Table 2) were taken from the Ukrainian Scientific-Research Institute of Medical Rehabilitation and Balneology (Odessa, Ukraine).

To ensure the reliability of analytical data Quality Assurance (QA) and Quality Control (QC) criteria are known as an effective tool (Geboy and Engle, 2011, Shuttler, 1995, Taylor, 1981). The main principles of QA and QC have been discussed in numerous papers, standards and guidance documents published by the Environmental Protection Agency (EPA), the Association of Official Analytical Chemists (AOAC), the American Society for Testing Materials (ASTM),

Table 2. Natural ground water samples

	Salinity g/L	pH	Location
1	5.31	6.6	City Tyachiv, Zakarpatska region
2	0.70	8.2	City Belgorod-Dnestrovsk, Odessa region
3	0.62	7.2	Storozhynets district, Chernovtsy region
4	0.59	7.3	City Lipovets, Vinnitsa region
5	0.94	8.0	Ovidiopolskij district, Odessa region
6	0.53	7.3	City Mirgorod (1), Poltava region
7	3.15	7.7	City Mirgorod (2), Poltava region
8	0.61	7.7	City Mirgorod (3), Poltava region
9	6.79	6.5	City Svalyava, Zakarpatska region
10	0.75	7.4	Gorodetskiy district, Khmelnytsky region
11	1.21	7.8	City Odessa, Odessa region
12	0.82	7.4	Settlement Mykulyntsi, Ternopol region
13	1.19	5.7	City Truskavec (2), Lvov region
14	3.64	7.7	Village Kuyalnik (1), Odessa region
15	3.70	7.1	Village Kuyalnik (2), Odessa region
16	0.75	7.2	City Zhashkiv, Cherkassy region
17	1.22	9.0	City Kamenka, Dniester Moldavian Republic
18	0.96	7.1	Village Petrine, Kirovograd region
19	0.53	7.4	City Cherkassy, Cherkassy region
20	2.35	7.9	City Saki, Crimea region

the International Organization for Standardization (ISO) with the Dutch Standardization Institute (NEN), etc. In the present study, in order to achieve QA and QC, we followed the procedures of sample collection, treatment, sample preparation, measurements and evaluation of the obtained results, based on the methods ISO 5667-3; ISO 17294; NEN 6427:1999; EPA Method 6020A.

During sample collection, treatment and preparation, procedures were carried out in order to minimize possible contamination. Prior to sample collection, all sample containers were cleaned using 5% HNO₃, rinsed with MilliQ water and finally rinsed three times with individual groundwater samples. All natural ground waters were collected directly from the springs (Table 2), which are pumped continuously for water supply. In order to preserve the integrity of the original sample for the analysis of the total content of elements, the filtration procedure was excluded. Two parallel sets of samples were collected at every site: 1) acidified with HNO₃ for further ICP-SFMS analysis (0,5 mL of concentrated nitric acid per 100 mL of a sample to prevent precipitation onto container walls); 2) unacidified for pH and salinity (electric conductivity) measurements using a pH-meter CP-103 and conductivity-meter CC-103.

Before the analysis, the water samples were diluted tenfold with 5% nitric acid to reduce the influence of matrix effects. All the samples and standard preparation procedures were performed in a clean room under a laminar flow bench DAIS using the gravimetric method. For ICP-SFMS measurements, a washing step with 5% HNO₃ was applied for 2 min between each sample.

Prior to the sample analysis, the ICP-SFMS instrument was optimized daily and an accurate mass calibration in high, medium and low-resolution modes was performed by adding In (1.0 µg/L) as an internal standard. To evaluate the effects of acidification, dilution and addition of the internal standard, the measurements of corresponding blank solutions (the same acid and water used) were performed before standards and samples analyses, and all of the blank values were respectively subtracted. The ICP-SFMS measurements were performed using the following isotopes: ⁴³Ca, ⁵²Cr, ⁵⁶Fe, ⁵⁹Co, ⁶⁶Zn, ⁶⁹Ga, ⁸²Se, ⁸⁵Rb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁴Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶²Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ²⁰⁵Tl, ²⁰⁹Bi, ²³²Th and ²³⁸U. These isotopes were chosen because they are naturally more abundant and have less interference than others (EPA Method 6020A:1998, ISO 17294-2:2002, May and Wiedmeyer, 1998, NEN 6427:1999).

Although the selected isotopes are almost free of isobaric interferences the medium-resolution mode (m/

Δm ~ 4000) was applied to Ca, Cr, Fe, Co, Zn, Ga, and the high-resolution mode (m/Δm ~ 10000) to Se, Eu and HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu) during ICP-SFMS measurements.

As an additional check, the REE-Oxide/REE ratios were found to be <1% when a solution of 1 µg/L of REEs was measured before sample analysis, and the RSD of REE measurements were lower than 1.5%. Also, there was no increase in REE concentrations, when 10 µg/L of Ba were added to the samples.

Table 3 shows the figures of merit obtained for ⁴³Ca, ⁵²Cr, ⁵⁶Fe, ⁵⁹Co, ⁶⁶Zn, ⁶⁹Ga, ⁸²Se, ⁸⁵Rb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁴Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶²Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ²⁰⁵Tl, ²⁰⁹Bi, ²³²Th and ²³⁸U using ICP-SFMS (Element 2).

The limits of detection and quantification were defined as a concentration of the listed elements equal to 3 and 10 times the SD of the blank solution (5% HNO₃ Romil, Cambridge, UK). For all calibration curves, the linearity was ~ 99.9%.

The precision (triplicates) and accuracy of the method were verified by analyzing the following CRM: SLEW-3; SLRS-4; TMRAIN-04. The results and certified values for Ca, Cr, Fe, Co, Zn, Se, Rb, Ba, Tl, Bi and U are presented in Table 4.

The results obtained for the selected isotopes in the CRM were within the range of standard deviation (SD) for certified values, and analytical precision (RSD) of the analysis was < 7%. This can be accepted as a proof that accurate and precise results can be obtained for the further analysis of natural water samples.

RESULTS & DISCUSSION

The results of the measurement of trace elements in ground water samples are presented as plots in Fig. 1. The RSD of all measurements did not exceed 10%.

The distribution of Ca, Cr, Co, Zn, Se, Fe, Ga, Rb, Ba, Tl, Bi, U and Th in the investigated waters shows significant variability (from 0.001 to 180000 µg/L). This variability in ground waters is mainly related to mobilization mechanisms, such as reductive dissolution of oxides, desorption minerals, as well as complexate with HCO₃⁻, H₂PO₄⁻, OH⁻, F⁻ (Haas et al., 1995). Transition elements Cr, Zn and Fe were found within the range ~ 0.2-45 µg/L, whereas Co was present at concentrations from ~ 0.07 to 0.90 µg/L. Non-transition elements, such as Tl and Bi, showed a plateau in concentrations at ~ 0.03 – 0.11 µg/L. Selenium was between 0.5 and 8 µg/L. Alkali and alkaline earth metals Rb, Ca and Ba were found to be the most abundant, especially in samples 1, 9, and varied between ~ 0.4 – 180000 µg/L. Significant variability was also observed

Table 3. Figures of merit for ⁴³Ca, ⁵²Cr, ⁵⁶Fe, ⁵⁹Co, ⁶⁶Zn, ⁶⁹Ga, ⁸²Se, ⁸⁵Rb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁴Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶²Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ²⁰⁵Tl, ²⁰⁹Bi, ²³²Th and ²³⁸U using ICP-SFMS (Element 2)

Isotopes	LOD, ng/L	LOQ, ng/L	Linearity, %
⁴³ Ca	215	710	99.95
⁵² Cr	3,9	12,9	99.96
⁵⁶ Fe	2,7	8,9	99.96
⁵⁹ Co	0,11	0,36	99.98
⁶⁶ Zn	0,95	3,1	99.98
⁶⁹ Ga	0,56	1,9	99.99
⁸² Se	44	145	99.96
⁸⁵ Rb	9,8	32	99.94
¹³⁷ Ba	0,83	2,7	99.97
¹³⁹ La	0,56	1,9	99.99
¹⁴⁰ Ce	1,1	3,6	99.98
¹⁴¹ Pr	0,47	1,6	99.98
¹⁴⁴ Nd	0,94	3,1	99.97
¹⁴⁷ Sm	0,62	2,1	99.99
¹⁵¹ Eu	0,21	0,69	99.97
¹⁵⁷ Gd	0,58	1,9	99.97
¹⁵⁹ Tb	0,22	0,73	99.96
¹⁶² Dy	0,6	2,0	99.98
¹⁶⁵ Ho	0,18	0,59	99.99
¹⁶⁶ Er	0,53	1,8	99.96
¹⁶⁹ Tm	0,11	0,36	99.98
¹⁷² Yb	0,4	1,3	99.97
¹⁷⁵ Lu	0,2	0,66	99.98
²⁰⁵ Tl	0,5	1,7	99.96
²⁰⁹ Bi	3,6	11,9	99.98
²³² Th	0,19	0,63	99.96
²³⁸ U	2,1	6,9	99.98

Table 4. Certified and measured values in SLEW-3, SLRS-4 and TMRAIN-04 by Inductively Coupled Plasma Sector Field Mass Spectrometry of Ca, Cr, Fe, Co, Zn, Se, Rb, Ba, Tl, Bi and U

Isotopes	SLEW-3 Estuarine Water		SLRS-4 River Water		TMRAIN-04 Rain Water	
	ICP-SFMS, µg/L	Certified value, µg/L	ICP-SFMS, µg/L	Certified value, µg/L	ICP-SFMS, µg/L	Certified value, µg/L
⁴³ Ca	-	-	5.93±0.15 ^a	6.2±0.2 ^a	-	-
⁵² Cr	0.184±0.002	0.183±0.019	0.33±0.01	0.33±0.02	0.892±0.006	0.866±0.165
⁵⁶ Fe	0.489±0.034	0.568±0.059	111±8.5	103±5	26.3±1.3	24.7±4.12
⁵⁹ Co	0.051±0.002	0.042±0.010	0.029±0.001	0.033±0.006	0.249±0.002	0.245±0.058
⁶⁶ Zn	0.23±0.01	0.201±0.037	0.96±0.03	0.93±0.10	9.22±0.24	8.47±2.11
⁸² Se	-	-	-	-	1.03±0.06	0.836±0.236
⁸⁵ Rb	-	-	-	-	0.037±0.001	0.03 ^b
¹³⁷ Ba	-	-	11.81±0.11	12.2±0.6	0.83±0.06	0.87±0.12
²⁰⁵ Tl	-	-	-	-	0.391±0.006	0.377±0.059
²⁰⁹ Bi	-	-	-	-	0.683±0.010	0.6 ^b
²³⁸ U	1.55±0.08	1.8 ^b	0.051±0.001	0.050±0.003	0.289±0.006	0.292±0.026

^a concentration in mg/L

^b information value only

for Ga, which ranged from 0.16 to 164 µg/L. Cluster analysis (CA) was performed to quantify the similarity of ground water quality parameters (pH, salinity, trace elements and REEs) (Abu-Khalaf et al., 2013,

Hosseinimarandi et al., 2014) by using the software STATISTICA®. Prior to CA, all data were standardized to provide a normal distribution of all variables. The dendrogram of CA is shown in Fig. 2.

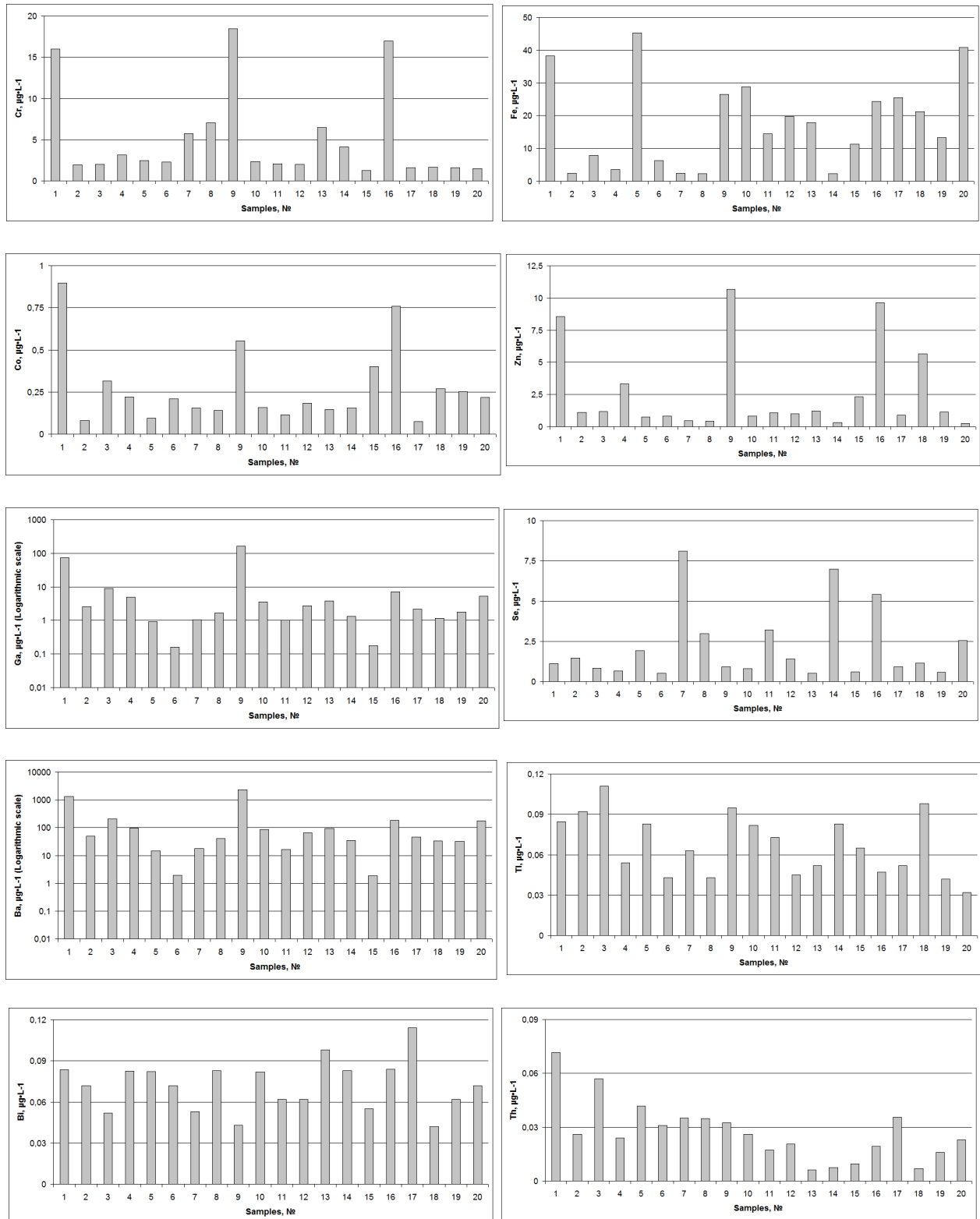


Fig.1. Plots of trace elements distribution obtained by Inductively Coupled Plasma Sector Field Mass Spectrometry in natural ground water samples (1-20)

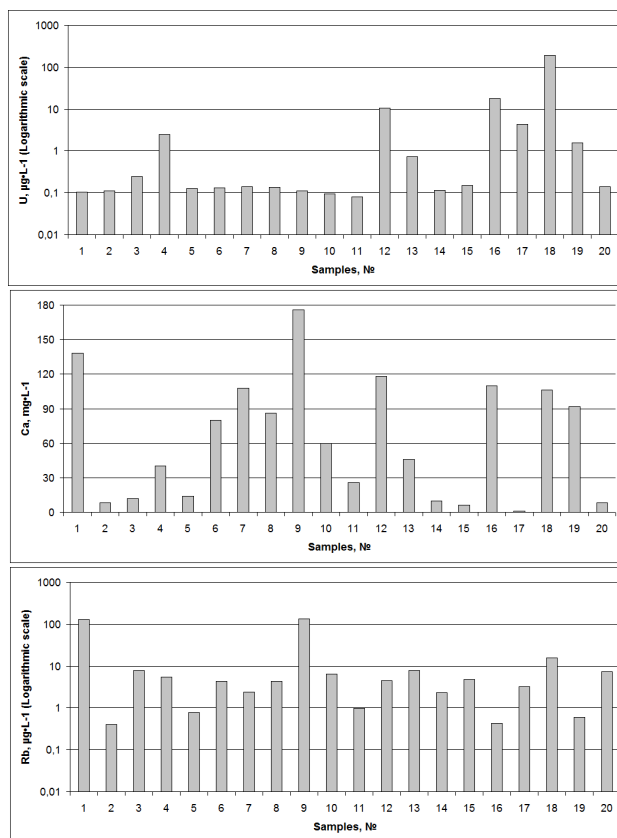


Fig.1. Plots of trace elements distribution obtained by Inductively Coupled Plasma Sector Field Mass Spectrometry in natural ground water samples (1-20)

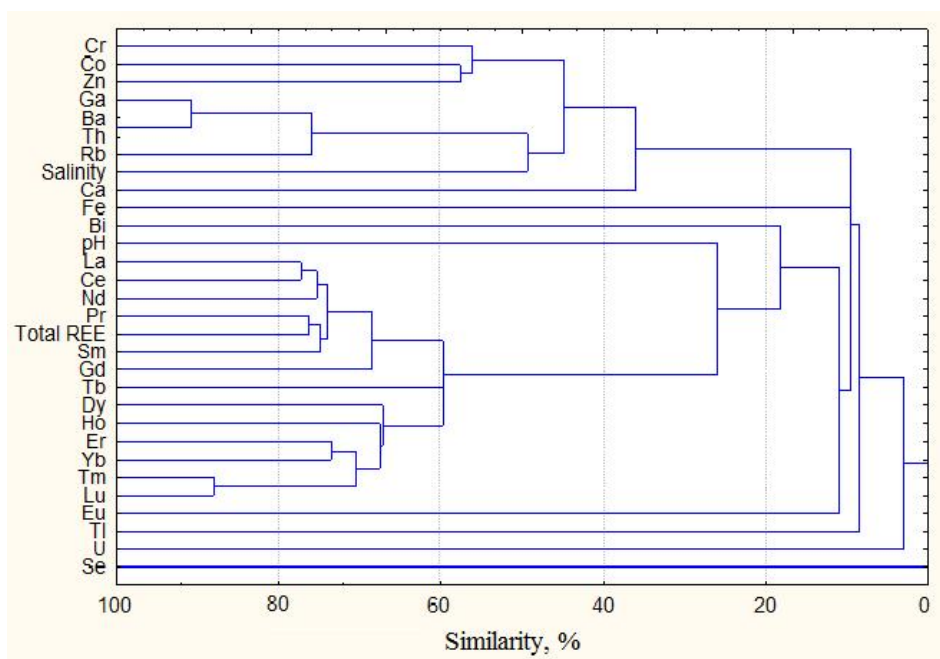


Fig.2. Dendrogram of CA for 30 ground water quality parameters

The dendrogram (Fig. 2) indicates that ground water quality parameters could be divided into three clusters with over 55% similarity level. The first cluster had the largest number of variables (REEs) with 60% similarity. Cluster II shows a high correlation between Rb, Ga, Ba

and Th with 75% similarity. The geogenic elements Rb, Ga and Ba are the main constituents of some tectosilicates and hence are useful tracers of granite rock minerals (quartz, orthoclase, microcline, albite to oligoclase, micropertite) in local aquifers (Carroll,

1970). Here, the presence of Th may also be associated with granite rock minerals. The third cluster shows about 55% similarity between Cr, Co and Zn, which could be related to their similar behavior as transition elements. It should be noted that, in general, groundwater samples ¹1 and 9 contain much higher concentrations of Ca, Cr, Co, Zn, Ga, Rb and Ba in comparison to other investigated waters, which shows the corresponding dependence on salinity (Table 2).

In addition, Cr, Fe and Se concentrations obtained in all investigated ground natural waters were compared to the threshold values for drinking waters (Cr - 50, Fe - 200 and Se - 10 µg/L) established by Directive 98/83/EC. It was found that the concentrations of the listed elements (Fig. 1) do not exceed their threshold values.

The U and Th contents in the investigated natural ground waters range from 0.1 to 10.7 and 0.001 to 0.07 µg/L, respectively, with the exception of sample ¹18 whose U concentration (195 µg/L) is considerably higher than the World Health Organization (WHO) provisional guideline value of 15 µg/L for U in drinking waters. This guideline value was identified as provisional due to the unclear epidemiology and toxicology of U, and to the difficulties regarding its technical attainability in smaller supplies (WHO, 2003).

As noted in other studies (Kringel et al., 2010), U is widely present in ground waters as a result of its leaching from crystalline rocks and was found in a range from 2 to 528 µg/L in alluvial ground water samples from Khan River and the Swakop River valleys, where only 21% of ground waters had U below the provisional WHO guideline value. The value of U obtained in our study (195 µg/L) in ground water sample ¹18 is in agreement with its geochemical distribution in the central part of Ukraine and may be associated with natural enrichment in the surrounding areas (Cuney et al., 2012, Voitsekhovych and Lavrova, 2009). It should also be noted that no correlation between U and Th was observed (Fig.2). The differences between U and Th indicate that Th is poorly soluble in natural waters and that its enrichment occurs in carbonate rocks during weathering and deposition processes, while U is easily soluble in almost all natural waters through complex formation (e.g., $(\text{UO}_2(\text{CO}_3)_3)^+$, $(\text{UO}_2(\text{CO}_3)_2)^2-$, UO_2CO_3) (Dabous et al., 2002, Kelepertsis, 1981, Kopylova et al., 2015).

According to Nakajima and Terakado (2003), Otsuka and Terakado (2003) chondrite normalization has been extensively employed in groundwater studies. In the present study, the results of ICP-SFMS measurement of REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in ground water samples were normalized by

the average chondrite values and are plotted in Fig. 3. The values of an average chondrite composite are tabulated in Schmidt et al. (1963).

Most of the samples are characterized by a predominance of HREEs, a negative Ce anomaly ($\text{Ce}/\text{Ce}^* = 2\text{Ce}_N/(\text{La}_N + \text{Pr}_N) \sim 0.4 - 0.9$) and a positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 2\text{Eu}_N/(\text{Sm}_N + \text{Gd}_N) \sim 1.2 - 17.5$). However, some samples (¹1, 9, 16, 17, 20) show LREE enrichments. For sample ¹13, the Eu anomaly is very conspicuous. On the contrary, for sample ¹17, the normalized values decrease almost linearly from La to Lu without significant Ce and Eu anomalies.

The Eu anomaly could be related to pH values, as suggested by the lack of Eu anomaly for sample ¹17 (pH = 9.0) and, in contrast, a significant Eu anomaly for sample ¹13 (pH = 5.7). Here (sample ¹13) the contribution of Eu from minerals such as feldspars during water-rock interaction processes is considered to be suspect (Jianfei et al., 2014, Kurian et al., 2008, Marmolejo et al., 2007, Michael and Kamber, 2006).

LREE enrichments were observed in several samples, including ¹1, 9 and 16 (Fig. 3b). Those samples have relatively high Cr, Co, Zn and Ca content, compared to other investigated waters (Fig. 1). As discussed in previous studies (Nakajima and Terakado, 2003), the abundance of dissolved Ca could be associated with a weak weathering process; moreover, a higher level of transition elements such as Cr, Co and Zn, due to their better solubility in anoxic conditions, could be suggested (Laluraj and Nair, 2009).

There was a correlation between low Fe contents (Fig. 1) and negative Ce anomalies in samples ¹2-4, 6-8, 14 (Fig. 3), which may be associated with an oxic condition in which precipitation of CeO_2 as well as insoluble Fe(III) oxides occurs. Besides that, Ce anomaly basically associated with HREEs enriched samples, which is evident in the plots (Fig. 3a). HREE enrichments could be explained on the one hand by precipitation of LREEs with solids (Johannesson et al., 1999, Kuss et al., 2001) and on the other hand by formation of stronger HREE complexes in liquid form due to an increase in atomic number (Byrne and Li, 1995, Lee and Byrne, 1993). It should also be noted that HREE enriched samples have a lower Ca content, except for samples ¹6-8, 10, 12, 18 and 19.

As previously supposed, the REE concentrations in waters from strongly weathered areas should be relatively high, while waters from weakly weathered areas should have lower REEs content. Also, the inverse tendency should occur for Ca data: in other words, Ca abundances in waters from weakly weathered areas should be higher than in waters from

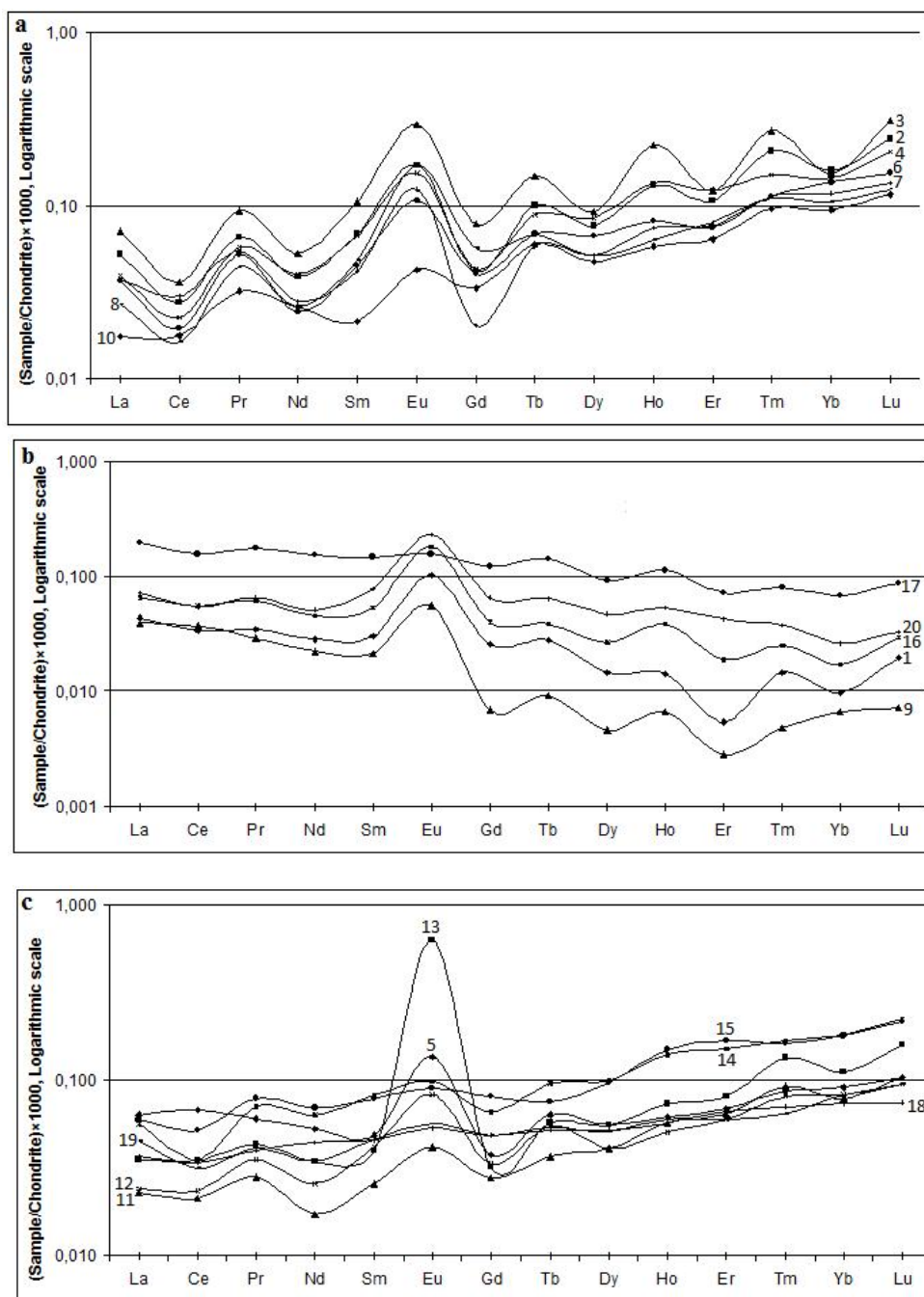


Fig.3. Chondrite-normalized rare-earth patterns for natural ground waters: a) ¹ 2-4, 6-8, 10 exhibiting heavy rare-earth-enrichment; b) ¹ 1, 9, 16, 17, 20 exhibiting light rare-earth-enrichment and c) ¹ 5, 11-15, 18, 19 exhibiting heavy rare-earth-enrichment

strongly weathered ones. To evaluate such an inverse tendency for the investigated ground waters samples, the sum of all REEs concentrations (Σ REE) for each sample was plotted against Ca contents (Fig. 4). The Ca contents in the listed samples range from 1 to 180 mg/L and the sums of REEs range from 75 to 470 ng/L.

Fig. 4 indicates an inverse correlation between Ca and Σ REE, which could be expressed by the power function ($y=447,9.X^{-0,27}$). Hence, the investigated samples could be relatively separated into two groups: 1) waters from strongly weathered areas ¹ 2, 3, 4, 5, 13, 11, 14, 15, 17, 20 (Σ REE ~ 200 – 470 ng/L) and 2) waters

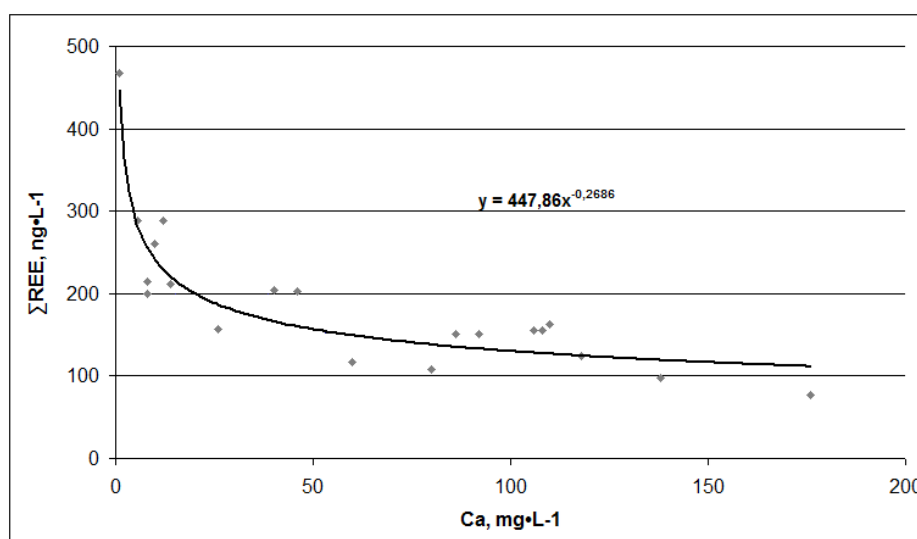


Fig. 4. Variation diagram for natural ground waters (1-20): “REE (ng/L) plotted against Ca (mg/L)

from weakly weathered areas 1, 6-10, 12, 16, 18, 19 (“REE ~ 75 – 155 ng/L).

CONCLUSIONS

The distributions of trace elements and REEs in natural ground water samples from the Ukraine are presented in this study. The investigated ground waters are characterized by near-acidic to alkaline pH (5.7 – 9.0) and significant variability in the concentration levels of trace elements and REEs. The relationship between REEs and trace elements, including Ca, allowed us to describe the major processes of water-rock interaction.

Natural ground waters 11 (City Tyachiv, Zakarpatska region) and 19 (City Svalyava, Zakarpatska region) were found to be enriched in Ca, Cr, Co, Zn, Ga, Rb, Ba as well as higher salinity compared to other investigated waters. Also, cluster analysis shows a correlation (55% similarity) among transition elements such as Cr, Co and Zn, and 75% similarity for geogenic elements (Ga, Rb, Ba and Th), which could provide useful information about natural abundances of silicate minerals such as quartz, orthoclase, microcline, albite to oligoclase, and microperthite in the investigated areas. Negative correlations were observed for U and Th data, which could be interpreted in terms of a low solubility of Th due to its precipitation in carbonate rocks and of a good solubility of U, caused by carbonate complex formation.

For all analyzed samples, we found a negative Ce anomaly, ranging from 0.4 to 0.9, a positive Eu anomaly from 1.2 to 17.5 and mainly HREE enrichments. Ce anomalies are correlated with a low level of transition elements such as Fe. This can be explained by an oxic

condition in which a precipitation of insoluble oxides of Fe and Ce occurs. At the same time, the Eu anomaly is mainly associated with pH values.

The chemical composition of the investigated natural ground waters is a result of water-rock interaction processes and the relatively low Ca and high “REE concentrations indicate significant calcite consumption during the weathering process, as well as the increase in REE-bicarbonate complex formation. On the contrary, relatively high Ca and low “REE abundances could be associated with a weakly weathering process. This inverse tendency can be a useful tool to investigate chemical weathering processes between calcite rocks and ground waters.

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