
CHEMISTRY PROFIL OF SOME LOCAL SOIL SAMPLES

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ABSTRACT

Chemical analysis of soil samples collected from six different sites in Tarhuna region that has been investigated using flame emission spectroscopy, atomic absorption spectroscopy and UV/visible spectrophotometry techniques. The investigated elements includes: Sodium, Potassium, Calcium, Magnesium, Chromium, Iron, Copper, and Zinc. The eight elements was extracted by the acid digestion method. The obtained experimental results of chemical analysis indicate that the maximum concentration of the metals are more than 11835, 5258, 3355, 1565, 699, 27, 20.05, and 15.9 ppm for Ca, Fe, Mg, Na, K, Cr, Zn, and Cu respectively. PH value of the examined soil solutions is at the range of (8.64-9.11) and hence, all samples is alkaline. The total metal ion concentration ($\sum M^{n+}$) as nitrate/chloride for different sites was calculated and the maximum value was found at Al syed area. The elemental concentration can be arranged as $Ca > Fe > Mg > Na > K > Zn > Cr > Cu$.

Keywords: Local soil, elemental analysis, spectrophotometry, heavy metals

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1. INTRODUCTION

In analytical chemistry, Flame emission, atomic absorption and UV/visible spectroscopy are the major techniques for determining the concentration of a particular metal element in a sample. Flame emission spectrometer can be used to determine alkali and alkaline earth metals. Atomic absorption and UV/visible spectroscopy can be used to determine the concentration of over 62 different metals especially transition elements in a solution [The Perkin-Elmer Corporation, 1996]. Soil is the material which nourishes and supports growing plants; it includes rocks, water, snow, and air. From chemical point of view, soil contains mainly mineral inorganic matter in the form of cations/anions and organic matter. The percentage of

inorganic minerals, air, water and organics in soil is about $\approx 45, 25, 25$, and 5% respectively [Marc Pansu and Jacques Gautheyrou 2006]. Physicochemical characterization of any soil should depend upon texture, chemical composition, color, and bulk density. The main factor affecting the soil texture is the presence of sand, silt and clay [Marc Pansu and Jacques Gautheyrou 2006]. In ecosystem, soil is considered as basic environmental element and also the important material basis for human being survival and development. But it also becomes a sink for contaminants entering the environment, independently if the contamination derives from air pollution, water pollution or soil pollution itself. The soil contamination is spreading due to various agricultural and industrial activities e.g. using of fertilizers and pesticides in agriculture, fossil fuel combustion, mining and milling wastes, and landfill leaching. Potential harmful contaminants have been accumulated in the upper soil during thousands of years, starting from the mining for precious metals, heavy metals, hematite, and later for copper.

In terms of their mobility and bio toxicity on living ecosystem, removing metals from soil is an essential task. Soil contamination has become a serious problem with the economy and industry development. Heavy metal soil contamination is more dangerous than any other soil contamination [Abumaizar, R.J., and Smith, E.H. 1999, PP-71-86]. Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline, paints, application of fertilizers, animal manures, normal sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition [Abdel-Aziz, R.A., et al. 1997, PP-217-234]. Heavy metals are toxic to all organisms if

presented in a high concentrations. The concentrations of heavy metals in soils may vary widely, even in uncontaminated soils. Marked differences in the geochemical composition of the rocks which form the parent materials of soils and variations in the intensity of soil-forming processes can result in wide ranges of total and available concentrations of most elements in soils, even in those unaffected by contamination. Nevertheless, contamination from many sources can often give rise to some very high concentrations of heavy metals which can cause toxicity in soil organisms and susceptible plants, but this depends on the factors affecting the bioavailability of the elements.

The present work aimed to analyze and evaluate the chemical composition of six local soil samples using different spectroscopic techniques. The study has been done to determine the concentrations of alkali metals (Na, K), alkaline earth metals (Ca, Mg) and transition metals (Cr, Fe, Cu, and Zn) of the soil samples collected from Tarhuna region which located in the south of Tripoli city, north-west of Libya.

2. EXPERIMENTAL

2.1. Materials and Sampling

Five soil samples were collected from six different locations around Tarhuna city. The region was divided into six agricultural zones, namely, Suq Alahed, Fam Mulga, Apyar Megi, Seedi Alsyed, Centre of Tarhuna and the Green Area. The five soil samples of the same location were mixed together to reach homogeneity. The depth of all samples is about 15 cm and the weight of the individual sample is approximately 50 g. Characterization of investigated soil samples was shown in Table 1. Analar nitric acid and hydrochloric acid in pure and analytical grade were used for digestion process.

Table1 Characterization of investigated soil samples

Sample notation	Site	Location	Number of samples	Total weight of mixed samples	color
(A)	Suq Alahed	Centre of Tarhuna city	5	250 g	Mud Color
(B)	Fam Mulga	East of Tarhuna city	5	250 g	Mud Color
(C)	Apyar Megi	West of Tarhuna city	5	250 g	Mud Color

(D)	Seedi Alsayed	South of Tarhuna city	5	250 g	Mud Color
(E)	Centre of Tarhuna	North of Tarhuna city	5	250 g	Mud Color
(F)	Green Area	Around Tarhuna city	5	250 g	Mud Color
Total			30	1500 g	-----

2.2. Instruments and Measurements

A single beam Flame Emission Spectrophotometer (FES), Model Corning 400, Corning, Halstead, England was used to analyze and measure the concentration of Sodium, Potassium, Calcium, and Magnesium in soil samples. A Varian Model Spectr A A 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for measuring the concentration of Zinc, Iron and Copper with the appropriate metal hollow cathode lamp. The operating parameters were set as recommended by the manufacturer. Atomic absorption measurements were carried out in an air-acetylene flame. UV/Vis. Spectrophotometer, model Evolution™ 201/220 Italy, was used for the determination of Chromium.

2.3. Procedure and analysis

Acid digestion method was used for leaching process of investigated elements from soil samples. Preparation of the investigated metal ion as concentrated solutions for analysis has been carried out according to the following steps:

1. Three portions of 2 grams of each soil sample were weighted and transferred onto three 100 ml beakers.
2. Stock, concentrated solution of aqua regia containing a mixture of 6M HCl and 6M HNO₃ (1:1 v/v ratio) was prepared and 10 ml from the prepared mixture was added to each beaker.
3. Samples were gently digested at 100-115°C for 30 min to almost dryness in a thermostatic water bath in a good ventilated atmosphere.
4. About 10 ml of the concentrated stock solution was added one again to each sample beaker and heated again to almost dryness.
5. Samples were left to cool, then the desired amount of double distilled water was added and stirred with a glass rod for 15 min to dissolve the

residue of the investigated metal ion which will dissolves to a metal nitrate or chloride.

- 6.The solution was left for 24 hours and allowed it to settle down avoiding vibrations.
- 7.Finally, dissolved samples were filtered using a whatman No.3 filter paper into 100 ml volumetric flasks and completed to the mark with bi-distilled water.
- 8.The used glassware and filter papers was washed continuously by a smallest amount of bi-distilled water to ensure that all metal ions are completely leached out from soil samples and the glassware and filter papers which are used become free from the metal ions.
- 9.For quantitative analysis, the metal ion concentration for solutions containing Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cr^{3+} , Fe^{3+} , Cu^{2+} , and Zn^{2+} ions was measured by transferred them directly to the appropriate instruments.
- 10.The standard calibration curves for each metal ion was generated first, separately, in a very wide range of concentrations. Several optimization experiments has been done to obtain the optimum conditions and results.
- 11.Before measuring Iron and Copper, a little amount of hydrogen peroxide H_2O_2 (30 %) was added to the solution to oxidize both the ferrous ions Fe^{2+} to ferric ions Fe^{3+} and cuprous ions Cu^+ to cupric one Cu^{2+} .
- 12.The sample was aspirated and the measurements was done, then the reading was recorded.
- 13.From the standard calibration curve, the concentration of the unknown samples was determined.
- 14.To get accurate and precise results, standardization and calibration curves was taken into consideration before measuring the metal ion concentration individually.
- 15.The final reading is the mean of the three measurements.

3. RESULTS AND DISCUSSIONS

The pH values and the chemical composition in terms of part per million (ppm) of the six soil samples collected from Tarhuna city has been measured and presented as shown in Table 2.

From the obtained results in this table, we can notice that all investigated soil sample solutions are slightly alkaline and the pH values are in the range from 8.64 for sample (F) to 9.11 for sample (B). In general, pH value of

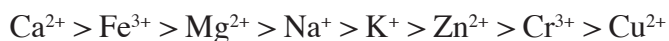
Table 2: Elemental concentration and pH of the investigated soil samples

Sample notation	Elemental concentration (ppm)										ΣM^{n+}	pH
	Alkali metals		Alkaline earth metals		Transition metals							
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cr ³⁺	Fe ³⁺	Cu ²⁺	Zn ²⁺				
(A)	890.24	565.60	6872.50	1604.50	15.15	3511.25	8.48	12.47	13480.18	8.95		
(B)	1565.18	599.99	10842.50	2020.00	21.78	4846.25	15.90	20.05	19931.65	9.11		
(C)	992.20	497.15	7785.00	3355.50	27.85	5258.75	6.28	17.78	17940.50	9.03		
(D)	1330.33	602.21	11835.00	1859.25	9.30	4790.63	7.85	17.28	20451.84	8.82		
(E)	1321.14	699.50	9555.00	2067.75	11.43	4596.25	4.75	13.73	18269.55	8.90		
(F)	1455.50	665.97	10295.00	1613.50	10.75	4980.63	5.58	15.92	19042.84	8.64		
ΣM^{n+}	7554.59	3630.42	57185.00	12520.50	96.25	27983.80	48.83	97.22	-----	-----		
Average	1259.09	605.07	9530.83	2086.75	16.04	4663.96	8.14	16.20	-----	-----		
λ_{max} (nm)	589	766	423	285	358	510	325	213	-----	-----		

samples (A), (D), (E), and (F) are nearly the same which is around 8, but the pH value of samples (B) and (C) seems to be closely related to each other. PH values for sample (A) and (E) is equal to ~ 8.9 , whereas, pH value of sample (B) and (C) is around 9. The suitable pH range for growing up the cultivated plant is 5-9 [Ibrar Khan et al. 2015, PP 96-105]. In general, alkalinity of the investigated soil samples may be attributed to the relatively high concentration of alkaline and alkali metals.

The maximum concentration of alkali metals is equal to 1565.18 ppm (Na^+) and has been found in sample (B), the maximum concentration of alkaline earth metals is equal to 11835.00 ppm (Ca^{2+}) and has been found in sample (D), and the maximum concentration of transition metals (heavy metals) is equal to 5258.75 ppm (Fe^{3+}) and has been found in sample (C). According to the total metal ion concentrations ($\sum \text{M}^{n+}$), the average value of the metal ion concentration, and the above mentioned results, the investigated metal ions can be arranged as follows:

Alkaline earth metals > alkali metals > heavy metals (except iron)



A relatively high concentration of calcium and magnesium ions in almost soil samples may reflects the presence of naturally occurring calcium and magnesium rich minerals such as: calcite/limestone, chalk, marble/stone CaCO_3 , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, natural phosphorite $\text{Ca}_3(\text{PO}_4)_2$, manmade synthetic rock $\text{Ca}_3(\text{PO}_4)_2$, magnesite MgCO_3 , dolomite MgCO_3 , CaCO_3 , asbestos $\text{CaMg}_3(\text{SiO}_3)_4$, Epsom salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and soapstone (talc) $\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$ [Abdul Waheed, et al. (2005)]. Calcium and magnesium in naturally occurring minerals were found as carbonate, sulphate, phosphate and silicates. On the other hand, the relatively high concentration of ferric ions may be due to the presence of iron rust as iron oxides in different forms $\text{Fe}_x\text{O}_y \cdot z\text{H}_2\text{O}$ such as hematite Fe_2O_3 , limonite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, magnetite Fe_3O_4 or may be due to the presence of iron pyrite FeS_2 . In fact, natural feldspar $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and kaolin $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ itself is a white aluminous-silicate mineral oxide clays, but if it mixed with iron oxides of different forms give a mud color appearance [Frederick H. Pough. 1995].

The average concentration of heavy metal ions, Zn^{2+} , Cr^{3+} , Cu^{2+} , does not exceed more than 16.2 ppm for Zn^{2+} ion. The minimum average concentration of heavy metal ions is 16.04 and 8.14 ppm for Cr^{3+} , Cu^{2+} ions respectively. The above mentioned data refer to the absence or restricted industrial activity around the area under investigation. In our opinion, these studies suppose that

the soil of Tarhuna region does not suffer from environmental contamination or pollution and hence, it is a cleaning area and free from heavy metal contamination.

In Denmark, it has been reported that the average concentration of heavy metal ions, Zn^{2+} , Cr^{3+} , and Cu^{2+} , is 107, 51, and 42 ppm respectively [Peter. E. H. et al. 2005, PP-43-52], while in Romania the minimum concentration of the same heavy metal ions recorded 149 and 19 ppm for Zn^{2+} and Cu^{2+} [Mihaly Cozmuta 2005, PP 358-362]. The concentration gape of Zn^{2+} ion between the investigated area and Denmark is equal to 90.8 ppm, this means that the concentration of Zn^{2+} ion in Tarhuna city is less than Denmark by ≈ 6.6 times. Also, the concentration gape of Cr^{3+} ion between the investigated area and Denmark is equal to 35 ppm, and the concentration of Cr^{3+} ion in Tarhuna city is less than Denmark by ≈ 3.2 times. Again, the concentration gape of Cu^{2+} ion between the investigated area and Denmark is equal to 33.87 ppm, and the concentration of Cu^{2+} ion in Tarhuna city is less than Denmark by ≈ 5.2 times. However, the concentration gape between the investigated area and Romania is equal to 132.8 and 10.87 ppm for Zn^{2+} and Cu^{2+} ions respectively, while and the concentration of Zn^{2+} and Cu^{2+} ions in Tarhuna city is less than Romania by ≈ 9.2 and 2.3 times.

In order to express the concentrations by units of gram metal ion per one gram soil sample (g/1g), so many calculations has been done to calculate the actual concentration of each metal ion in each soil samples, here is an example for the first sample which have the notation (A) [David Harvey. 2000]:

$$\therefore \text{the concentration of } Na^+ = 890.24 \text{ ppm}$$

$$\therefore \text{the concentration of } Na^+ = \frac{890.24 \text{ mg}}{L}$$

$$\therefore \text{the concentration of } Na^+ \simeq \frac{0.89 \text{ g}}{L}$$

$$\therefore \text{the concentration of } Na^+ = \frac{0.89 \text{ g}}{1000 \text{ ml}}$$

$$\therefore \text{the concentration of } Na^+ = \frac{0.089 \text{ g}}{100 \text{ ml}}$$

$$\therefore \text{the concentration of } Na^+ \text{ in 2g soil sample} = \frac{0.089}{2 \text{ g sample}}$$

$$\therefore \text{the concentration of } Na^+ \text{ in 1g soil sample} = \frac{0.0445 \text{ g}}{1 \text{ g sample}}$$

The obtained results expressed by the unit g metal ion per 1g soil sample (g/1g) has been summarized in Figure 1, from which we notice that the relatively high concentration of calcium ion is more than ≥ 0.5 g/1g and was found in sample (B), (D) and (F). The concentration of calcium ion was found below this value in sample ((A), (C), and (E). These results is in agreement with the alkalinity data of the samples. In accordance, we can conclude that the concentration of calcium ion is the main operating chemical factor affecting the alkalinity of the investigated soil. Nevertheless, the increasing concentration of calcium ion will appear as more alkalinity of the soil and vice versa. For all samples, except sample (C), Na^+ , K^+ , Mg^{2+} , Cr^{3+} , Cu^{2+} and Zn^{2+} ion concentration is found below 0.1 g/1g. Also, for all samples, except sample (A), the concentration of Fe^{3+} is found more than 0.2 g/1g. The total calculated metal ion concentrations $\sum M^{n+}$ for each soil sample refer to the following sequence:

Sample (D) > Sample (B) > Sample (F) > Sample (E) > Sample (C) >
Sample (A)

Finally, this sequence refer to that sample (D) from Seedi Alsayed site, south of tarhuna, contains the maximum total mineral contents ($\sum M^{n+}$) that equal to more than ≈ 20451 ppm or about 1g/1g, while the low mineral contents was found in sample (A) which is Suq Alahed. This may be attributed to the warm weather in south of Tarhuna region.

4. CONCLUSION

Several conclusions can be written depending upon the above mentioned results as follows:

- 1.The soil in Tarhuna region was classified as alkaline soil and suitable for plant growth.
- 2.The most abundant elements in the soil samples are calcium and iron, calcium is a natural occurring mineral and iron may be present due to modern human activities and life.
- 3.Chemical analysis of the samples indicates that Tarhuna area contains a

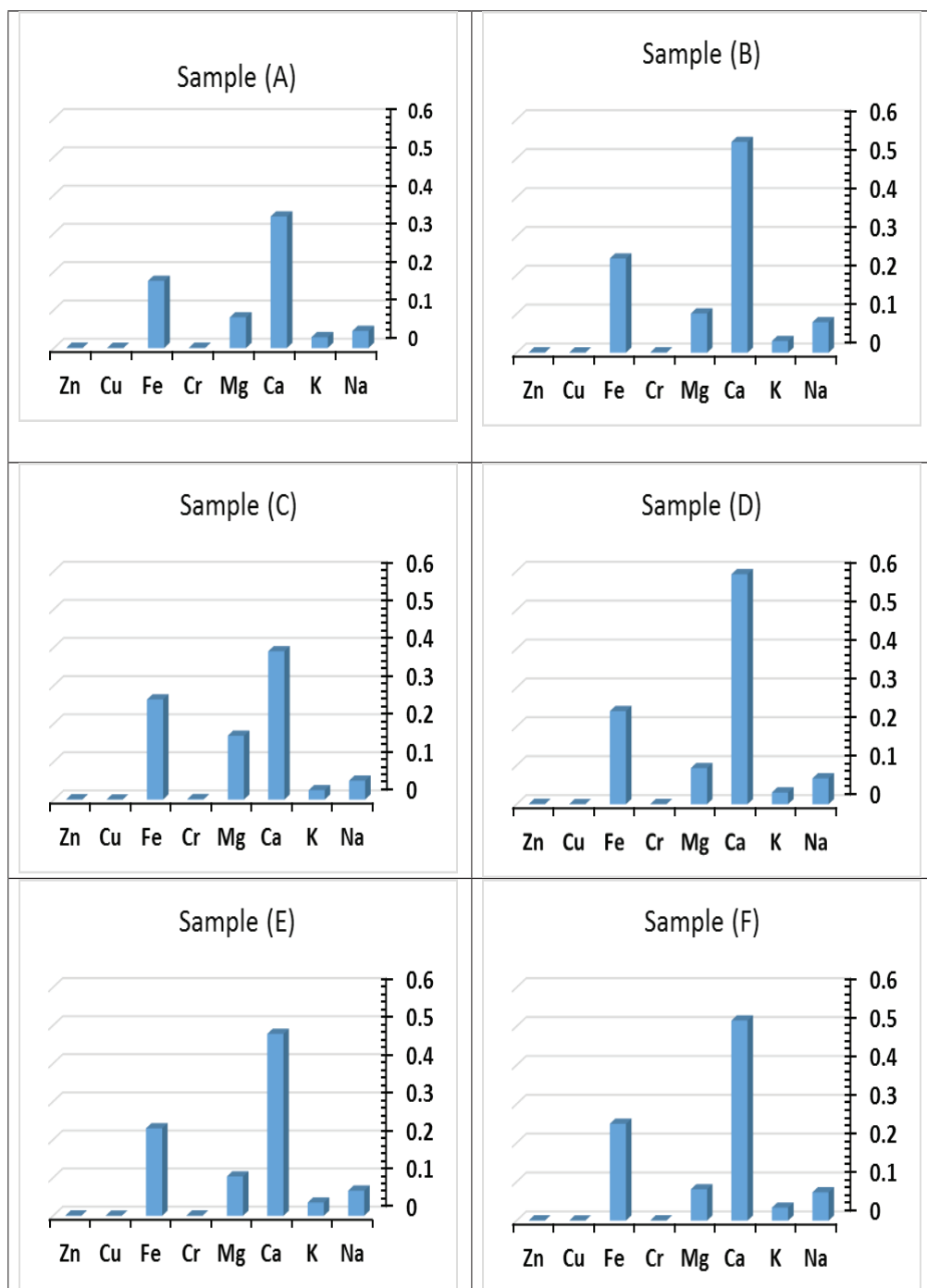


Fig. 1: Metal ion concentration expressed in gram per one gram of soil (g/1g)

free heavy metal cleaning soil.

4. Spectrophotometric techniques succeeded and was able to give us a brief about chemistry profile of local soils.
5. Seedi Alsayed site (south of Tarhuna) contains the maximum mineral content.
6. Further researches and more studies must continue in the nearest time to insure that the local environment is in a good state for our future generation.

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التحليل الكيميائي لبعض عينات من التربة المحلية

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الملخص

في هذا البحث تم إجراء مسح كيميائي لعينات من التربة التي تم جمعها من ستة مواقع مختلفة بمنطقة ترهونة باستخدام ثلاث طرق للتحليل الطيفي وهي: طيف انبعاث اللهب (لتحليل الصوديوم والبوتاسيوم والكالسيوم والمغنسيوم)، طيف الامتصاص الذري (لتحليل الحديد والنحاس والزنك)، وطيف الأشعة فوق البنفسجية والضوء المرئي (لتحليل الكروم). واستُخدمت طريقة الهضم بالأحماض القوية والمركزة لاستخلاص هذه العناصر الثمانية من العينات. أظهرت النتائج التجريبية للتحليل الكيميائي للعينات أن أعلى تركيز للعناصر هو 1565 ، 699 ، 11835 ، 3355 ، 27 ، 5258 ، 15.9 ، 20.05 جزء في المليون (ppm) وذلك بالنسبة لكل من الصوديوم ، البوتاسيوم ، الكالسيوم ، المغنسيوم ، الكروم ، الحديد ، النحاس ، والزنك على الترتيب. كما أثبتت القياسات أن قيمة الأس الهيدروجيني (pH) لمحلول جميع عينات التربة تتراوح في المدى 8.64-9.11 ومن ثم فإن العينات لها خواص قلوية خفيفة وهو المدى المناسب للأنشطة الزراعية والرعية. لقد تم حساب التركيز الكلي للعناصر ($^{+Mn} \gamma$) على صورة النترات (NO_3^-) والكلوريدات (Cl^-) لكل المواقع المختارة وتبين أن الموقع المعروف باسم الصيد يحتوى على أعلى نسبة من العناصر الكيميائية. وبالنسبة لتركيز العناصر الكيميائية المقاسة فجاءت النتائج لتؤكد على أن العنصر الأوسع انتشاراً في منطقة ترهونة وما حولها هو عنصر الكالسيوم يليه الحديد ، بينما العنصر الأقل انتشاراً في هذه البيئة هو النحاس والكروم ويمكن ترتيبها على النحو التالي: $Ca > Fe > Mg > Na > K > Zn > Cr > Cu$.

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