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Letter to the Editor

LETTER TO THE EDITOR

Far-reaching governance of electrode potential: The case of priority in metal exploitation

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Abstract: Is the priority applied during metals introduction in mankind's service responsible for the forthcoming crisis in raw materials supply? Was the priority erroneous? To solve this dilemma, the relevant characteristics of GCIAL metals were compared, the acronym standing for gold, copper, iron, aluminum and lithium. These five metals were ranged according to: 1) the time of their incorporation in exploitation, 2) their abundance in the Earth's crust, 3) reserves of mineral resources, 4) their stability and, partially, 5) the achieved level of mankind's scientific highlights and technical expertise in that period. It was shown that the start of exploitation of the GCIAL metals does not correlate at all with their abundance, or their reserves in nature, but there is a straight correlation with their stability in the metallic state, as expressed by the corresponding values of the normal electrode potential. This is an expected behavior because the electrode potential is an alternative way of expressing the Gibbs energy change during the oxidation/reduction electrode reaction. Such a result also eliminates any doubt of error mentioned above. Thus, it is clear that the introduction of metals in human use was determined by their nature only and has nothing in common with insufficient abundance not only for the GCIAL metals, but probably for all other 'technical metals', the main pillars of our technical standard.

Keywords: raw materials; metals in human use; abundance; stability; reserves.

INTRODUCTION

Metals are among the top raw materials that mankind uses to build its high standard of living, and they will probably keep the front running position, despite the attacks of new materials that are being engineered continually. This is why the depletion of metal resources makes more serious the concern about their availability in the future.[1–7] Justification of such concern was confirmed by the

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world's leading institutions, such as UNESCO, IUPAC, EUCheMS, *etc.*, who declared the year 2019 as the International Year of the Periodic Table, IYPT2019.[8]

Their basic message reads: "**The 90 natural elements that make up everything. How much is there? Is that enough?**" It is followed by an originally modified Periodic Table where the elements are presented according to their abundance, importance, application, *etc.*

The IYPT2019 alarm confirms that the natural reserves of our raw materials are being seriously attacked. This is a normal consequence of the prolonged habits in the sectors of consumption, rate of population growth and individual human behavior. Mankind's population registers a permanent increase. The consumption of raw materials follows a similar pattern, but with further rise of per capita consumption, yesterday's quotas are no longer sufficient for today's consumers.[9] Hence, contemporary society is faced with the puzzle: satisfy the ever-growing needs of ever-growing population with – continuously depleting natural resources!

Being aware of such a state, a search was made to find and apply a number of measures to counteract these trends.

Let them be analyzed one by one, starting with the population. Frankly, it is not an easy task to convince the entire population to undergo strict demographic control, without imposing rigorous restriction (as has already been seen in the world's most populated country). Thus, the population will keep growing governed by its random patterns.

The situation with the *per capita* consumption of goods is similar. Voluntary restriction is of low probability, unless some *force majeure* implies it.

The only remaining segment is the relation to the consumption of raw materials, *i.e.*, increasing the availability of raw materials. This issue is regularly on the agenda of mankind's summits, but hitherto with poor chances for some promising solution. The situation is so bad that the search must include not only reasonable sources, but also some extraordinary ones, as shown later.

SURVEY OF THE INTRODUCTION OF METALS INTO USE

Thus, this paper is concerned with the order of the introduction of metallic materials into human use, in a search of any eventual error in the prioritization of metals and its consequences for the present crisis.

Avoiding previous materials, the start is a survey of the material base of civilization with the use of metals. Remember that most of the Ages are named according to the newest metal in use, *e.g.*, the Bronze Age and the Iron Age. Native metals, such as gold, silver and copper were hammered into decorative objects in the cradle days of human civilization. Later on, native metals joined them. Further, with primitive melting of bronze, metallurgy started its career in producing and shaping metals for use as tools, weapons, *etc.* The number of metals in use grew continually but slowly until the 19th century when it reached the present set of 90 stabile chemical elements, the dominant part of them being metals. For the sake of this paper, it should be mentioned that aluminum was introduced into wider usage by the end of that century, when its extraction was effected by molten salt electrolysis; lithium was also introduced into use a long time after its discovery.[10]

In order to answer the question of the prioritization of metals in human use, information is need on the formation, evolution and composition of our solar system, and its planets, especially the Earth. The composition of the Universe is shown in Fig. 1, as abundance of chemical elements plotted *vs*. their mass number.[11]

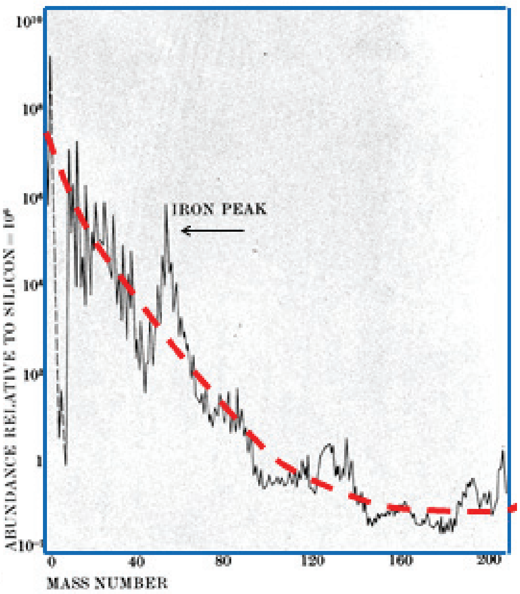

Fig. 1. Abundance of chemical elements in the Universe *vs.* mass number.[11]

Several important data are to be seen from Fig. 1, as, *e.g.*:

- General trend: The abundances of the elements decrease exponentially with their mass number,
- Exception 1: Light elements lithium, beryllium and boron show much lower abundance than the value suggested by the general trend in Fig. 1,
- Exception 2: Iron and its neighbors ("iron group" in Fig. 1) show abundance up to the thousand times higher than the trend in Fig. 1,
- The most abundant are hydrogen and helium, the only two elements that are not formed in cosmic nuclear furnaces or explosions.[11]

One should know more about the chemical composition of planets in our Solar system, because they will be the ultimate choice in case the mankind is forced to look for raw materials sources in the surrounding universe. For the sake of this study, it is sufficient to provide only data for the availability of the resources that will be badly needed when the reserves of Earth vanish.

The location of the planets around the Sun is shown in Fig. 2. Smaller planets, *i.e.*, Mercury, Venus, Earth and Mars, are situated nearer to the Sun and are built out of metals (such as iron, nickel, aluminum, *etc.*), and some nonmetallic materials, such as rocky silicates. Thus, they are potential sources for the materials needed in the menu of mankind. Unfortunately, these planets are a tiny part of the solar system, only 0.6 mass %.[12] The vast majority, 99 % of mass, belong to Jupiter, Saturn, Uranus and Neptune, so-cold Giant planets, situated beyond the frost line, and thus containing abundant quantities of frozen water and methane, as well as hydrogen and helium captured by the extreme gravity these planets possess. Hence, metallic compounds are not present in significant quantities in these planets. Smaller bodies, such as meteors, asteroids, *etc.*, do contain metals, but they are not necessarily part of our solar system.

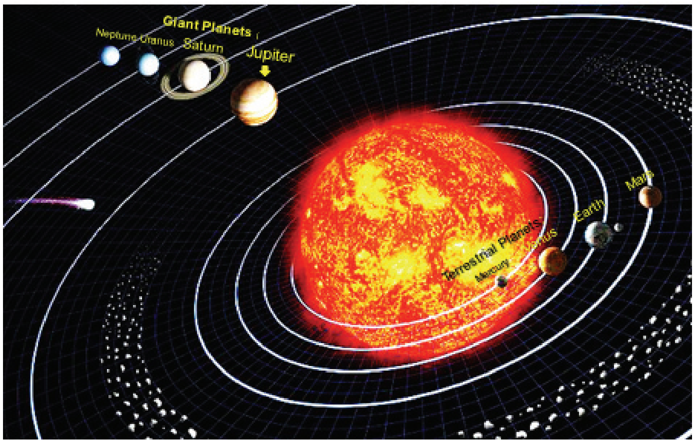

Fig. 2. Schematic of location of solar system planets around the Sun (by Harman Smith and Laura Generosa (*nee* Berwin), graphic artists and contractors to NASA's Jet Propulsion Laboratory, *via* Wikimedia Commons).

Finally, let summarize the data that characterize the Earth as our regular and, until present time, the exclusive source of raw materials. Earth is:[13]

- The largest and densest of the Inner planets,
- The only planet with oxygen in the atmosphere, liquid hydrosphere and geological activity and plate tectonics,
- Composed of mainly metallic and silicate minerals.

During the molten youth of the Earth, heavy elements were pulled into its core by gravity, thus depleting the crust of valuable chemical elements. This is preferably true for the siderophilic ("iron-loving") elements. Over the rest 4 billion years of Earth's life, a rain of asteroids re-infused valuable metals into the depleted crust, such as, *e.g.*, gold, cobalt, iron, manganese, nickel, *etc.*[13,14]

Recent Earth's dominant chemical constituents are as follows:[7]

Earth, crust: 98 % made of 8 elements: O, Si, Al, Fe, Ca, Mg, Na, and K

Earth, core: iron – 88 %

Earth, total: iron – 32.1 %; oxygen – 30.1 %; silicon – 15.1 %; magnesium – 13.9 %

Earth, mantle: olivine (Fe+Mg silicates)

Density, crust: 2,400 kg m^{-3}

Density, Earth: 5,500 kg m^{-3}.

A more detailed insight into the composition of Earth's crust is shown in Fig. 3.[16] Major "industrial metals" are abundant in an interval of 1 to 10^{-6} %.

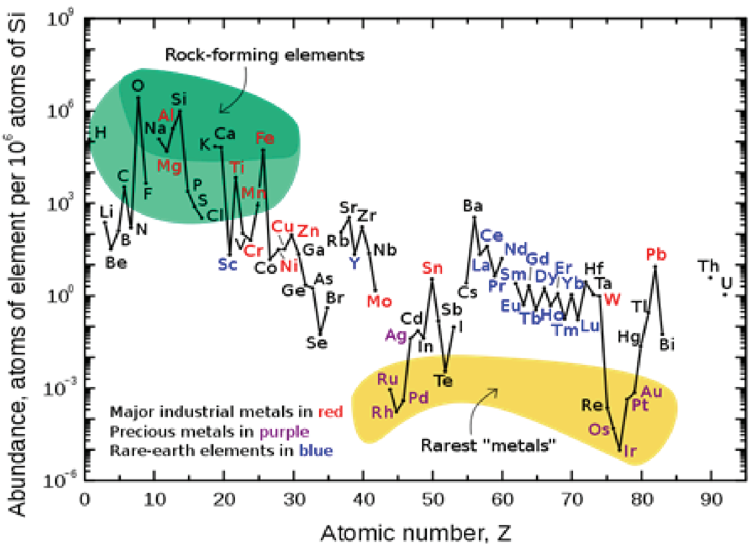

Fig. 3. Abundance of chemical elements in the Earth's crust.[16]

Man has been exploiting Earth's mineral resources over a span of some five millennia. No matter how long this sounds, it is only one millionth part of Earth's total life. Over such a short period, man succeeded in endangering (depleting) reserves of useful raw materials in the Earth's crust. The process started sometime in the pre-history, and was further intensified, especially with the Industrial Revolution. Recently, in the Consumer Society period, the exploitation was further multiplied. Metals were used all over this period, as shown in Table I.[7]

For practical reasons, only fife metals are the subject of further analysis. They represent different periods of human civilization and are well known. An acronym GCIAL was coined to stand for gold, copper, iron, aluminum and lithium.

The metals compared in Table I somehow represent trademarks of human civilization. The first one, gold, is a precious metal with properties that made it attractive and highly prized from the early days of civilization until today. Next are copper and iron, probably among the most significant metals in human history. The last two, aluminum and lithium, are also of high significance, but only in the 20th, resp. 21th century.

TABLE I. History of use of GCIAL metals[7]

Metal	When	Where–Who	Application
Gold	Prehistory 5000 BC	Ancient civilizations	Jewelry, precious metal
Copper	Bronze Age	Ancient civilizations	Armaments, tools,
Cu → bronze	3500 BC (5500 BC)		households
Iron	Iron Age	Hittite's	Armaments, tools,
	1500 BC (1,100 BC)	secret for 400 years	constructions
Aluminum	Age of electricity	1825 Hans Christian	Lightweight, stable:
	1825; 1886	1886 Hearult & Hall	aviation, constructions
Lithium	1923 – discovered	Metal Geselschaft	Batteries, ceramics, glass,
	21st Century – wide use	Germany	pharmaceuticals

The time of the introduction of these metals in use varies from many millennia up to only one century. The period of their introduction in exploitation provokes curiosity: was it just occasional or was there some regularity involved. The answer to this question could eventually help in solving the doubts of how to manage the forthcoming crisis in supply.

What was of crucial importance in determining the start of their exploitation:

- the abundance of the metal,
- the stability of metal's chemical compounds (precursors),
- necessity to satisfy some need of mankind, or
- achieved level of technology development?

Each of the possible causes is analyzed below. The start of exploitation *vs.* abundance of the metal is given in Table II.[14]

TABLE II. Plot of start of exploitation *vs.* abundance of metal[14]

Metal	Gold	Copper	Iron	Aluminum	Lithium
Used, years	7,000	5,500	3,100	130	< 100
Ranged	I	II	III	IV	V
Abundance, %[22-27]					
Mean value	2.7×10^{-7}	7×10^{-3}	5.22	8.17	1.9×10^{-3}
Interval	$(1.1–4.0)\times10^{-7}$	$(5.0–10.0)\times10^{-3}$	4.1–6.3	8.07–8.23	$(1.7–2.0)\times10^{-3}$
Ranged	V	III	II	I	IV

The start of exploitation of the metals under investigation varies from 7,000 years down to 100 years. Their abundance in the Earth's crust varies from 2.7×10^{-7} to 8.17 mass %. As seen in Table II, there is no proportionality between these two parameters. Thus, the metal abundance is not the determining factor for the start of their exploitation.

Information concerning exploitation *vs*. metal stability is given in Table III.

TABLE III. Start of exploitation *vs.* metal stability

Metal	Gold	Copper	Iron	Aluminum	Lithium
Used, years	7,000	5,500	3,100	130	<100
Ranged	I	II	III	IV	V
Stability E^o / V	1.5	0.34	–0,44	–1.67	–3.05
Ranged	I	II	III	IV	V

The metal stability is expressed in terms of standard equilibrium electrode potential of the metal in aqueous media. The more positive the electrode potential is, the more stable is the metal, *i.e.*, the metallic state is more preferable over the oxidized state. The winning of the metal from its compounds is easier to perform. In the opposite case, a less noble potential means that the precursor is more stable, so that its reduction to metallic state is thermodynamically burdened.

The studied electrode potential becomes more negative along the GCIAL series, and such a trend coincides with the order of the introduction of these metals into service. Thus, the metal stability is the factor that determines its priority in usage.

Reserves of some mineral resource, in conjunction with the annually extracted and further processed quantities, are an important parameter in providing a stable exploitation of the metal. The estimated reserves of the metals under consideration are given in Table IV.[15] It can be seen that next to the metals with reserves for many centuries production, there are also metals with reserves for only few decades of exploitation!

TABLE IV. Reserves of mineral resources[15]

Metal	Gold	Copper	Iron	Aluminum	Lithium
Reserves, 10^6 t	0.54	550	93,000	6,000	16
Production, years	–	56	200	375	27

PRACTICAL CONSIDERATION

It is a normal reaction to be alarmed with so short periods of exploitation as shown in Table IV. If all the used data and calculations are correct, then the end of usage of these metals is in front of us. How to prevent it?

The first step is to check again old mining sites or try to find new sites of mineral resources. One of the contemporary popular measures is to bypass the shortage of given metal by means of alternative materials that possess the required property of the exhausted metal, *e.g.*, to apply conducting polymers instead of copper metal.

Should all tried remedy measures fail, then one should be prepared for more drastic ones, such as, *e.g.*, a return back to the pre-metal civilization lifestyle (?), or adoption of a new, non-metal based lifestyle pattern (??).

It does not deserve to explain how plausible these measures are.

If the situation worsens further, there is an ultimate solution: Urgently seek a place to continue mankind's civilization – somewhere in the surrounding Space (!!!).

An important conclusion is that metals did enter into mankind's usage with priorities determined by their nature (stability), regardless of the abundance of the resources. Thus, there was no human error when a deficient category of raw materials was selected instead of some other, more available. It has to be accepted that the material's prioritization established over the past Ages was a valid and justified one. The only measure that could be applied against the forthcoming crisis in the supply of metals is to find the correct steps in the search for mineral (metal) sources.

In order to avoid any omissions, one should search for every new source, no matter how problematic it could seem now. This means to look at, *e.g.*, in the deep interior of Earth, but also at remote planets and eventually other bodies in the solar system. The search could benefit as well from the broad possibilities that new technologies offer.

Here is a short summary of such a long list of possible solutions.

Deep Earth's interior is known with the enormous reserves of metals, primarily iron, nickel, *etc*. stocked in the Earth's core. Unfortunately, these metals are and will keep being inaccessible for exploitation. Advance of mining possibilities in future may eventually enable operation at a depth of 6,000 km and temperatures of 6,000 °C?

Planet Mars has been present within space research programs for almost half a century and our knowledge of its characteristics (such as distance, trajectories, chemical composition, *etc.*) is increasing gradually. Thus, the Viking mission in 1976 did detect a titanium content of some 0.9 %. More sophisticated analysis produced in 2012 by the Curiosity mission improved further the exactness of chemical analysis and did detect a few other metals, such as, *e.g.*, Fe, Mg, Al, Ca, *etc.* in Mars soil.[16,17] Studies are ongoing, and our knowledge is becoming richer and more diversified. This encourages mankind to consider the planet Mars as an eventual future source of raw materials. However, conditions for harvesting metals at Mars are far from favorable: Mars is remote from Earth between 55 and 100 million km, *i.e.*, too far for any reasonable exploitation; its atmosphere contains only traces of oxygen (0.13 %) and this makes mining activities on its open surface rather limited. Other relevant Mars parameters are yet to be detected or confirmed. All this disqualifies Mars as a raw materials source in the near future.

Recently, a surprise was spread on the possible great benefit from a small sky body. The asteroid 16 Psyche was announced as a possible miraculous source of iron and some other metals.[18,19] It is the most massive between the metallic asteroids, made out of almost pure iron in a quantity that is some 100 times more valuable than the US economy (?). Its mass, estimated as 10^{10} megatons, could cover the terrestrial needs for "several million years", and so to turn up-side-down the global economy (!). Some of these yet non-confirmed qualities may be "too green to be true". Anyhow, it is important that the mankind did start thinking of mining in Space, to date only an attractive idea.

Another strange idea that could be of help in the centuries to come is: May mankind dream of reversing back the process of metal dissipation during exploitation and gather again the finest metal containing particles into a bulk metal stock? Against all sound reasoning and limitations implied by thermodynamics and its almighty entropy.

The history of technology is full of examples where scientific principles are somehow by-passed or double crossed. There are cases when thermodynamic blockage is outsmarted by kinetic aspects of a given process. Remember the phenomenon of "eternal" stability of diamond, despite the fact that the elementary state is not thermodynamically preferable for carbon in contact with oxygen.

Similar is the case with winning the potassium by cementation with sodium in molten salts.[20] In principle, the cementation reaction is not possible because sodium is nobler than potassium. However, the process is enabled by proper selection of reaction temperature, where the just gewonen potassium evaporates, thus leaving the reaction mixture and kinetically outsmarting the thermodynamic limitation.

The excellent example of agglomeration of dissipated metal particles is the formerly used gold winning process by dissolving the gold fine grains in mercury, followed by extraction of mercury by distillation. Unfortunately, mercury is banned from usage all over the world as an extremely dangerous metal.

The lack of proper extraction process is the reason why enormous quantities of gold (estimated as 6 million tons, *i.e.*, hundred times more than gold in mankind possession!) are spread in the ocean water.[21] Also, gold is not the only metal there. We need only a "minor ability", a method to extract the gold present in concentrations of 4.5×10^{-9} g L^{-1}! Contemporary metallurgy employs new methods of metal extraction able to exploit resources with further decrease of concentration of the desirable metal, so that the 10^{-9} g L^{-1} may one day become within the threshold of exploitation.

May mankind be blessed with scientific and technical achievements to start harvesting metals from so extremely poor secondary raw materials. If so, all troubles that are concerned with the exhaustion of natural resources will become history.

CONCLUSION

The primary aim of this study was the search for raw material sources. The performed consideration did not discover any new or certain source. It just listed some of the extraordinary places where to look for material's supply in future, or similar low probable processes for metal extraction from extremely poor sources. More and harder efforts may eventually provide some concrete data.

In elaborating this study, a proof was produced on a very important result: what/who was the crucial argument in determining the period of introducing metals in mankind's use. It was shown that metal's nature was the primary selection factor, *i.e.*, priority in metal's use was given to the more stable metals. In the more recent periods, the achieved level of human technical expertise was employed as well as bypassing nature's laws and priorities. This was illustrated with the cases of the winning of aluminum and lithium as metals. The further enabling the extraction of metals against the barriers imposed by the existing natural laws is welcomed.

ИЗВОД

ДАЛЕКОСЕЖНА ВЛАДАВИНА ЕЛЕКТРОДНОГ ПОТЕНЦИЈАЛА: СЛУЧАЈ ПРИОРИТЕТА У ЕКСПЛОАТАЦИЈИ МЕТАЛА

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Да ли је приоритет примењен током увођења метала у службу човечанства одговоран за надолазећу кризу у снабдевању сировинама? Да ли је приоритет био погрешан? Да би се решила ова дилема, упоређене су релевантне карактеристике метала GCIAL, акроним који стоји за злато, бакар, гвожђе, алуминијум и литијум. Ових пет метала распоређено је према: 1) времену њиховог коришћења у експлоатацији, 2) обиљу у земљиној кори, 3) резервама минералних сировина, 4) стабилности и, делимично, 5) достигнутом нивоу научног врхунаца и техничке стручности човечанства у том периоду. Показано је да почетак експлоатације GCIAL метала уопште није у корелацији са њиховим обиљем или њиховим резервама у природи, али постоји директна веза са њиховом стабилношћу у металном стању, изражена са одговарајућим вредностима стандардног равнотежног електродног потенцијала. Ово је очекивано понашање зато што је потенцијал електроде алтернативни начин изражавања промене Гибсове енергије током електродне реакције оксидације/редукције. Такав резултат такође елиминише сваку сумњу на грешку поменуту горе. Јасно је, дакле, да је увођење метала у људску употребу било одређено само њиховом природом и нема ништа заједничко с недовољним обиљем, не само за GCIAL, већ вероватно и за све друге „техничке метале“, главне стубове нашег техничког стандарда.

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