# Li, Te, Se, Nb-Ta – 21st CENTURY METALS

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The third millennium started under the new information era. Revolution IT (Information Technology) is dependent on new mineral resources that have become viable since 2000. Metals such as Li, Te, Se, Nb-Ta, through their properties and uses into the modern technology, generates an increasingly demand on the market, also being a challenge for the mining industry.
**Keywords:** lithium, tellurium, selenium, niobium, tantalum, application, resources, reserves, producing countries.

## Motivation

According to a European Commission report published on 17 June 2010, European Union will have lower access to some mineral resources essential to the manufacture of high technology and current use products, such as mobile phones, solar panels with thin-layer cells, Li-ion batteries, cables with optical fiber or synthetic fuels. Forecasts go to 2030 and show a group of 14 elements and materials are considered critical [9].

This is generated by economic growth in developing countries and new emerging technologies. The issue of ensuring the supply of these raw materials is mainly due to the fact that they exist in only a few countries in the world (Ex.: Democratic Republic of Congo for cobalt and tantalum, Brazil for niobium and tantalum etc..). In many cases, besides the concentration of production, a low degree of substitution and a low recycling rate can be remarked. Moreover, many emerging economies have adopted the strategy of industrial development based on commercial, tax and investment instruments so as to use only local resources [9].

## Application and uses

As stated, the demand on the market of these elements mostly dues the latest generation technologies, especially in the field of IT and communications. Every element among these has different uses, derived from their properties. Thus:

### *Lithium*

Although lithium and its compounds find utility in several applications (for example in industry - for heat-resistant glass and ceramics, high strength alloys and lightweight aircraft used, in nuclear physics - through the fission of lithium atoms, the use of deuterium as lithium and as a fuel for thermonuclear weapons) its main use in the context mentioned above, is related to the manufacture of batteries and accumulators. Banal and ubiquitous: mobile phone, laptop, digital camera, mp3 player, even the clock at our hand, all use batteries or rechargeable batteries. For several years, batteries / lithium batteries have seized the world market with a majority share in growth at the expense of those based on nickel-cadmium (Ni-Cd) or nickel-metal hybrid (Ni-MH). Visionaries, however, argue that the future of this metal will be in the auto industry, by manufacturing electric or hybrid cars. Naval and aviation industry where miniaturization of circuits and electrical energy storage devices are essential should not be neglected.

### *Tellurium*

Until recently considered waste material in the mining industry, tellurium is recently widely used in various fields, including: energy industry (thermoelectric devices), steel processing, coloring glass and plastics, manufacture of metal alloys (due to its ductility). Its most important using in terms of economic implications, however, remains manufacture of solar panels and semiconductors. Underlying solar cells as basis for the solar panels are used as semiconductor materials especially Si and also CdTe, GaAs combinations or CdTe cells use very expedient CBD technology (deposition of thin layers on large surfaces in the environment of pH, temperature and concentration of reagent control) which reached a yield of 16% in the laboratory, and less than 10% for modules produced so far [10].

### *Selenium*

Beyond the essential character that this element plays in the functioning of the human body, selenium has many uses, from manufacturing photovoltaic cells, photocopiers and cameras / cameras etc. to the recovery of electricity. It is obtained from: refining lead, copper, nickel. Selenium increases its conductivity easily a thousand times when it is moved from darkness to strong sunlight, which is used to build magnetic flow-meters. Selenium salts (selenite mercury for example) use in medical analysis laboratories for determination of total nitrogen in blood/serum.

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***Niobium and Tantalum***

These two metals, with antimony, beryllium, cobalt, fluorine, gallium, germanium, graphite, indium, manganese, platinum metals, rare earths and tungsten are considered "critical" for European industry, according to data presented by the first report so far in the EU on access to mineral raw materials [9].

From the world production of niobium and tantalum, 60% is used in the manufacture of mobile phones, and the rest, at everything that is last generation electronics: TVs, video games, batteries / accumulators, laptops, airplanes, GPS, optic fiber guided weapons, MP3 players, artificial satellites, cameras / digital video, medical devices.

Tantalum chemical inertia makes it extremely valuable for laboratory equipment and a replacement for platinum, but its main use is in implementing powdered tantalum capacitors and electronic equipment industry. By alloying with other metals, tantalum is used to create high-quality alloys used in nuclear reactors, missile components, jet engines production, etc. Because it does not cause irritation to the body, being a nonalergic a material, tantalum is widely used in the manufacture of surgical instruments and implants, and for jewels newly, mounted with gold [11].

Niobium is extracted by electrolysis or other complex processes, from niobium and tantalum, these minerals being, first, converted into double fluoride of niobium and potassium.

It is a silvery-gray metal, which possesses the property of easily absorbing gases, making it usable in absorbent compositions (getters) for tubes. It is also used in the preparation of alloy steels (as feroniobiu), or other alloys.

## GEOCHEMICAL Li, Te, Se, Nb-Ta

***Lithium***

Lithium is part of the alkali metals with sodium, potassium, rubidium and cesium, one of the rarest elements in the bark and having a strong lithophile character. Lithium contents of the various classes of magmatic rocks show that it tends to be concentrated in the latest products during crystallization, especially in granite rocks, while remarking “repulsion” toward the feldspatic structures.

Lithium however is concentrated in the mice, amphibole and pyroxene. With lithium fluoride, chlorine, phosphorus and manganese are often so focused on border and sientic nepheline pegmatite-forming minerals that are independent: criolitionit, trifilit, litiofilit, ambligonit, petalit, and its product spodumen encriptit alteration, micelles of lithium - lepidolit, and coockeit zinawaldit, lithium tourmaline, amphibole very rare - holmquistit etc. Minerals of the pegmatite, ambligolit (8-10% $Li_2O$) spodumen (4,6 - 7,5% $Li_2O$) and lepidotit (3-10% $Li_2O$) are important sources of lithium [7].

***Tellurium and Selenium***

Tellurium and selenium are calcofile elements (have high affinity for sulfur). In lava rocks selenium and tellurium come together with sulfur in separated sulfides of magma. After Noddack, selenium content of primary magmatic sulphides is 200 g/t and tellurium 2g/t.

Like sulfur, selenium and tellurium elements are pronounced sulfofile in the upper lithosphere. The average ratio S:Se in the early magmatic sulphides is 2.000:1 - 20,000:1 (Goldschmidt and Hefter, 1933) and in the sulphides pneumatolitic arsenide and high-temperature hydrothermal ratio is 400:1 - 20,000:1 (Goldschmidt and Strock, 1935). On the other hand selenium is less abundantly in rocks and hydrothermal minerals formed at intermediate and low temperatures in this report S:Se being 70.000:1 - 250.000:1 (Goldschmidt and Strock, 1935). The values of the S: It is shown that selenium is preferentially concentrated in sulphides and hydrothermal arsenide formed at high temperatures.

Tellurium also forms, in hydrothermal rocks, telluride of the mentioned elements and other elements. In addition, he has a tendency to combine with gold, which he accompanies in many mineral strands.

Among the products resulting from oxidation of terrestrial minerals there are known different telluriums, ex.: durdenitum- $Fe_2$ $(TeO_3)$-$4H_2O$; feroteluritum - Fe $(TeO_4)$ teinitum - With [(Te, S) O4] $2H_2O$ (all being rare minerals).

Like sulfur, selenium and tellurium elements are found in nature and natural state. In addition, they form mixed crystals of selenium-tellurium (Se, Te). Selenolitum oxides ($SeO_2$) and tellurite ($TeO_2$) are produced by oxidation of native elements or selenide and telluride. Selenium accompanies sulfur in volcanic emanations S:Se report of the sublimation of sulfur in volcanic regions varies between 600:1 and 140.000:1 S: Se (Goldschmidt and Hefter, 1933) so it is similar to the ratio in sulfides from magmatic rocks. Native sulfur content of selenium in volcanic regions may exceed 5%.

After Scerbina (1937), tellurium metal affinity decreases in minerals in the next order (gold, having the highest affinity): Hg-Au-Ag-Bi-Pb-Cu-Ni [7].

***Niobium and tantalum***

From the geochemical point of view, niobium and tantalum elements form a pair of pretty consistent elements, being separated by hardly by chemical analysis; in spite of this, the two elements are slightly separated in nature. Nb and Ta medium contents in magmatic rocks are 24 g/t Nb and 2.1 g/t Ta (Rankama, 1944, 1948), so the average of abundance Nb:Ta is 11.4.

In magmatic rocks it is known that Nb and Ta crystallize in the last stages of magmatic differentiation.

The concentration is very strong in the borders Ta presents the maximum concentration, while Nb, although appears in borders, has maximum concentration in syenite and nepheline – syenite.

Although in the basic and ultrabasic rocks the content of the two elements are smaller than those in the borders, in ultrabasic rocks sometimes we find remarkable amount of columbium (Niggli, 1932).

The dominant and typical feature in the Nb and Ta geochemistry is their pronounced concentration in pegmatite The most common minerals in the pegmatite Nb and Ta are columbitum and tantalitum [7].

In genetically terms, these elements are concentrated in magmatic deposits or the alteration products and their mechanical and physical concentration [2,4,5].

**Reserves and producing countries**

A report by the U.S. Agency for Mineral Resources shows that the total resources of lithium in the world by the end of 2008, would approach 30 million tones, of which around 750,000 tones would be in the United States, especially in Nevada. About 14 million tons in the global reserves would be exploitable resources. Almost half of what can exploited, 5.4 million tons, would be found in Bolivia, under Salar de Uyuni, a salt desert of 10,000 km$^2$. There are also, according to those estimations, reserves in Chile - 3 million tons (from which Americans massively import), 1.1 million tons in China and about one million in Brazil. The rest, 0.5 million tons as reserves, would be in Argentina, Australia, Canada, Zimbabwe and Portugal.

***Table 1*** *World production of lithium (according to WMD, 2010) [8]*

| Country / Year | 2004 | 2005 | 2006 | 2007 | 2008 |
|---|---|---|---|---|---|
| **Chile** | 17977 | 17900 | 20700 | 24111 | 22997 |
| **Australia** | 5922 | 8682 | 11105 | 9613 | 11976 |
| **SUA** | 3200 | 3200 | 3200 | 3230 | 3230 |
| **China** | 2700 | 2820 | 2820 | 3010 | 3100 |
| **Canada** | 650 | 630 | 700 | 707 | 707 |
| **Brazil** | 497 | 473 | 437 | 430 | 430 |
| **Portugal** | 346 | 311 | 339 | 372 | 375 |
| **Spain** | 30 | 20 | 42 | 45 | 0 |
| **Zimbabwe** | 1450 | 937 | 900 | 0 | 0 |
| **Total** | **32772** | **34973** | **40243** | **41518** | **42815** |

And in the case of this metal so wanted, paradoxes are evident. Although Chile has reserves be estimated as 250 times lower compared with the U.S., production records a seven times higher production, with a weight of more than 53% of world the production. The next state in order of production volume is Australia, with values that are approx. 28% of the world production. Tellurium and selenium are found in small quantities in the anode mud resulting from the copper electrolysis process. Unfortunately copper producers use only a part of the mud results for the extraction of tellurium and selenium.

***Table 2*** *World production of tellurium (according to WMD, 2010) [8]*

| Country / Year | 2004 | 2005 | 2006 | 2007 | 2008 |
|---|---|---|---|---|---|
| **Peru** | 29 | 33 | 34 | 35 | 28 |
| **Canada** | 40 | 28 | 11 | 8 | 19 |
| **Japan** | 33 | 23 | 24 | 41 | 4 |
| **Mongolia** | 2 | 1 | 0 | 0 | 0 |
| **Total** | **104** | **65** | **69** | **84** | **87** |

Economically exploitable reserves of selenium, however, are estimated at only 82,000 tones and 43,000 tones at tellurium opposite of copper which is estimated at 550 million tons. Many production processes use gallium, indium, selenium and tellurium in uneconomic ways. Unlike copper, where the recycling process is developed, at gallium, indium, selenium and tellurium recycling is not possible because these elements are included in finely distributed multilayer structures, where the recovery, apparently, even in future shall be impossible.

***Table 3*** *World production of selenium (according to BGS, 2010) [1]*

| Country / Year | 2004 | 2005 | 2006 | 2007 | 2008 |
|---|---|---|---|---|---|
| **Japan** | 599 | 625 | 730 | 806 | 754 |
| **Belgium** | 200 | 200 | 200 | 200 | 200 |
| **Canada** | 277 | 107 | 117 | 144 | 158 |
| **Sweden** | 131 | 122 | 135 | 126 | 130 |
| **Russia** | 85 | 100 | 110 | 110 | 110 |
| **Poland** | 83 | 84 | 87 | 85 | 82 |
| **Finland** | 65 | 66 | 70 | 52 | 65 |
| **China** | 65 | 65 | 65 | 65 | 65 |
| **Philippines** | 48 | 68 | 65 | 65 | 65 |
| **Peru** | 76 | 70 | 75 | 59 | 60 |
| **Kazakhstan** | 100 | 60 | 70 | 155 | 56 |
| **Uzbekistan** | 20 | 20 | 20 | 20 | 20 |
| **Germany** | 14 | 12 | 12 | 12 | 12 |
| **India** | 0 | 8 | 0 | 0 | 0 |
| **Total** | **3767** | **3612** | **3762** | **3906** | **3785** |

*– estimated production*

In addition to the table, it is considered that countries like Australia, Chile, Korea and Zimbabwe are also producing selenium.

About niobium and tantalum, R.D. Congo on the border with Burundi and Rwanda holds 80% of the world reserves, it records an annual production of only 0.21% of the global production. This state, situated at the end of 2008 on the 5th position from a total of 11 producers of niobium and tantalum, with a slightly increase of production. Brazil doubled its production of these metals in recent years, reaching at the end of the same year at a weight overreaching 93% of the world production.

***Table 4*** *World production of niobium and tantalum (according to WMD, 2010) [8]*

| Country / Year | 2004 | 2005 | 2006 | 2007 | 2008 |
|---|---|---|---|---|---|
| **Brazil** | 39296 | 56287 | 68850 | 81922 | 82000 |
| **Canada** | 3450 | 3704 | 4157 | 4368 | 4432 |
| **Australia** | 350 | 340 | 330 | 435 | 680 |
| **Ruanda** | 117 | 148 | 100 | 242 | 298 |
| **R.D. Congo** | 37 | 61 | 26 | 132 | 186 |
| **Mozambic** | 256 | 101 | 34 | 70 | 138 |
| **Etiopia** | 52 | 68 | 81 | 89 | 93 |
| **Nigeria** | 40 | 35 | 40 | 70 | 60 |
| **Burundi** | 10 | 17 | 6 | 19 | 33 |
| **Bolivia** | 11 | 4 | 3 | 2 | 2 |
| **Zimbabwe** | 4 | 0 | 0 | 0 | 0 |
| **Total** | **43623** | **60765** | **73627** | **87349** | **87922** |

As shown, there are many situations in which the main holders of these resources are not the major producers. Because the statistics shown above refer to the leading manufacturers of Li, Te, Se, Nb and TA in the following graphic the main areas of major economic interest will be highlighted (Fig. 1.).

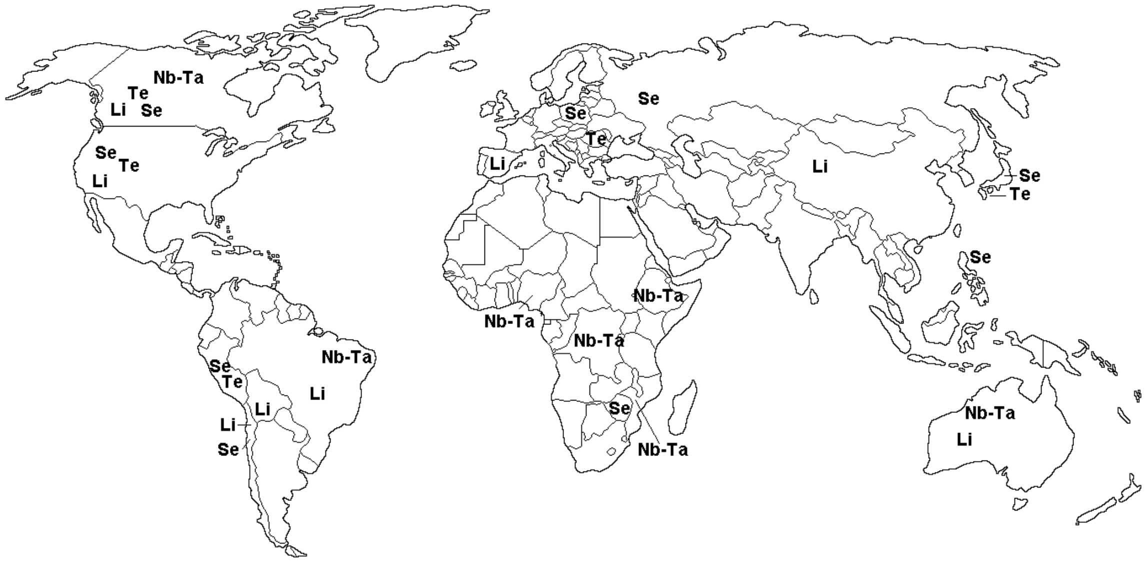


***Figure 1*** *Areas of major economic interest for the elements Li, Te, Se, Nb and Ta*

Therefore lithium reserves are outlined in the U.S., Bolivia, Chile, China, Brazil, Canada, Australia, Spain, Portugal, Argentina, Zimbabwe, tellurium in the U.S., Canada, Japan, Peru, Romania, selenium in Peru, Chile, Russia, Canada, USA, Japan, Philippines, Poland, Zimbabwe, Romania, and niobium and tantalum in Brazil, RD Congo, Australia, Canada, Mozambique, Ethiopia, Nigeria.

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