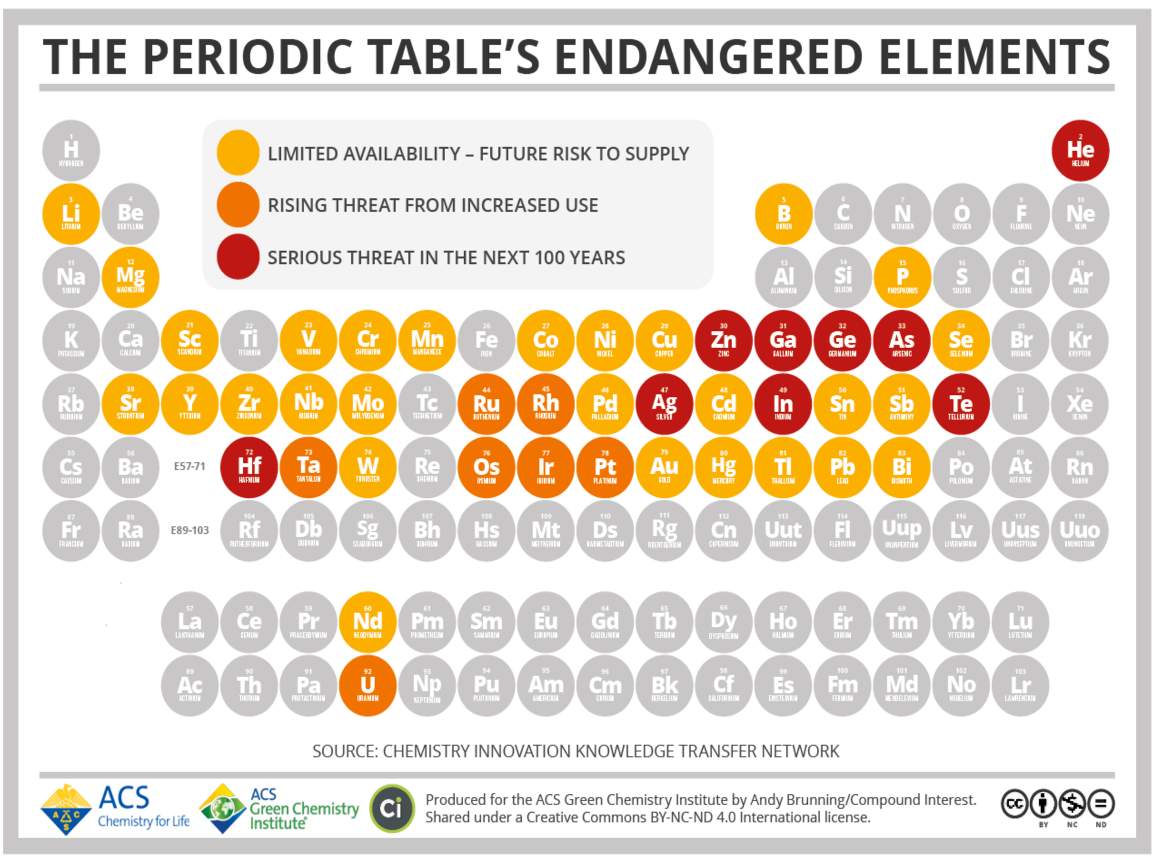
Protecting Endangered Elements Report

I attended this workshop co-hosted by **Ian Duncan MEP** and David Cole Hamilton EuCheMS President at the EuCheMS offices in Brussels on 22 September 2015.

Ian Duncan MEP gave the introduction to the workshop. He stressed the need to embrace the "Circular Economy" model, in other words, recycle as much waste as possible.

He mentioned that while parliament is progressive with conservation policy, the public, regional politicians and industry are slower to engage in conservation of materials. He suggested that material recycling should be worked into global trade agreements.

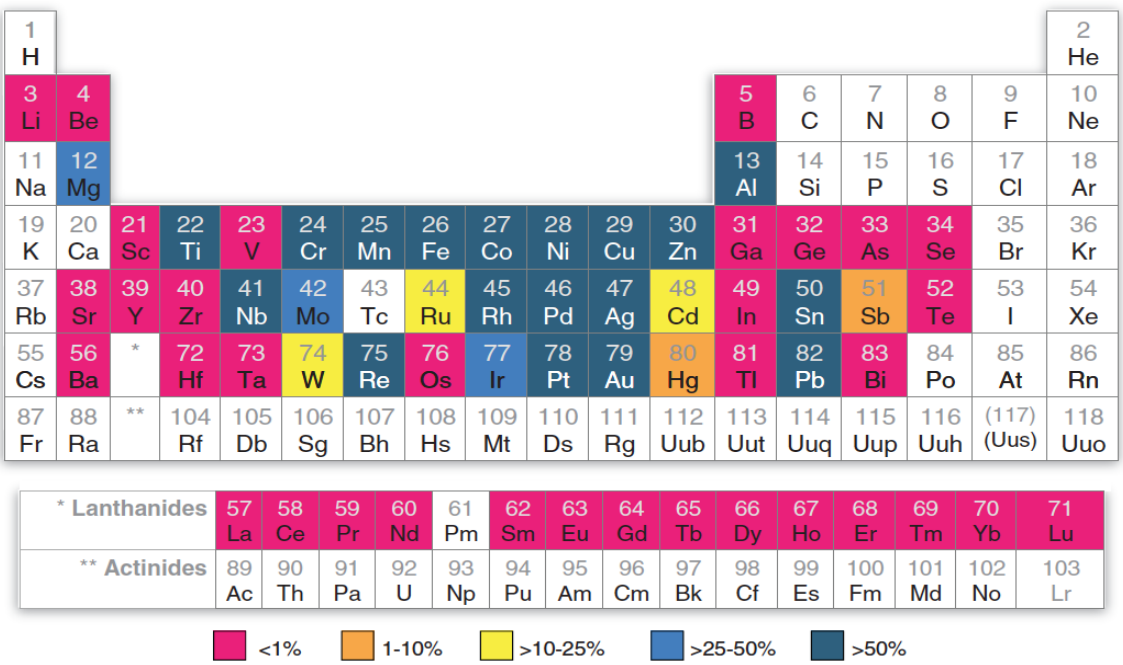
At present carbon is by far the most widely talked about element with respect to conservation due to its role in global warming. However, carbon is is not an endangered element. See periodic table below with the endangered elements highlighted:



The lanthanides should also be highlighted as having "Limited Availability"

Nicola Armaroli, The Institute of Organic Synthesis and Photoreactivity, Bologna gave a presentation entitled: <u>Hunting the Elements of the Periodic Table on Spaceship Earth</u>. He discussed how the escalated demand for electronic consumer goods over the past thirty years has led to the dramatically expanded use of several of the endangered elements. Whilst electronic devices have become miniaturised over this period resulting in "demateralisation", the reduction in material per device has been overcompensated by the increased demand of these goods.

There are several elements intensively mined now which were barely sought after thirty years ago. The alkali metal lithium (Li) is one of these and it has limited availability. This light metal has an extremely high electrochemical potential and is thus used in many rechargeable batteries today. Global supply at present is 36,000 tons per year. The largest producers are: Australia, Chile and China, but Bolivia has the largest reserves. If all cars sold today were electric and used lithium batteries then 700.000 tons of lithium would be required per year. Recycling, which is relatively easy for lithium, needs to be stepped up in order to keep the supply going in the future. To illustrate the poor rates for element recycling see the diagram below:



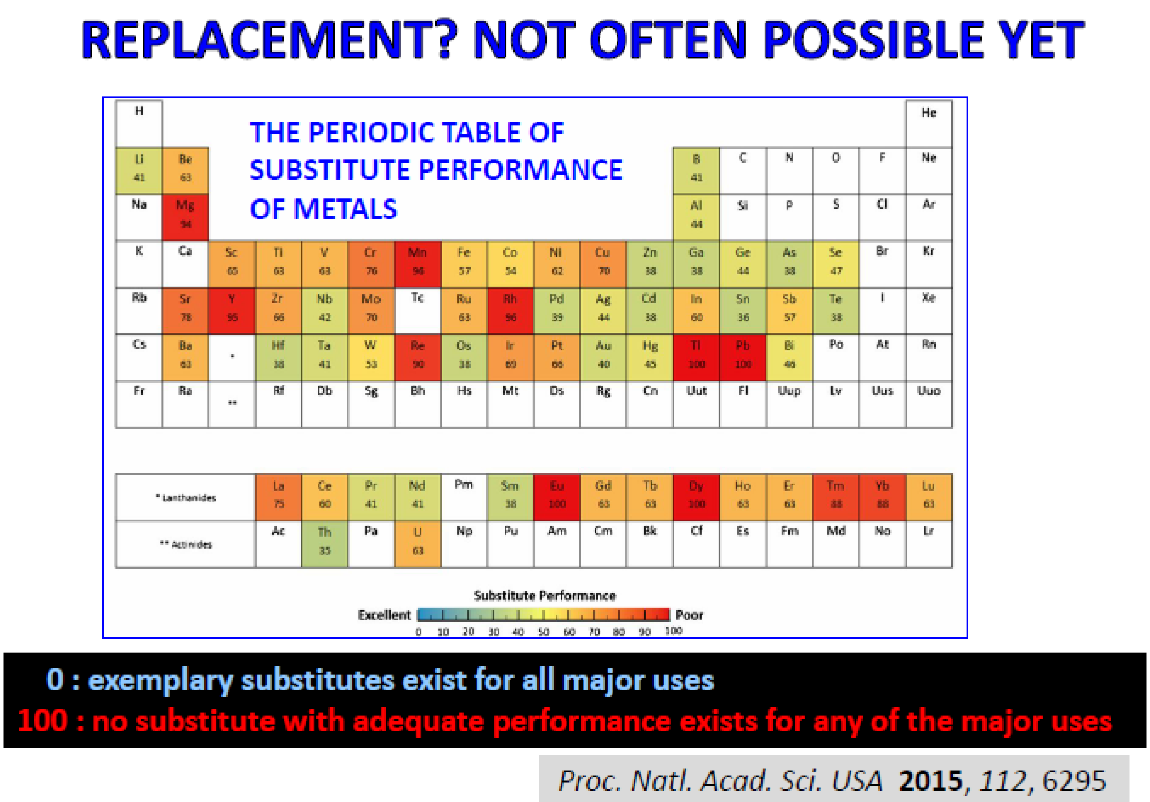
Rates of recycling

Another element the usage of which has increased recently is the metal indium (In). It is used in screens for various devices such as mobile phones due to its transparency and stability in air and water. The major producers are: China, South Korea and Japan, the amount of reserves are presently unknown. As this element is not mined directly but as a by-product of zinc, there is a risk of supply disruptions and price volatility.

The rare earth elements, though not particularly rare, are not very economic to recover, as they are not concentrated enough in any one place. The Chinese have a monopoly with 95% of world supply. China sold these metals at low prices and other mines around the world could not compete, now China is exporting much less as it's internal consumption has risen and this could lead supply issues. They have good magnetic, phosphorescent, catalytic and optical properties. They are widely used in smart phones, cars and many other devices. There are now over 40 elements present in an iPhone (8 are rare earths), while in the 90's there were only 20 elements in an entire house. http://www.rareelementresources.com Interestingly Tesla Motors deliberately avoided the use of rare earth metals in their recent all electric Model S car.

Solar radiation (photons) is both extraterrestrial and the most abundant energy source for planet earth, and it must be harnessed more efficiently in the future. Photovoltaic thin film solar panels for renewable energy use these endangered elements: indium (In), gallium (Ga) and tellurium (Te). LEDs are energy efficient lighting devices but use seventeen times more metals than the higher energy consuming CFL bulbs. The platinum group transition metal, iridium(Ir) is endangered due to increased demand and it being one of the least abundant elements. It is used in spark plugs and catalysts as well as electronic devices. Organic complexes of iridium(III) have been developed in Bologna and found to be very stable and tunable. These complexes have found applications in the low energy OLEDs.

Europe relies heavily on imports for most of its metal demands. However copper (Cu) is recycled in the EU resulting in its import being cut in half. Many endangered elements have no substitutes as shown in the periodic table below:



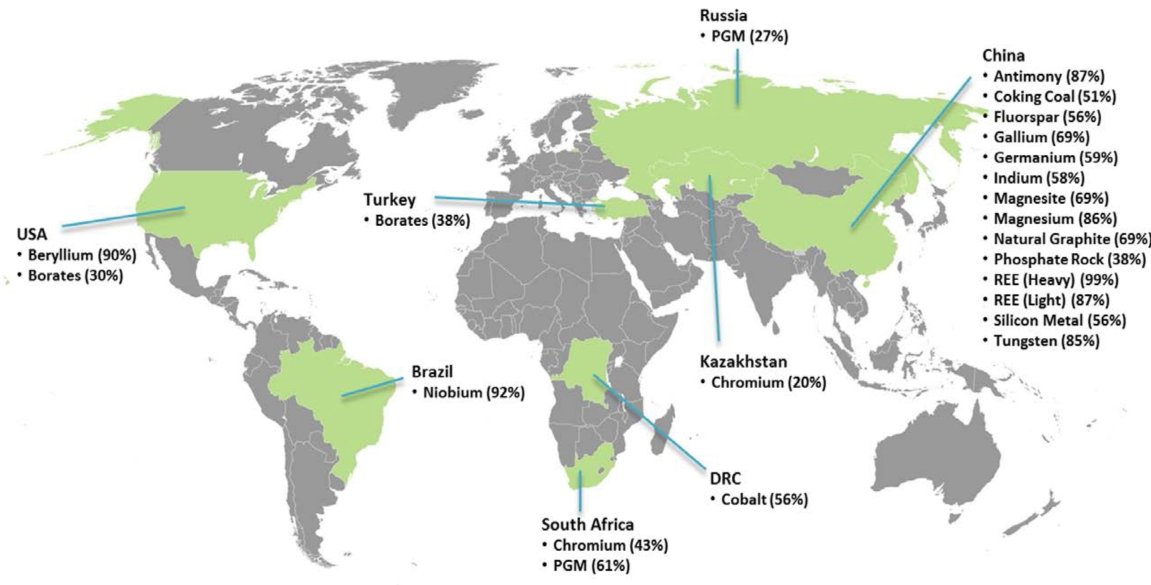
Claire Carmalt, University College London, gave a presentation entitled: <u>Sustainable Manufacturing of Transparent Conducting Oxide (TCO) Thin Films</u>.

Transparent conducting oxide thin films use many of the endangered elements in their oxide forms: In_2O_3, SnO_3, Ga_2O_3, ZnO. These oxides are doped with other elements such as fluorine to provide the desired properties of transparency and conductivity for the thin films. Such thin films are used in photovoltaics, solar panels, touch screen devices etc. There is a need to replace indium(In) and tin(Sn) due to reduce availability and price rises. 56% of indium usage is in flat panel devices. Titanium oxide (TiO_2), which is

much more plentiful has been successfully used as a substitute. Titanium can be doped with fluorine and the transition metal niobium (Nb) for use in TCO thin films.
Methods for manufacture of TCO thin films needed to be optimised to reduce costs. An efficient *aerosol-assisted chemical vapour deposition* process was developed and optimised by Claire Carmalt's team at UCL in collaboration with various faculties at Loughborough University. This has been brought to a commercial scale with significant cost savings over the previous *sputter deposition* process, which had resulted in a lot of waste.
Willem Schipper**,** Schipper Consulting, Netherlands, gave his presentation entitled: The Story of Phosphorus.
Phosphorus (P) although a ubiquitous element has limited availability. Its largest availability is in the form of phosphoric acid (H_3PO_4). It is essential for life and is endangered due to it going to waste in the ground and not being recovered. Phosphorus is relatively easy to recycle. It was placed on the European Commission Critical Raw Materials list in 2014. Morocco has 77% of phosphorus mine reserves, this could give rise to supply fluctuations if there was to be geopolitical instability.
The use of phosphorus needs to be limited where leaching into water ways is likely. The latter causes over enrichment (eutrophication), resulting in excess growth of algal bloom which has an adverse effect aquatic life. The largest use for phosphorus is in inorganic fertilizers, overuse of which gives rise to leaching. Phosphorus is also lost during slaughtering. There are various directives throughout the EU stating that fertilizers and animal slurry may not be applied to land during the winter months to reduce both phosphate and nitrate leaching. Also there have been soil phosphorus levels determined in order to prevent the over use of phosphorus containing fertilizers. Restriction of phosphorus levels in the soil by some EU member states involve control of livestock density and reduction of phosphorus in animal feedstuffs.
Incineration of phosphorus containing sludge (meat industry, sewage, manure, chemical/metallurgical) has been practised in Europe, however the ash goes to landfill. See www.recophos.org for recovery of phosphorus from sewage sludge by the monoincineration *Thermo-Reductive RecoPhos Process* in Austria. Some of the waste

residue is used as a binder for cement and as a high calorific syngas for thermal energy generation. The ash is used by ICL Netherlands to produce fertilizers.

Constantine Ciupagea, European Commission Joint Research Centre (JRC), gave a presentation entitled: Critical Raw Materials. http://www.criticalrawmaterials.eu He talked about the Circular Economy based on a life cycle approach. In 2014 the EC produced a list of 20 critical raw materials. These are critical because of their high economic value to the EU and because there could be a supply risk. See global locations diagram below: An EU report on critical raw materials predicts there will be a rapid increase in demand over the next 5 years. Previous research was focused mainly on the energy resources oil and gas. There is a Raw Material Knowledge Base held by the EU. Input to this Knowledge Base comes from international sources: EU-USA-Japan. They have focused on recyclability and substitution in their strategies based on the life cycle approach. Substitution is not only about finding replacement materials but also engaging in activities like reducing reliability on the critical materials. Looking at criticality of a material in the supply chain and how it is managed at end of life is also important.
The research of the Joint Research Centre on critical raw materials also feeds into EU industrial policy. To mitigate against potential supply issues the EU are incentivising European production of critical raw materials which stimulates the launching of new mining activities within the EU. Europe is the poorest continent in the world when it comes to minerals.

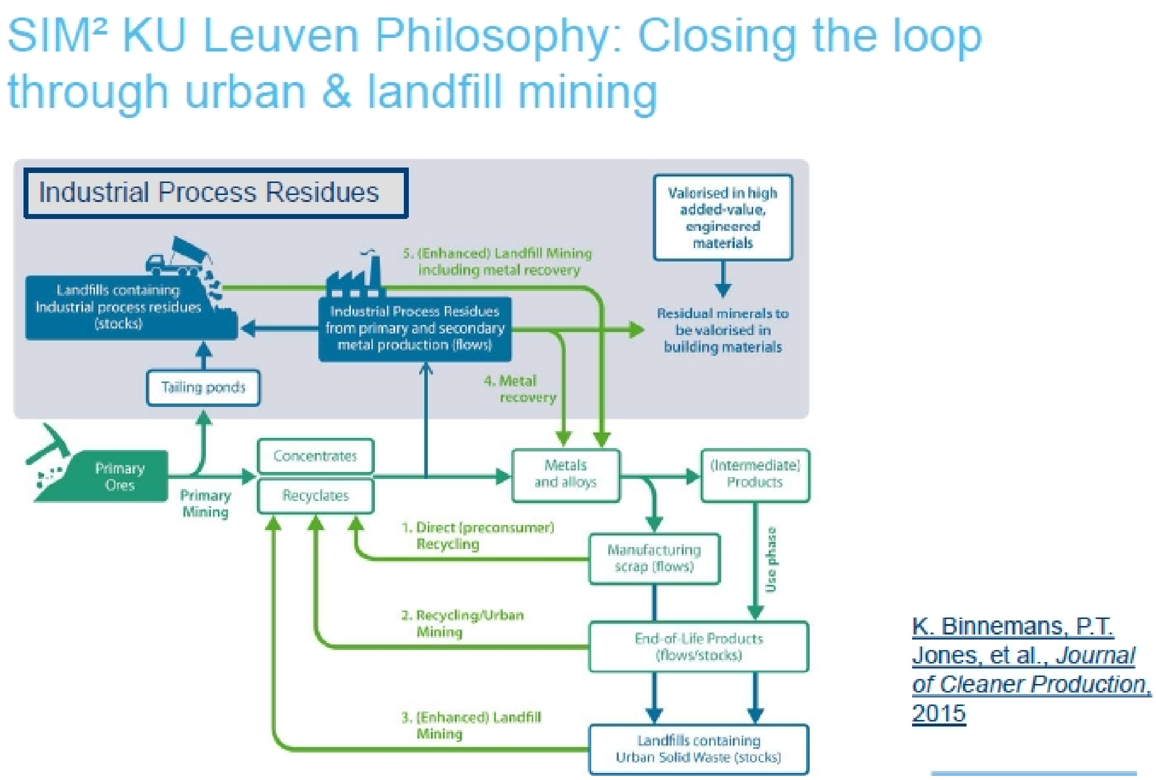


Critical Raw Materials

Ecodesign Regulation, which is part of the life cycle approach, will ensure manufactures design goods with ease of disassembly in mind. This makes recycling more efficient, for example components containing critical materials such as circuit boards (platinum group metals - PGM) can be placed in a specific recovery process when recycling.
Amsterdam council in cooperation with numerous other local bodies have established a successful recycling facility based on the “Circular Economy” It is still not complete in all features of recycling such as electricity and heat but it works well so far. The next update of Critical Raw Material list is 2017, the EC is monitoring endangered elements more closely now than at any time before.

Peter Tom Jones, Katholieke Universiteit Leuven, Flanders, gave a presentation entitled: Towards Zero-waste Valorisation of Fresh Landfilled Wastes and Residues.

He discussed the philosophy behind the recovery of value-added materials from landfill with the aid of flow diagrams, see flowchart below:



There are many practices where landfill recovery has been successful. For example, in Flanders which has approximately 12000 landfill sites and several metal processing companies which now have the ability to recover high value low concentration metals. Metallo-Chimique and KU Leuven invested in a fumer to clean landfilled fayalite slag which yielded new binders.

A new SUPERMetalEXtractor has been built in Flanders. This facility processes the residue, goethite, produced from zinc smelting by Nyrstar. After extraction of the main element iron (Fe), high value endangered metals such as indium (In), germanium (Ge), thallium (TI), cadmium (Cd), manganese (Mn), copper (Cu) and silver (Ag) are recovered.

CFL bulbs contain expensive rare earth elements which are normally difficult to recover. A new simple three step process was developed at KU Leuven which involves using an ionic liquid to selectively dissolve yttrium and europium (Y_2O_3 :Eu(III)) from the matrix, and recover the expensive Y:Eu phosphor in a purity comparable with that commercially available. Rare earth elements were at their highest price in 2011 but since have dropped, making it less attractive to recycle them.

After extraction of aluminium from bauxite there remains the bauxite residue known as red mud. This residue contains several metals including iron (Fe) and endangered rare earth elements. It has been mainly used in the construction industry after the extraction of iron. However, there exists 2.7 billion tonnes of red mud in holding ponds worldwide thus providing further opportunity to recover rare earths such as scandium (Sc) which is in a relatively high concentration. The first zero-waste valorisation process on bauxite residue has been achieved by KU Leuven. This process yields: aluminium (Al), iron (Fe), titanium (Ti), scandium (Sc) and some other rare earth elements.

The outcome of this workshop is summarised as follows:

The amount of recycling of endangered elements must be greatly stimulated as it is very poor at present It remains as an opportunity for technological innovation.

Substitution of components which use rare elements with components that use more plentiful elements is just in its infancy. Collaboration of public and private bodies and higher education research institutes must become more widespread in order to come up with solutions to conserve rare materials. EU directives need to focus more on gathering information on the landfill sites in Europe in order to have an good estimate of reserves for reworking into useful materials. It is estimated that 70% of toxic pollution in landfill comes from electronic waste. This leaves huge opportunity for recovery of rare metals.

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