Critical Minerals, Recoverable from Radioactive Materials for Value-Addition: Indian Examples

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Abstract— Critical Minerals (CMs) are mostly metals and a few non-metals, which have diverse, important industrial uses and, thus, are vital for the economic well-being of the Society, but their supply may be at risk due to several factors. They occur in three sources, viz., primary, from ore deposits, recoverable mostly as by-products and less as main products; secondary, extractable from waste materials like the electronic waste and tertiary, in imports. The list of CMs is dynamic and depends upon their availability and perspective of each country, and, hence, may change with time. For India, 33 CMs were proposed earlier by the author‒ Sb, As, Be, Bi, Cs, Cr, Co, Ga, Au, C (natural), Hf, He, In, Li, Ni, Nb-Ta, PGMs, REEs, Re, Rb, Sc, Se, Ag, Sr, Te, Sn, Ti, W, U, V and Zr, and potash, and phosphate (proposed now, making the total 34), required for the fertilizer industry. Of these, > 60% CMs may be recoverable from radioactive materials (RMs). Examples of these with their contents in diverse RMs from various parts of India are presented and discussed. From such RMs, the CMs-carrying minerals are to be first recovered and concentrated by physical beneficiation techniques of gravity/magnetic/EM. Next, the CMs in such minerals are to be extracted and purified by appropriate methods of chemical-/biochemical-/nano-technology, for which extensive R&D is to be carried out. By this swadeshi (indigenous) way under the Prime Minister's Make in India programme, the Country's requirement of critical/strategic minerals can be met to a notable extent, besides value-addition during the processing of RMs for their main products.

Keywords— Critical Minerals, Radioactive Materials, Value-Addition, Indian Examples.

INTRODUCTION

Critical Minerals (CMs) are mostly metals and a few non-metals, which are vital for the economic well-being of the world's major and emerging e-economies. But their supply may be at risk due to geological scarcity, geopolitical issues, trade policy, supply-chain problems and other factors. CMs ranked as most critical for the world's major industrial economies due to their use in futuristic developments in energy, health, construction and transportation sectors as well as in space, nuclear and defence industries, and artificial intelligence of the developed countries, such as the USA, Japan, Republic of Korea, European Union (EU) and the UK include rare earth elements (REEs), platinum group metals (PGMs), lithium (Li), beryllium (Be), gallium (Ga), germanium (Ge), indium (In), tungsten (W), cobalt (Co), niobium–tantalum (Nb–Ta), molybdenum (Mo), antimony (Sb), vanadium (V), nickel (Ni), tellurium (Te), chromium (Cr), tin (Sn), thorium–uranium (Th–U), zirconium (Zr), hafnium (Hf), selenium (Se), rhenium (Re), phosphate, potash, etc. (Critical Minerals, Geoscience Australia). From the perspective of each country, the list of CMs may change. For example, USA lists 35 CMs in the year, 2018 (Dept. of the Interior, US Geological Survey, 2018) and increased to 54 CMs in their draft for the year 2021, based on the lowest supply chain risk and quantitative evaluation (Federal Register, 2021: Ga, Nb, Co, Nd, Ru, Rh, Dy, Al, fluorspar, Pt, Ir, Pm, Ce, La, Bi, Y, Sb, Ta, Hf, W, V, Sn, Mg, Ge, Pd, Ti, Zn, graphite, Cr, As, barite, In, Sm, Mn, Li, Te, Pb, potash, Sr, Rh, Ni, Cu, Be, feldspar, phosphate, Ag, mica, Se, Cd, Zr, Mo, Au, He and, iron ore [54]; besides 12, based on qualitative evaluation - Cs, Er, Gu, Gd, Ho, Lu, Rb, Sc, Te, Th, U and Yb), as these are considered critical to its economic and national security (President of the United States, Executive order13817, 2018; US Geological Survey, 2018). For Australia, its critical commodities include Sb, Be, C (graphite), He, In, Li, Mn, Mo, Nb–Ta, Th, Sn, Ti, W and Zr, besides phosphate and potash used in fertilizers (Critical Minerals, Geoscience Australia) and this list is increased to 27 comprising two categories: High Criticality: REE, Ga, In, W, PGE, Co, Ni, Mg, Mo, Sb, Li, V, Ni, Ta Te, Cr and Mn; Moderate Criticality: Se, Ti, Sr, graphite, Sn, Ge, Be, Zr, Bi and F) (Australian Government, Dept. of Industry, Science, Energy and Resources). In India, 10 strategic minerals (S, Pb, petroleum, Zn, Hg, Pt, Ni, graphite, Sn and ferrotungsten) have been identified and their present status and future challenges are discussed by Ranadive and Jawadan (2019). From the Indian perspective, the present author has earlier suggested 33 CMs (Dhana Raju, 2020) and now adds one (phosphate) more taking the total to 34, viz., antimony, arsenic, beryllium, bismuth, caesium, chromium, cobalt, gallium, germanium, gold, graphite (natural), hafnium, helium, indium, lithium, nickel, niobium, phosphate, platinum group metals (PGMs), potash, rare earth elements (REEs), rhenium, rubidium, scandium, selenium, silver, strontium, tantalum, tellurium, tin, titanium, tungsten, uranium, vanadium and zirconium. Of these, over 60% CMs, due to their notable content, are recoverable from diverse radioactive materials (RMs) – rock, ore, mineral, mineral sand/concentrate. Examples of these recoverable CMs from the Indian RMs, their industrial uses and their contents are presented in this article, together and purification of CMs by appropriate R&D, under the Prime Minister's Make in India programme, so as to meet the Country's requirement of critical/strategic minerals to a notable extent, besides value-addition during the processing of RMs.

CRITICAL MINERALS, RECOVERABLE FROM RADIOACTIVE MATERIALS, AND THEIR INDUSTRIAL USES

Radioactive Materials (RM) are diverse in nature and include rock, ore, mineral, mineral sand and mineral concentrate, with their radioactivity ascribed to the presence of radio-elements, viz., Uranium (U), Thorium(Th) and radio-isotope of potassium (40K), in them in concentrations much higher than their crustal average. Some of the Critical Minerals (CMs, cited above), due to their geochemical affinity, are associated with the radio-elements in RMs e.g., REEs with U and Th in radioactive minerals like uraninite, zircon, thorianite, monazite, allanite etc. If such radioactive minerals are in notable concentration in diverse RMs, some of the CMs in them may be recovered, first by separating/concentrating the constituent radioactive minerals by subjecting the RMs to physical beneficiation, using the gravity, magnetic and electro-magnetic etc., techniques, and next the CMs in the separated/concentrated radioactive minerals can be extracted, enriched and purified by a combination of techniques of diverse methods such as hydro-/pyro-metallurgy, chemical-/bio-technology, nano-/laser-technology, smelting etc. The CMs that are recoverable from diverse RMs are broadly categorized under 7 heads, viz., REEs, Battery Metals, Precious Metals, Nuclear Metals, Alloy Metals, Toxic Metals and Fertilizer Commodities, and their important industrial uses are given in Table 1.

Table 1. *Critical Minerals (recoverable from Radioactive Materials) and their Industrial Uses*

Critical Minerals Symbol & At. No.	**Industrial Uses***
1. REEs: Lanathanum, La-57 Cerium, Ce-58, Prasodymium,Pr59 Neodymium,Nd-60 Promythium,Pm-61 Samarium, Sm-62 Europium, Eu-63 Gadolinium, Gd-64 Terbium, Tb-65 Dysprosium, Dy-66 Holium, Ho-67 Erbium, Er-68 Thulium, Tm-69 Ytterbium, Yb-70 Lutetium, Lu-71 Yttrium, Y-39 and Scandium, Sc-21	La: in hybrid engines, H-storage batteries, green phosphors, metal alloys, laser crystals (Y-La-fluoride); La-rich compounds in FCC catalysts, mainly for making low-octane fuel from heavy crude oil; La-stabilized zirconia in electronics. Ce: in glass & glass-polishing, phosphors (as a sensitizer), ceramics (in dental compositions and as a phase stabilizer in zirconia-based products), catalysts (FCC- catalysts, as a stabilizer in catalytic converters, as a promoter of the water-gas shift reaction & as an O-storage component), metallurgy, steel manufacturing (to remove free O/S by forming stable oxysulphides & by tying up undesirable trace elements); Ce-doped glass (to block out UV light) in manufacturing medical glassware & aerospace windows, to prevent polymers from darkening in sunlight & to suppress discoloration of television glass, and as optical components to improve performance. Pr: in magnets, ceramics, pigment (bright yellow), in scintillator for medical computed tomography scans; Pr-doped zirconia. Nd: in lasers (Nd-based YAG lasers in medical fields, drilling, welding & material processing), glass colouring & tinting, dielectrics, electronic equipment, Nd2Fe14B permanent magnets (in HEVs, EVs & renewable energy generation), Y-Al-garnet solid-state lasers, automotive industry, in the voice coil motors required for computer disk drives &, in protective lenses for welding goggles. Sm: in manufacturing of Sm-Co permanent magnets (replacing expensive Pt-Co magnets), laser applications due to its dielectric properties (as stable Sm-titanate compounds for coatings), in the filter glass on Nd: YAG solid state lasers (to envelope laser rod to improve efficiency by absorbing stray emissions) & in capacitors at microwave frequencies. Eu: has a unique luminescent property that is used for emission of visible radiation & in medical, surgical & biochemical fields, energy-efficient fluorescent lighting (yields both red & blue light), commercial red phosphors for color TV, computer screens & fluorescent lamps.

	Gd: for both high magnetic moment and phosphors & scintillated materials, when mixed with EDTA dopants, it is used as an injectable contrast agent for patients undergoing magnetic resonance imaging, can reduce relaxation times (due to its high magnetic moment) and enhances signal intensity and as an inert phosphor host for x-ray cassettes & scintillated materials for computed tomography. Tb: used in phosphors, particularly in fluorescent lamps, & as high intensity green emitter, used in projection televisions (Tb: YAG), as an x-ray phosphor & Tb-alloys in magneto-optic recording films & magnets. Dy: mainly in Nd-Fe-B high strength permanent magnets & hybrid engines and in special ceramic compositions. Ho: Due to highest magnetic moment of any naturally occurring element, it is used to create the highest known magnetic fields by placing it within high strength magnets as a pole piece or magnetic flux concentrator, in YIronGarnet YIG) lasers for microwave equipment, in a variety of medical and dental fields in both YAG & YLF solid state lasers, applications in silica fibers designed for shorter wave-lengths, while still providing the cutting strength of longer wavelength equipment. Er: in phosphors, glass colouring, lasers for medical/dental use & in eye-ware, decorative glassware, as amplifier for fiber optic data transfer, lasers (Er: YAG) for surgical applications due to its ability to deliver energy without producing heat in tissue. Tm: Most Tm-products used in making crystals & lasers, for production of portable X-ray sources as tools for medical & dental diagnosis, for detecting defects in inaccessible mechanical & electronic components and in magnetic & ceramic materials (like Y-Fe alloys, required in the microwave technologies). Yb: in fiber amplifier/optic technologies & lasers, is useful in silicon photocells for converting directly radiant energy to electricity, as metal increases its electrical resistance on being subjected to very high stresses & used in stress gauges for monitoring ground deformations from earthquakes & nuclear explosions and as thermal barrier system bond coatings on Ni, Fe & other transition metal alloy substrates. Lu: is the best host for X-ray phosphors as it produces the densest known white material (Lu tantalite), as a dopant in comparing crystallographic parameters of certain substrate garnet crystals (indium-gallium-garnet, IGG) as it lacks in a magnetic moment. Y: (highest thermodynamic affinity for O) in ceramics as crucibles for molten reactive metals, fluorescent lighting phosphors, computer displays & automotive fuel consumption sensors; Yttria-stabilized Zr-oxide in high temperature applica-tions (thermal plasma sprays for safety of aerospace component surfaces at high temperatures), YIG) crystals for the equipment of microwave communication &YAG crystals with Nd in a variety of laser applications; Yttria enhances the strength of metallic alloys; and Eu:Y2O2S phosphor produces red color in televisions. Sc: in ceramics, lasers, phosphors & certain high-performance alloys.
2. Battery Metals Lithium, Li-3 Cobalt-27 and Nickel-23	Li: Primarily for Li-ion/-polymer batteries for electric-vehicles; in ceramics and glass industries; nuclear fusion and for many chemical compounds. Co: Co-oxide nano-particles in Li-ion batteries for electric vehicles and Co in super-alloys. Ni: For batteries, alloys, coins, cars, mobile phones, jet engines, cutlery and bathroom tops and shower heads.
3. Precious Metals PGMs: Platinum, Pt-78, Palladium, Pd-46, Osmium, Os-76, Rhodium, Rh-45, Ruthenium, Ru-44 & Iridium, Ir-77) Gold, Au-79 Silver, Ag-47	PGMs: Pt catalysts in the production of silicones, high-octane gas & petrochemical feedstocks that are used to make plastics, synthetic rubber & polyester fibres; Pt as oxygen sensors & spark plugs in automobiles; Pd in almost all electronics & in the manufacture of raw materials to make nylon & synthetic rubber because of its H-absorbing qualities; Pt & Pd in applications requiring stability at high temp., such as jet engine & missile parts; Os is the densest of all elements & used for production of very hard alloys for fountain pen tips, instrument pivots, needle & electric contacts: Pt & Rh catalysts in the manufacture of nitic acid, a key ingredient in fertilizer; Ir to make high-purity crystals that have applications in medical, petroleum & security industries; Ir& Ru catalysts in making acetic acid.

	Au: for jewelry; in electronics & computers, medicine & dentistry, and medals & statues. Ag: In electronics, coins, jewelry and medicine.
4. Nuclear Metals Uranium, U-92 Thorium, Th-90 Zirconium, Zr-40 Hafnium, Hf-72 Beryllium, Be-4	U: As fuel for nuclear fission reactors; in defense to power nuclear submarines and in nuclear weapons. Th: As fuel for Th-based nuclear reactors like breeder & MSR (molten salt reactors), which are under development. Zr: In high-temperature ceramic industries, Hf-free Zr as cladding material; in alloys, chemical industry, refractories (steel and glass works), medicine, tanning and oil industries. Hf: For nuclear control rods, alloys and high-temperature ceramics. Be: As metal: as an alloying agent in aerospace and defense industries; X-ray window, as canning material in nuclear reactors; for high-speed computers and audio components As oxide: electrical insulator, in microwave communications, alloys (Be-Cu in electrical and electronic industries; Be-Al as hardener in Al-Mg alloy melting).
5. Alloy Metals Titanium, Ti-22 Vanadium, V-23 Chromium, Cr-24 Nickel, Ni-23 Niobium, Nb-41 Tantalum, Ta-73 Tin, Sn-50	Ti: As metal: as an alloying agent in aerospace and defense industries; X-ray window, as canning material in nuclear reactors; for high-speed computers and audio components As oxide: electrical insulator, in microwave communications, alloys (Be-Cu in electrical and electronic industries; Be-Al as hardener in Al-Mg alloy melting). V: For Ti-, Ferrovanadium- and V-steel alloys; minor alloy metal which toughens steel; by adding V to any steel, helps remove oxygen and nitrogen, and gives uniform grain size; V2O5 is used as a mordant, a material that permanently fixes dyes to fabrics. Cr: Primarily in stainless steel and super-alloys. Nickel: For alloys, batteries, coins, cars, mobile phones, jet engines, cutlery and bathroom taps and shower heads. Nb: In making steel; Zr-2.5% Nb alloy for pressure tubes in heavy water nuclear reactor, Zr-Nb-Cu for garter springs, SS super-alloys, superconductors, micro-alloyed steel; magnetic films of Fe-Nb nitride used in corrosion resistance. Ta: In electric components, most capacitors; transmitting and vacuum tubes, heating elements and heat shield; carbides for tools, magnetic films of Fe-Ta nitride used in corrosion resistance Sn: As protective coatings and alloys such as soft solder, pewter, bronze, phosphor bronze & steel; Nb-Sn alloy for superconducting magnets.
6. Toxic Metals Lead, Pb-82 Arsenic, As-33	Lead: For batteries, cable sheaths, machinery manufacturing, shipbuilding, light industry, lead oxide, radiation protection. Arsenic: Lumber preservatives, pesticides and semiconductors.
7. Fertilizer Commodities Phosphate	Phosphate: Major amount for the manufacture of phosphate-fertilizers and feed. Minor amount for industrial phosphates that have broad range of end-uses such as food, detergents, personal hygiene and construction.

(*Source: (1) REEs: Singh, Yamuna, 2020, Table 1.6, pp. 20-22; and Rest (2 to 7): Dhana Raju, 2020, Table 2, p. 924).

Coordinates of the places, in the alphabetical order, cited in the text and Tables – 2 to 5: Ajmer-26.4499°N,74.6399°E; Allapatna-12.3194°N,76.755°E; Bastar-19.1071°N,81.9535°E; Bhatin-22.6643°N,86.3250°E; Boleng-28.3360°N,94.9617°E; Challanpara-8.88483°N,81.5661°E; Chavara-8.9908°N,76.5404°E; Chhatrapur-19.3597°N,84.9887°E; Diguvapalle-14.8586°N,77.9625°E; Domiasiat-25.3367°N,91.2258°E; Giddankipalle-4.3122°N,78.3572°E; Gogi-16.7321°N,76.7481°E; Gomaghat-25.21267°N,91.46732°E; Jahaz-27.7377°N,75.6343°E; Kalingapatnam-18.3387°N,84.1211°E; Keruadungri-22.213207°N,85.876770°E; Kollam-8.9969°N,76.8721°E; Kotalu-4.3353°N,78.225°E; Malkangiri-18.3436°N:81.8825°E; Marlagalla-2.3031°N,76.755°E; Mewar-25.25°N,74.75°E; Narwapahar-22.6962°N,86.2584°E; Nimidih-22.9917°N,86.1459°E; Pdengshakap-25.2191°N,92.1504°E; Rachakuntapalle-4.3075°N,78.2967°E; Rohil-27.5569°N,75.49028°E; Surda-22.5540°N,86.4466°E; Tal-25.6238°N,74.0564°E; Teri sand complex-8.00°-9.50°N,77.30°-79°E; Tummalapalle-14.3214°N,78.2678°E; Ukinal-16.7575°N, 76.6635°E, Vattalakki-11.1283°N,76.7253°E and Wahkyn-25.3214°N,91.0833°E.

INDIAN EXAMPLES OF CRITICAL MINERALS, RECOVERABLE FROM RADIOACTIVE MATERIALS

There are numerous Indian examples of critical minerals (CMs), recoverable from diverse radioactive materials (RMs). Some of these on which the author has the information and work-experience are presented, together with the contents of such CMs in RMs and a brief geological account of each occurrence, in the following, which by no means is exhaustive and may be taken as a guide for more comprehensive future work by interested young geoscientists.

1. Rare Earth Elements (REEs) and Associated other CMs in Radioactive Materials (RMs)

Of the REEs, the Light REEs have been recorded (i) mostly in the mineral (M), Th-bearing monazite in the coastal heavy mineral sand (HMS) deposits along both the eastern and western coasts and less in the inland HMS deposits in the states of Odisha, Andhra Pradesh, Tamil Nadu and Kerala; (ii) in the uraniferous sandstones (whole-rock, WR and bromo-heavies, Br.H.) of the U-prospects of Pdengshakap (for the coordinates of places cited in the text and Tables – 2 to 5 see at the end of Table 1) and Gomaghat and U-deposit at Domiasiat, Meghalaya, (iii) in the fossil-placer (WR) from Boleng, Arunachal Pradesh; (iv) in the collophane (M) from the phosphatic limestone from Ukinal, Karnataka; and (v) in the U-minerals of the U-ore (O, Uraniferous Phosphatic Siliceous Dolostone, UPSD) of the U-deposit at Tummalapalle, Andhra Pradesh; and the Heavy REEs from (vii) the xenotime (M) of inland RE-placers in the states of Chhattisgarh and Jharkhand; (viii) the garnet (M) in the coastal HMS deposits and Teri inland sand complex, Tamil Nadu and (ix) Uraninite-concentrates (MC) from the U-deposits of Narwapahar, Bhatin, Keruadungri and Surda in the Singhbhum Shear Zone (SSZ), Jharkhand (Table 2).

An examination of Table 2 points out the following:

(i) The CMs like REEs, U-Th, Pb, Zr, Ti, As and P are in notable concentrations in diverse radioactive materials (RMs), such as whole-rock (WR), ore (O), mineral (M), heavy mineral sands (HMS) and mineral concentrates (MC), and could be recovered by adopting appropriate techniques of ore dressing and extractive metallurgy.

(ii) For the extraction of REEs, the two minerals, namely monazite and xenotime, are the well-known candidates, respectively, for LREEs and HREEs, besides bastnasite for LREEs which, however, is rare in India. Of these, monazite is a low-content (usually < 1 wt. % in raw sand), ubiquitous heavy mineral, mostly in the coastal and less in the inland placer heavy mineral sand (HMS) deposits, both along the east and west coasts of India, and their offshore regions. Detailed information on the placer HMS deposits of India can be had from the papers published in the edit-volumes of Dhana Raju et al. (2001) and Dhana Raju (2021). The Indian resource of monazite is 12.47 Mt (IBM yr. book, 2019). As monazite contains > 50% LREEs (Table 2, item no. 1), a resource of nearly 7 Mt of LREEs is, thus, available for their recovery and extraction of individual LREEs.

***Table 2.** REEs and Their Associated Other CMs, recoverable from diverse types of Radioactive Materials (RMs)*

REEs and Their Associated Other CMs in diverse types of RMs	Reference
A. Light REEs: 1. Monazite (M) from coastal (i, ii and iii) & inland (iv) placer HMS deposits: (i) Chhatrapur, Odisha: (wt. %, av., n=10): La2O3-11.66, Ce2O3-27.46, Pr2O3-3.23, Nd2O3-11.25, Sm2O3-1.97, Eu2O3-0.08, Gd2O3-1.08, Y2O3-0.48, ThO2-10.18, UO3-0.26 & PbO-0.31.(ii) Kalingapatnam, Andhra Pradesh: (wt. %, av., n=6): La2O3-11.39, Ce2O3-27.17, Pr2O3-2.73, Nd2O3-10.32, Sm2O3-1.58, Gd2O3-0.9, Dy2O3-0.03, Er2O3-0.07, Y2O3-0.21, ThO2-14.72 and UO2-0.29. (iii) Chavara, Kerala: (wt. %) La-10.3, Ce-17.4, Nd-9.4, Sm-1.4, Eu-0.012, Tb-0.04, Yb-0.004, Th-5.80, U-0.32 and Sc (ppm)-4,500. (iv) Siri river, Chhattisgarh: (wt.%, av., n=15) La2O3-12.2, Ce2O3-26.6, Pr2O3-2.7, Nd2O3-8.8, Sm2O3-1.6, Gd2O3-1.3, Dy2O3-0.5, Er2O3-0.2, ThO2-11.3, UO2-0.5	Mohanty et al., 2003, Table 1. Panda et al., 2003, p. 434. Krishnan et al. 2001, p.12 9. Sarbajna et al., 2007
2. Lower Mahadek Uraniferous Sandstone, Meghalaya (WR in ppm; Br. Heavies. in wt. %): (i) Pdengshakap: WR: La-210, Ce-368, Nd-NA, Sm-7.8,Eu-1.7,Tb-2.0,Yb-4.5,Lu-0.26,Y-58. BrH: La-2.148, Ce-3.513,Nd-1.51,Sm-0.305,Eu-0.0576,Tb-0.028,Yb-0.077,Lu-0.013,Y-1.07. (ii) Gomaghat: WR: La-92,Ce-137,Nd-33,Sm-11,Eu-1.20,Tb-2.20,Yb-37,Lu-1.70,Y-NA. Br.H: La-0.030,Ce-0.05,Nd-ND,Sm-0.005,Eu-0.0002,Tb-0.001,Yb-0.045,Lu-0.001,Y-0.043. (iii) Domiasiat: WR: La-224, Ce-381, Nd-165, Sm-24, Eu-1, Tb-2,Yb-2.8, Lu-0.35, Y-NA. BrH: La-1.55, Ce-2.90, Nd-1.05, Sm-0.19, Eu-0.003, Tb-0.014, Yb-0.012, Lu-0.002,Y-0.21. NA: Not analysed; ND: Not determined. Analytical Method: INAA.	Dhana Raju et al., 1989, Tables 7,6 (Sample Nos. 916, 927, 934)

3. Fossil-placer (cyrtolite-Ti ht. ironstone, WR), Boleng, E. Siang dist., Arunachal Pradesh: (In wt. %, av., n=3), (RE, Y)2O3:0.58-3.1, ZrO2:1.66-5.4, ThO2:0.13-0.5, U3O8:0.02-0.087, TiO2:13.3-15.0, Fe2O3:41.84-60.31, FeO: 1.33-1.6. Sp. Gr.: 3.96-4.66; 60-84% heavy min.	Singh et al, 1994, p. 410.
4. Collophane (M) from (a) Phosphatic Limestone, Ukinal, Karnataka: (In wt. %, av., n=4) La2O3-0.02, Ce2O3-0.03, Pr2O3-0.06, Nd2O3-0.01, Sm2O3-0.10, Gd2O3-0.06, Yb2O3-0.05, UO2-0.16, ThO2-0.07, PbO-0.06 and P2O5-40.61.	Dhana Raju et al., 2002 p.313.
5. U-phases in the UPSD (Ore),Tummalapalle, Andhra Pradesh (in wt. %, av., n: no. of spots) (a) Pitchblende (n:8): Ce2O3-0.33,Gd2O3-0.05,Dy2O3-0.06,Y2O3-0.07,V2O5-0.28,As2O3-0.30 (b) Coffinite (n:18): Ce2O3-0.40,Gd2O3-0.11,Dy2O3-0.10,Y2O3-0.29,V2O5-0.41,As2O3-0.28 (c) U-Si Complex(n:6) Ce2O3-0.45,Gd2O3-0.10,Dy2O3-0.08,Y2O3-0.24,V2O5-0.28,As2O3-0.08	Roy and Dhana Raju, 1999, p. 69.
6. REE-Th-Zr-Ti-rich Tremolite-Actinolite rock, Vattalakki, Kerala: (WR, in ppm, av., n:5): La-9022, Ce-14780, Pr-1972, Nd-5707, Sm-345, Eu-15, Gd-150, Tb-51, Dy-105,Yb-8.4,Y-245,Cr-571,Sc-29,Co-46 and Ce/Yb:1863; TiO2-8.86%, ThO2-0.88%.	Madhuparna et al., 1990, p. 138,136.
7. Heavy REEs: 7. Xenotime (M) from Siri River RE placers, Chhattisgharh (in wt. %, av.) (n:25) Y2O3-43.9, La2O3-0.0, Ce2O3-0.1, Pr2O3-0.1, Nd2O3-0.3, Sm2O3-0.1, Gd2O3-3.1, Dy2O3-4.4, Er2O3-4.6, Yb2O3-5.4, ThO2-0.6 UO2-1.6, PbO-0.6 and P2O5-33.4.	Sarbajna et al., (2007)
8. Garnet (M) from Kalingapatnam beach placers, Andhra Pradesh (in wt. %, av., n: no. of points) (n: 5): Y2O3-0.04, La2O3-0.01, Ce2O3-0.02, Nd2O3-0.03, Gd2O3-0.05, Dy2O3-0.06, Er2O3-0.10, Lu2O3-0.11, ∑LREEO-0.07, ∑HREEO-0.32 and ∑REEO-0.39.	Panda et al., 2017, p.133
9. Uraninite-concentrates (MC) from U-deposits* in the Singhbhum shear zone, Jharkhand. (In wt. %, n: 5, range): UO2:40.02 to 51.14, UO3: 22.95 to 31.18, ThO2: 0.18 to 0.84, ∑RE2O3: 4.59 to 8.68, with predominance of heavy (Gd, Dy & Er) over light lanthanides. *Narwapahar, Bhatin, Keruadungri and Surda.	Rao & Rao, 1980, p. 388.

(iii) Of the LREEs in the Lower Mahadek sandstone, the whole-rock samples contain REEs in ppm level with the highest content of Ce being 381 ppm, whereas their bromoform-heavies (Br. H.) contain in %-level, with the highest content of Ce being 3.513% (Table 2, item no. 2) in the Domiasiat U-ore; the % Br. H. in the whole-rock sandstone is usually < 1% with a maximum of 4.9%. This pattern demonstrates that for recovering the REEs in notable content from low-content whole-rocks, physical beneficiation, involving separation and enrichment of REE-bearing heavy minerals like monazite and zircon using the gravity, electrical and electro-magnetic methods should be the first step in mineral progressing. Detailed account of these sandstones from the U-prospects of Pdengshaka and Gomaghat, and the sandstone-type U-deposit of Domiasiat can be had from Dhana Raju et al., (1989), Sen et al., (2002) and Dhana Raju (2019).

(iv) The cyrtolite-Ti-hematite ironstone (Table 2-item no. 3) from Boleng, Arunachal Pradesh is a rare fossil-placer (Sp. Gr. 3.96-4.66) containing 60-85% heavy and resistant minerals comprising 46-61% opaque minerals (mostly Ti-hematite), 9-13 rutile, 3-9% cyrtolite, 0.7-4.5% monazite and 0.2-0.9% thorite, all set in 10-30% sericitic matrix. With such dominant heavy mineral assemblage, it is no surprise that it contains notable contents of critical minerals of Ti, Zr and REEs in major amounts. Physical beneficiation of this rock will lead to much higher concentrations of these critical minerals. In view of the importance of this rock for the above critical minerals, it is suggested that a detailed exploration should be carried out in the area for locating more bodies of this rock. The rock is recorded in association with the quartzite and metagraywacke of the Proterozoic Miri Group (Singh et al., 1994).

(v) The critical mineral (P, LREEs, U-Th-Pb) data of collophane from the Ukinal area in Karnataka (Table 1-item 4) points out that this rock, near to the Gogi high-grade U-deposit, needs to be re-explored to evaluate the resource of critical minerals listed above.

(vi) Data on the critical minerals (REEs, V and As) in the U-phases of the rare carbonate-hosted U-deposit at Tummalapalle (Table 2 - item 5) highlight the importance of extracting them as by-products of U during the ongoing mineral processing of this deposit, which will be an important value-addition.

(vii) The REE-Th-Zr-Ti-rich tremolite-actinolite rock from Vattalakki, Kerala (Table 2 -item 6) is another rare rock that is important for the above critical minerals. As this rock occurs as a sill-like intrusive body in the gneisses in the area, in association with dolerite sill, it is recommended that a detailed exploration in the area should be undertaken for such exotic rocks to enhance the resource position of important critical minerals, listed above.

(viii) As xenotime is the HREE-mineral with notable contents of CMs of individual HREEs, together with other CMs like U-Th, Pb and P (Table 2 - item 7), AMD has been exploring and exploiting since long the potential inland riverine placer bodies for both xenotime and monazite in the states of Chhattisgarh and Jharkhand, with their source rocks being granites and granite pegmatites.

(ix) An HM concentrate comprising 2-5% xenotime, 22-54% monazite, 45-50% Fe-minerals, 5-24% garnet, 2-6% zircon and 12% other minerals, and analyzing 1.5-3.5% Y_2O_3 and 2.0-12.81% Ce_2O_3 has been recovered by mobile pilot-scale recovery plants (Ramesh Babu, 2021). More details on the Indian RE-inland placer deposits, exploration, exploitation, resources etc., can be had from the papers in (Eds.) Mahadevan and Dhana Raju (1999), Singh (2020) and (Ed.) Dhana Raju (2021).

(x) Garnet (Table 2 - item 8), a major heavy mineral in the coastal and some inland (like Teri HMS deposits in Tamil Nadu) is a known host for REEs though in minor content ($\sum$REEO ~ 0.3-0.4%), with HREE/LREE being 4-5. As the garnet resource in the Indian placers is 187 Mt (IBM Indian Mineral Year Book 2018/2019), taking its $\sum$REEO around 0.3%, an REE resource of 0.56 Mt is available for recovery and extraction, with 5/6th of it being HREEs. Hence, recovery of HREEs from more available garnet than xenotime should also to be taken up, along with the recovery from xenotime.

(xi) The uraninite-concentrate from different U-deposits of the Singhbhum shear zone (SSZ), Jharkhand (Table 2- item 9) contains notable content of $\sum RE_2O_3$: 4.59 to 8.68, with predominance of heavy (Gd, Dy & Er) over light lanthanides, and, hence, extraction of REEs as by-products from uraninite during the processing of U-ore should be taken up under value-addition so as to improve the resource base particularly of HREEs. At the Jaduguda U-mine in SSZ, a by-product recovery plant was in operation for recovering Cu, Ni, Mo and Fe (as magnetite) from U-ore (IAEA, 2001).

2. Battery Metals and Precious Metals as CMs in Radioactive Materials (RMs)

Of the three battery metals that can be recovered from radioactive materials (RMs), Li occurs in the form of its discrete minerals, viz., spodumene, lepidolite and amblygonite in the granite-related rare metal pegmatites of Marlagalla, Karnataka (Krishna and Thirupathi, 1999) and Bastar – Malkangiri Pegmatite Belt (BMPB) in Chhattisgarh and Odisha (Ramesh Babu, 1999; 2021); and Co and Ni occur in the sulphides of in the U-ore of Gogi, Karnataka (Dhana Raju et al., 2002). Among the precious metals, PGMs at ppb level occur in the rare REE-Th-Zr-Ti-rich tremolite-actinolite rock in the Vattalakki area, Kerala (Dhana Raju et al., 1998), whereas Au and Ag at per cent level occur in the sulphides of the U-ores at Gogi, Karnataka (Dhana Raju et al., 2002) and Tummalapalle (Roy and Dhana Raju, 1999) (Table 3).

An examination of the data on the three battery CMs (Table 3) points out the following:

(i) Li occurs in its discrete minerals such as spodumene, lepidolite and amblygonite, which are hosted usually by the granite-related rare metal pegmatites that occur as well-defined belts, groups and clusters in the states of Chhattisgarh, Odisha and Karnataka.

(ii) AMD has been extensively exploring and exploiting these pegmatites with recovery of spodumene mostly from the rare metal pegmatites in the Marlagalla area, Karnataka, and lepidolite and amblygonite from those in the states of Chhattisgarh and Odisha by field-based mobile plants (Krishna and Thirupathi, 1999; Dwivedy, 1996; Ramesh Babu, 1999 and 2021).

(iii) Of the above three Li-minerals, the Li-content ranges from 4.6 to 9.1%, with the lowest, intermediate and highest contents, respectively, in lepidolite, spodumene and amblygonite.

(iv) The other two battery CMs, namely Co and Ni occur in recoverable amounts in the sulphides of the U-ore (hosted both by limestone and granite) at Gogi, Karnataka. These sulphides include pyrite (euhedral and framboidal), chalcopyrite and galena.

(v) Of these three sulphides, chalcopyrite and pyrite host higher contents, and galena carries low contents of Co and Ni. Between the two forms of pyrite, viz., euhedral and framboidal, the euhedral one in granite and the framboidal one in limestone carry relatively higher contents of both Co and Ni (Dhana Raju et al., 2002).

(vi) These patterns indicate that both the pyrite and chalcopyrite should be separated and concentrated from the Gogi U-ore by appropriate mineral processing and extraction techniques to recover Co and Ni as high-value by-products required for the battery industry.

Table 3. *Battery Metals and Precious Metals, recoverable from Radioactive Materials (RMs)*

Battery Metals and Precious Metals as CMs in RMs	**Reference**
A. Battery Metals	
1. Lithium (Li): (in wt. %) (i) Marlagalla, Karnataka: Li_2O: (M) Spodumene: 6.55-7.35, av. 7.14 (n=4), (ii) Govindpal, BMPB, Chhattishgarh & Odisha: Lepidolite: 4.55, Amblygonite: 9.12	Krishna & Thiru-pathi,1999,p. 146 Dwivedy, 1996, p. 113, 114
2. Cobalt (Co) & Nickel (Ni): (a) Sulphides in Gogi U-ore: (in wt. %, av., n=6-45), Pyrite (euhedral): (i) in L.St.: Co-0.04, Ni-0.04, (ii) (in Gr.): Co-0.10, Ni-0.06 Pyrite (framboidal): (i) in L.St.: Co-0.36, Ni-0.14, (ii) (in Gr.): Co:0.03, Ni:0.0 Galena (i) in L.St.: Co-0.02, Ni-0.01, (ii) (in Gr.): Co-0.01, Ni-0.01 Chalcopyrite (i) (in L.St.): Co-0.28, Ni-0.18 (L.St: Limestone, Gr.: Granite)	Dhana Raju et al., 2002, p.312
(b) Sulphides in Tummalapalle U-ore: (in wt. %, av.), Pyrite (euhedral): Co-0.02, Ni-0.07 (n=19), Pyrite (framboidal): Co-0.03, Ni-0.085 (n=14)	Roy & Dhana Raju, p.70
B. Precious Metals	
3. Platinum Group Metals (PGMs) (in ppb, av., n=4), REE-Th-Zr-Ti-rich tremolite-actinolite rock, Vattalakki, Kerala: Pt: 3.125, Ir: <0.5-0.5, Rh: <0.5, Ru:1.0, Pd-2.25	Dhana Raju et al., 1998 p. 525
4. Gold (Au) in sulphides of the U-ore at Gogi, Karnataka (in wt. %, av., n=6 to 45) Pyrite (euhedral): (i) in L.St.: Au-0.00, (ii) (in Gr.): Au-0.04 Pyrite (framboidal): (i) in L.St.: Au-0.00, (ii) (in Gr.): Au:0.09 Galena (i) in L.St.: Au-0.04, (ii) (in Gr.): Au-0.07 Chalcopyrite (i) (in L.St.): Au-0.00, (L.St: Limestone, Gr.: Granite)	Dhana Raju et al., 2002, p.312
5. Silver (Ag) in sulphides of the (a) Gogi U-ore, Karnataka (in wt. %, av., n=6 to 45) Pyrite (euhedral): (i) in L.St.: Ag-0.04, (ii) (in Gr.): Ag-0.02; Pyrite (framboidal): (i) in L.St.: Ag-0.09, (ii) (in Gr.): Ag:0.04; Galena (i) in L.St.: Ag-0.00, (ii) (in Gr.): Ag-0.02; Chalcopyrite (i) (in L.St.): Ag-0.26 (L.St: Limestone, Gr.: Granite)	Dhana Raju et al., 2002, p.312
(b) Tummalapalle U-ore, A.P.: Pyrite (euhedral): 0.04%, Pyrite (framboidal): 0.03%	Roy & Dhana Raju, 1999, p. 70

(vii) Amongst the precious CMs, as expected, the contents of Ag > Au >> PGMs, with the first two being in notable, low per cent grade in the sulphides of the Gogi U-ore (Dhana Raju et al., 2002), whereas the contents of PGMs in the rare tremolite-actinolite rock at Vattalakki, Kerala (Dhana Raju et al., 1998) appear to be of academic interest; however, detailed exploration in the area and its contiguous areas is suggested for more possible such bodies.

(viii) Regards Au and Ag in the Gogi area, pyrite and galena in granite-hosted U-ore carry higher contents of Au than those in the limestone-hosted U-ore, whereas pyrite and chalcopyrite in the limestone-hosted U-ore carry higher contents of Ag, with chalcopyrite carrying the highest content at 0.26% Ag. These data, thus, cumulatively demonstrate the importance of separation and concentration of sulphides from the Gogi U-ore to recover both precious and battery CMs as valuable by-products as and when the ore is processed for U as the main-product.

3. Nuclear Metals as CMs in Radioactive Materials (RMs)

Of the five nuclear metals as CMs in RMs, uranium (U) occurs in India in low-grade (< 0.2% U_3O_8) deposits, with source of U mostly in granitic rocks and hosted by diverse rock types such as (i) granite and limestone (hydrothermal type) in the Neoproterozoic Bhima basin in the Gogi area, Karnataka, (ii) impure carbonate-sediment (UPSD – uraniferous, phosphatic, siliceous dolostone – in the Tummalapalle - Rachakuntapalle - Giddankipalle sector (and its contiguous areas (rare strata-bound, syn/dia-genetic type with a large-tonnage

[> 1.5 lakh tonnes U_3O_8, accounting for > 50% of Indian U-resources of > 3 lakh tonnes U_3O_8]) along the SW, S and W margins of the Mesoproterozoic Cuddapah basin in Andhra Pradesh, (iii) basement granite and its overlying quartzite of the unconformity-proximal type along N- and NE-margins of the Cuddapah basin in parts of Telangana and Andhra Pradesh; (iv) diverse low-medium grade tourmaline-apatite-magnetite-biotite-chlorite-quartz schists, quartzite, sheared conglomerate etc., along the Singhbhum Shear Zone (SSZ) in Jharkhand; (v) Upper Cretaceous, Lower Mahadek sandstone in the Domiasiat area, Meghalaya; (vi) albitites and albitised associated rocks (Albitisation-related, metasomatic hydrothermal type) in Rajasthan, etc. From these U-ores, U as the main product is recovered by mineral processing either through acid-route in case of silicate rocks as host (e.g., U-ores of different deposits in SSZ, Jharkhand) or alkali-route in case of carbonate-rocks as host of U-minerals (e.g., Tummalapalle U-deposit in Andhra Pradesh). For more details, see the papers in AMD's EARFAM, v. 14, 2002, (Eds. R. Dhana Raju et al.,) and Dhana Raju, (2019). In India, most of Thorium (Th) is in the mineral, monazite (4-15% ThO_2) that is a fine-grained constituent (< 1% in raw sand) of the placer heavy mineral sand (HMS) deposits along the east and west coasts, and less in the inland HMS deposits in the states of Odisha, Andhra Pradesh, Tamil Nadu and Kerala (for details, see the papers in AMD's EARFAM Spl. Vol. 13 on 'Beach and Inland Heavy Mineral Sand Deposits of India', (Eds.) Dhana Raju et al., 2001) and in the book on 'Indian Placer Deposits' (Ed.) Dhana Raju (2021). Zirconium (Zr) and hafnium (Hf) in recoverable contents occur mostly in the form of fine-grained mineral, zircon in the HMS deposits cited above, and beryllium (Be) occurs in the mineral, beryl in the Rare Metal Pegmatite deposits in the states of Chattisgarh, Odisha and Karnataka, from which it can be recovered as the main product (for details see papers in the AMD's EARFAM Spl. Vol. 12 on 'Rare Metal and Rare Earth Pegmatites of India', (Eds. Mahadevan and Dhana Raju (1999) and in the book on 'Indian Placer Deposits' (Ed.) Dhana Raju, 2021) (Table 4).

An examination of the data in Table 4 points to the following:

(i) Out of different U-deposits in India, the one at Tummalapalle is the lowest (0.045% U_3O_8) and that at Gogi is the highest (0.18% U_3O_8) in the U-grade. The U-ore in different deposits of the SSZ, Jharkhand contains many CMs, some of which like Cu, Ni and Mo have been under recovery as by-products, whereas Co, Zr and Y, and Re from the molybdenite-concentrate may be recovered by appropriate extraction technologies that may need R & D.

Table 4. *Nuclear Metals and Their associated other CMs, recoverable from different types of Radioactive Materials (RMs)*

Nuclear Metals as CMs, recoverable from RMs	**Reference**
1.Uranium (U)	Dhana Raju, 2019
(i) Gogi U-deposit, Karnataka: U-ore: U_3O_8: 0.013-1.678%, av. 0.18%	p. 126
(ii)Tummalapalle U-deposit, Andhra Pradesh: U-ore: U_3O_8: av. ~ 0.045%	-do-, p. 246
(iii)Unconformity-proximal type, Telangana, AP: U-ore: U_3O_8: 0.05-0.1%	-do-, p. 185
(iv)Jaduguda-Bhatin-Nimdih U-deposits in SSZ: U-ore: eU_3O_8: 0.05-0.07%; (in ppm, av. of 359 samples) Ni-402, Cu-70, Mo-47, Co-47, Y up to 290 and Zr up to 230;	Dhana Raju, 2019, p. 68
by-product molybdenite-concentrate (UCIL-recovery plant) contains upto180 ppm Re	Singh et al., 1979
(v) Sandstone-type U-deposits in Meghalaya: U-ore: (a) Domiasiat: U_3O_8: 0.098%, (b) Wahkyn: 0.124% eU_3O_8	Dhana Raju, 2019, p. 395-do- , p.326
(vi) Albitisation-related type U-deposit: Rohil, Rajasthan:U-ore: U_3O_8: 0.05-0.08%	
2. Thorium (Th): mostly in monazite of HMS deposits: 5-15% ThO_2 (see Table 2-A 1)	Ravi, 2021, p. 527
3. Zirconium (Zr) content (in wt.%) of Zircon from HMS deposits: (i) OSCOM, Chhatrapur, Odisha: 64.5, (ii) Manvalakuruchi, Tamil Nadu: 65.8, (iii) Chavara, Kerala: 65.3 and Kollam, Kerala: 64.8	Krishna &Thiru-pathi, 1999, p. 136
4. Beryllium (Be) & associated other CMs (wt.%) in Beryl from RM pegmatite deposits	
(i) Marlagalla, Karnataka: BeO-11.89, Li_2O-0.55, Cs_2O-0.66 and Rb-799 ppm	Ramesh Babu
(ii) Challanpara (in BMPB), Chhattisgarh: BeO-13.20, Cs_2O-0.06and Rb_2O-0.005	1999, p.17
(iii) Ajmer, Rajasthan: BeO-13.41, Cs_2O-986 ppm and Rb_2O-41 ppm	Maithani & Nagar, 1999, p. 105

(ii) From the mineral monazite in the HMS deposits, both LREEs and Th, which occur as major constituents, are recoverable.

(iii) The CMs, zirconium and its ubiquitous associate, Hf in the mineral, zircon from the HMS deposits have been under recovery in the nuclear industry.

(iv) As the CM, Be is associated with the other CMs, namely Cs and Rb in recoverable contents in the mineral, beryl of the Rare Metal pegmatites, R & D may be required to extract both Cs and Rb as by-products, when Be is recovered as the main product from the mineral, beryl.

4. Alloy metals as CMs in Radioactive Materials (RMs)

Of the alloy metals, Ti, Nb-Ta and Sn occur usually in major amounts, whereas V, Cr and Ni occur in minor to trace contents in the radioactive materials (RMs). Thus, Ti is a major constituent and Cr is in minor to trace amounts (< 1%) in the mineral, ilmenite ($FeO.TiO_2$) that is normally in the maximum amount amongst the valuable heavy minerals (ilmenite-sillimanite-garnet, each > 1% and zircon-rutile-monazite, each < 1%) in the HMS deposits along the east and west coasts of India (see papers in the volumes edited by Dhana Raju et al., 2001 and Dhana Raju, 2021). Nb-Ta occur together in major amounts in some rare minerals such as columbite-tantalite, microlite, ixiolite and wodginite, and Sn in major amount in the mineral, cassiterite; all these minerals are valuable constituents in the rare metal pegmatites in the BMPB in the states of Chhattisgarh and Odisha (Ramesh Babu, 1999 and 2021) and in the Marlagalla – Allapatna area in Karnataka (Krishna and Thirupathi, 1999). V, Ni, Cu and Mo in notable contents occur in the sulphides (pyrite, chalcopyrite, pyrrhotite and molybdenite) of the uraniferous albititites and related rocks in the albitisation-related U-deposits of Rohil - Jahaz in Rajasthan (Padhi et al., 2016) and U-ores of Tummalapalle and Gogi, and in relatively higher contents in their sulphides (Dhana Raju, 2019) (Table 5).

Table 5. *Alloy Metals and Their associated other CMs, recoverable from different types of Radioactive Materials (RMs)*

Alloy Metals as CMs, recoverable from Radioactive Materials (RMs)	**Reference**
1.Titanium, Chromium and Vanadium in HMS deposits	
(i) Chhatrapur HMS deposit, Odisha: Ilmenite: (wt. %, range, n=20) TiO_2-45.67 to 55.41, Cr_2O_3-0 to 0.089, V_2O_5-0.247 to 0.306	Rao & Sengupta, 2014, p. 5
(ii) HMS deposits in Andhra Pradesh: Ilmenite: (wt. %, range, n=7) TiO_2-48.0 to 50.8, V_2O_5-0.07 to 0.25; Cr (in ppm, n=3): 650-1178 (Jagannadha Rao et al., 2015)	Ravi, 2021, p. 411
(iii)HMS deposits in Tamil Nadu: Ilmenite: (wt. %) (a) Coastal beach & dune sands: (range, n=68) TiO_2: 49.7-57.8, Cr_2O_3: < 0.1 to 0.7, V_2O_5-0.1-0.3; (b) Inland Teri sands (n=20): TiO_2-49.7 to 54.5, Cr_2O_3-0 to 0.2, V_2O_5-0.2-0.25	Chandrasekaran & Murugan, 1999, pp. 94-95
(iv)Chavara HMS deposit, Kerala: Ilmenite: (wt. %, n=9) TiO_2-58.4 to 65.0, Cr_2O_3-0.15-0.25, V_2O_5-0.15-0.25	Krishnan et al., 2001, p. 128
2.Niobium-Tantalum in Nb-Ta Ores of Rare Metal Pegmatites (i) BMPB, Chhattisgarh and Odisha: (wt. %) (a) Columbite-Tantalite: Nb_2O_5-35.2, 32.6; Ta_2O_5-31.2, 37.1; (b) Ixiolite: Nb_2O_5-11.0, 8.5; Ta_2O_5-57.1, 60.5; (c) Niobian Ixiolite: Nb_2O_5-58.8, Ta_2O_5-14.2; (d) Wodginite: Nb_2O_5-2.0, 32.6; Ta_2O_5-67.8; (e) Microlite: Nb_2O_5-3.8, Ta_2O_5-69.8	Ramesh Babu, 1999, p. 19
(ii)Marlagalla-Allapatna, Karnataka: (wt. %) (a) Columbite-Tantalite (n=8): Nb_2O_5:18.66-68.67,Ta_2O_5:16.34-59.56;(b) Microlite: Nb_2O_5- 4.04, 4.31; Ta_2O_5-73.40, 73.01	Sarbajna et al., 1999
3.Tin in Sn-ore of Rare Metal Pegmatites	
(i) BMPB, Chhattisgarh and Odisha: Cassiterite: (wt. %, range, n=4) SnO_2-79.62 to 91.40, Nb_2O_5- 0.78 to 2.60, Ta_2O_5-4.01 to 12.40, WO_3-<0.01 to 0.10	Dwivedy, 1996, p. 116
4. Nickel, Vanadium and their other associated CMs in U-ores/phases and sulphides	
(i) Albitites-microclinites-pyroxenites from Mewar-Gujarwas to Tal, Rajasthan U-Ore (n=14, ppm): U- 116 to 13,600, Ni- 22 to 180, Cu- <5 to 2,165, Mo- < 5 to > 1,000,	Singh et al., 1998, p.5
(ii)Tummalapalle U-ore, Andhra Pradesh: (wt. %) V_2O_5 (av.) in U-phases: Pitchblende-0.28 (n=8), Coffinite-0.41 (n=18), U-Si Complex-0.28 (n=6) and U-Si-Ti Complex-0.35 (n=6)	Roy & Dhana Raju, 1999, p. 69
(iii)Gogi U-ore, Karnataka: (wt. %) (a) Ni (range, av.): pyrite: 0.0 to 1.47, 0.06 (n=76), Galena: 0.0 to 0.07, 0.01 (n=19), Chalcopyrite: 0.03 to 0.28, 0,12 (n=6);	

(b) Cu (range, av.): Chalcopyrite: 28.59-34.12, 31.16 (n=6); pyrite: 0.0 to 0.94, 0.04 (n=76); Galena: 0.0 to 0.32, 0.07, n=19)	Dhana Raju et al., 2002, p. 312

An examination of the data in Table 5 points to the following:

(i) Of the ilmenite in the HMS deposits of India, TiO2 content is the highest (65%) in the Chavara deposit and lowest (45.67%) in the Chhatrapur deposit, whereas Cr2O3 is the highest (0.7%) in the Tamil Nadu deposits and lowest in the Chhatrapur deposit (0-0.09%) and V2O5 is the highest in the Chhatrapur deposit (0.25-0.31%) and comparable (~ 0.1 to 0.25%) in the deposits of Andhra Pradesh, Tamil Nadu and Kerala. As the India's ilmenite resource is 630 Mt (IBM yr. book, 2019), recovery of Cr and V from ilmenite will add substantial amounts to their resource base. Furthermore, as the V2O5 content in the U-phases in the Tummalapalle U-ore is appreciable (0.28 to 0.41%), it should be recovered as a by-product for value-addition during the processing of this U-ore.

(ii) In the columbite-tantalite, the ones from Marlagalla deposit contain both Nb and Ta in higher amounts as compared to that in the BMPB deposits. Besides, Ta > Nb occurs in the minerals like ixiolite, wodginite and microlite, and the inverse pattern (Nb > Ta) in the niobian-ixiolite in the BMPB.

(iii) Cassiterite in the BMPB contains notable amounts of both Nb and Ta, which may be recovered as valuable by-products during the processing of cassiterite for tin as the main product.

(iv) Ni is in recoverable amounts from the sulphides such as pyrite and chalcopyrite of the Gogi U-ore, whereas from the sulphides in the U-ores hosted by the albitite-pyroxenite-microclinite in Rajasthan, Cu and Mo may be recovered as main-products and Ni as a by-product.

5. Toxic Metals and Fertilizer Commodity as CMs in Radioactive Materials (RMs)

The toxic metals – lead (Pb) and arsenic (As) – occur in notable concentration in different RMs, with radiogenic Pb in all U-phases in genetically diverse U-ores and As in sulphides in these ores, as demonstrated by the following examples:

(i) In the stratabound, syn/dia-genetic impure dolostone-hosted Tummalapalle U-ore (UPSD), Andhra Pradesh, the average contents (in wt. %) of radiogenic Pb in different U-phases are as follows: pitchblende: 4.82 (n=8), coffinite: 2.48 (n=18), U-Si complex: 1.75 (n=6) and U-Si-Ti complex: 5.58 (n=6) (Roy and Dhana Raju, 1999, p. 69);

(ii) In the hydrothermal type Gogi U-ore, hosted both by basement granite and its overlying limestone, the average contents (in wt. %) of radiogenic Pb in different U-phases are as follows: pitchblende: 6.28 (n=9) in limestone and 2.48 (n=14) in granite; coffinite: 3.20 (n=16) in limestone and 1.27 (n=20) in granite; and U-Ti complex in granite: 0.04 (n=6) (Dhana Raju et al., 2002, p. 310). In the uraninite-concentrates from hydrothermal type of different U-deposits in the SSZ, Jharkhand, PbO ranges from 6.29% (Surda) to 13.64% (Narwapahar) (Rao and Rao, 1980, p. 388). Besides radiogenic lead, non-radiogenic Pb occurs as the major constituent in the sulphide, galena, e.g., in the Gogi U-ore, av. 83.74% (n=6) in the limestone and av. 85.59% (n=13) in the granite.

(iii) Arsenic (As) in lower concentration occurs in the sulphides of U-ores, e.g., in the Gogi U-ore, framboidal pyrite in both limestone and granite, respectively, contains average contents of 0.28% (n=7) and 0.17%, whereas the euhedral pyrite in limestone and granite, respectively, contains average contents of 0.23% (n=45) and 0.04% (n=7) (Dhana Raju et al., 2002, p. 312).

(iv) The non-metal CM, phosphate used as a fertilizer commodity occurs in notable content in the phosphatic RMs containing major amount of a phosphatic mineral like collophane and apatite. e.g., UPSD in the different U-deposits of Diguvapalle, Tummalapalle, Gidankipalle and Kotalu along the SW-margin of the Cuddapah basin in Andhra Pradesh contains usually 1-9.4% P2O5 with a maximum of 28.58% P2O5 in that from Kotalu (Roy and Dhana Raju, 2012, p. 183) and, hence, the phosphate in the large tonnage (> 1.5 lakh tonnes) dolostone-hosted U-ore should be recovered as a by-product for agricultural use during the processing of this ore in the Tummalapalle plant. Another example of notable phosphate content in RA material is the radioactive limestone from the Ukinal area (near the Gogi U-deposit), Karnataka that contains 25.64% P2O5 (average, n=15) (Dhana Raju et al., 2002, p. 302).

DISCUSSION

Recovery of Critical Minerals (CMs) from Radioactive Materials (RMs)

An examination of the data (Tables – 2 to 5) and information, presented in the earlier sections, points out that out of the 33 Critical Minerals (CMs) identified from the Indian perspective (Dhana Raju, 2020) plus phosphate as one more CM, > 60%, viz., As, Be, Cs, Cr, Co, Au, Hf, Li, Ni, Nb-Ta, REEs, Sc, Rb, Ag, Sn, Ti, W, U, V and Zr metals, and non-metal phosphate are in contents recoverable (mostly as by-products under value-addition and a few as main products) from diverse radioactive materials (RMs) that include whole-rock and its constituent heavy minerals, U-ores and their constituent U-phases and sulphides, rare metal minerals, mineral concentrates and heavy mineral sands. This is illustrated by the following examples:

(i) The LREEs in the whole-rock Lower Mahadek sandstones in Meghalaya are in ppm level, whereas they are in per cent level in their bromoform-heavies (Br. H.) (Table 2 - item 2), which are usually < 1% in their host sandstone. This pattern points out that when the CMs like LREEs in a rock are in ppm level, it is advisable to identify first the minerals in the rock which account for such CMs, followed by their physical separation so as to enhance the concentration of these CMs for their better recovery as by-products as value-addition during the processing of the whole-rock. Furthermore, in rare rocks like the fossil-placer from Boleng, Arunachal Pradesh and tremolite-actinolite rock from Vattalakki, Kerala (Table 2 - items 3 and 6, respectively), ∑REEs and Ti are in recoverable, major amounts.

(ii) All the diverse types of U-ores, such as hydrothermal, stratabound syn/dia-genetic, unconformity-proximal, albitisation-related, sandstone etc., contain some CMs (other than U and/or Th [radio-element CMs] and radiogenic Pb [toxic CM, section 5, item nos. i and ii]) in lower concentration that increases substantially in their constituent mineral phases like U-minerals and sulphides. This pattern is illustrated by the following examples of the U-ores of Gogi (Karnataka) and Tummalapalle (Andhra Pradesh): (a) In the Tummalapalle U-ore, its U-phases contain per cent level REEs, V and As (Table 2 - item 5) and its sulphides contain recoverable grade (% level) Ag (Table 3 - item 5) and Co and Ni (Table 3 - item 2). (b) In the Gogi U-ore, its sulphides contain per cent level Co & Ni, Au and Ag (Table 3 - items 2, 4 and 5, respectively) and arsenic (As, section 5 - item iii).

(iii) The uraninite-concentrates from different U-deposits in the Singhbhum shear zone, Jharkhand, contain per cent level ∑REEs, with HREE >> LREE (Table 2 - item 9).

(iv) The rare metal minerals in the pegmatites of BMPB in the states of Chhattisgarh and Odisha, and Marlagalla-Allapatna in the state of Karnataka contain the CMs of Li, Cs, Nb-Ta, Be and Sn in recoverable, major amounts from their respective minerals (spodumene, lepidolite and amblygonite for Li; pollucite for Cs; columbite-tantalite, ixiolite, niobian ixiolite, microlite and wodginite for Nb-Ta; beryl for Be and cassiterite for Sn), besides other CMs in minor (per cent level) contents, e.g., cassiterite containing Nb-Ta and W (Table 5 - items 2 and 3) and beryl containing Li, Cs and Rb (Table 4 - item 4).

(v) The coastal and inland heavy mineral sand (HMS) deposits along the east and west coasts of India in the states of Odisha, Andhra Pradesh, Tamil Nadu and Kerala contain some CMs in major amounts in their respective minerals (e.g., Ti in ilmenite [Table 5 - item 1], Zr in zircon [Table 4 - item 3] and LREEs in monazite [Table 2 - item 1]), and a few other CMs in minor amounts (e.g., HREE in garnet [Table 2 - item 8]; Cr and V in ilmenite [Table 2 - item 1]). Furthermore, the inland riverine placer bodies in the states of Chhattisgarh and Jharkhand contain both xenotime and monazite, from which HREEs and LREEs, respectively, can be recovered (Table 2 - items 1[iv] and 7).

(vi) Non-metal CM, Phosphate: This fertilizer commodity is in major amounts in the Tummalapalle U-ore (Andhra Pradesh) and the Ukinal U-ore (Karnataka) (section 5 - item iv) and during the processing of such ores, phosphate can be recovered as a co-product of uranium. Furthermore, as the radioactive, RE-minerals – monazite and xenotime – contain major amounts of P2O5 (25-35%, Sarbajna et al., 2007), phosphate can be obtained as a co-product during their mineral processing for REEs.

Recovery of CMs from RMs by Ore Dressing and Extractive Techniques

As majority of the CMs are in major contents in their respective, usually heavy and/or magnetic minerals in diverse radioactive materials (RMs), e.g., LREEs in monazite and HREEs in xenotime in mineral sands, recovery of CMs from RMs should start with the identification of specific minerals for their contained

CMs. This is to be followed by a general, sequential procedure involving (i) separation and concentration of such minerals from their RMs, using the mineral beneficiation techniques of gravity (e.g., hydro-cyclones and spirals), magnetic (e.g., low and high intensity magnetic separators) and electrostatic (e.g., high tension separator) separations, which are based on the physical parameters of minerals, such as density, magnetic susceptibility and conductivity; (ii) extracting next the CMs by techniques like hydro-/pyro-metallurgy and bio-/nano-technology and (iii) purification of different CMs in a smelter/refinery. In India, the Indian Rare Earths Ltd. (IREL) is processing placer monazite for value-added products like RE-chloride, RE-Th oxide cake and Th-concentrate, and the composite RE-chloride is further processed to obtain high purity oxides of La, Pr, Nd, Sm-Gd and Y, and Ce-carbonate. As the REs in monazite comprise basically LREEs, IREL is interested in sourcing HREEs and is willing to collaborate with foreign companies in this quest (Patra, 2014). In Australia, the mineral sand industry major, Iluka is planning to produce separated rare earth oxides at its rare earth refinery at the Eneabba mine site in Western Australia, with its Wimmera project serving as long-life rare earth concentrate feed source to the above refinery (Australian Mining, Jan. 12, 2022). Some important CMs like the battery metals, Co and Ni along with Cu and Mo are recoverable from sulphides in RMs. For example, the Rohil-Ghateswar multi-metal U-ore (~ 0.04% U_3O_8, 0.14% Cu and 0.024% Mo) in arid Rajasthan contains the above four CMs in the sulphides of pyrite, pyrrhotite, chalcopyrite, molybdenite and covellite. Sreenivas et al., (2018) have undertaken the process development studies to recover multi-metals from a composite feed of this sample, for which four options have been formulated, out of which the fourth option comprising 'Comminution – separation of ferromagnetic pyrrhotite by magnetic separation – hydrometallurgical recovery of U – gravity separation of leach residue for non-magnetic heavy sulphide minerals recovery – tailings disposal' is found to be the best due to maximum recovery of both U (80-83%) and by-products of Cu and Mo (~ 75% at the pre-concentration stage) with minimum water inventory due to easy recyclability of water, used in both the stages of magnetic and gravity separation. The sulphide mineral concentrate comprising Cu, Mo and Fe with traces of Ni and Co was subjected to 'roasting-leaching process' for quantitative separation of Cu, Mo, Ni and Co, while keeping the Fe-oxide phases as an insoluble fraction. Roasting converts the sulphides of Cu, Ni and Co to their respective sulphates and transforms the sulphides of Mo and Fe to their respective oxides by careful control of the roasting temperature. The sulphates of Cu, Ni and Co are soluble in mild acidic aqueous medium and MoO in alkaline medium, whereas FeO is insoluble. A forward integration approach helped in treating low-grade concentrates for maximum overall recovery of Cu and Mo Sreenivas et al., (2018). These examples illustrate the recoverability of CMs in RMs. It is desirable that more such studies are required for recovering CMs from RMs, followed by their purification by appropriate methods of chemical-/biochemical-/nano-technology, for which extensive R&D is to be carried out. By this swadeshi (indigenous) way under the Prime Minister's Make in India programme, the Country's requirement of critical/strategic minerals can be met to a notable extent, besides value-addition during the processing of RMs. Lastly, it is suggested that the AMD should actively work for the CMs recoverable from the RMs, as a part of their presently mandated exploration for radioactive (atomic) minerals.

CONCLUSIONS

Critical Minerals (CMs) are (i) mostly metals and a few non-metals, (ii) ranked as most critical for the world's major industrial economies, (iii) vital for the economic well-being of the Society (iv) extensively used in (a) futuristic developments and (b) diverse conventional, high-tech and cutting-edge technologies; but their supply may be at risk due to several factors. The list of CMs is dynamic and depends upon their availability and perspective of each country.

From the point of availability in and perspective of India, 34 CMs were identified. Of these, > 60% is recoverable from diverse radioactive materials (RMs), and their important industrial uses are presented. Many Indian examples of the CMs recoverable from diverse RMs are given and discussed. A brief account on the methods of recovery, extraction and purification of these CMs with a few examples is presented. The need for further work, including R & D, in this field is highlighted, which may be taken up under the Prime Minister's Make in India programme for swadeshi supply of these CMs to meet much of their demand within the Country, besides value-addition during the processing of RMs.

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