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Preliminary Resource Potential Assessment of Placer Light Rare Earth Elements (LREEs) from mid-Siwalik Sediments of a late Miocene Himalayan Foreland Basin, Pakistan

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Abstract: The present study has assessed the preliminary placer LREEs resource potential of mid-Siwalik Group Dhok Pathan Formation from Surghar-Shingar Range of NW Himalayan foreland Fold-and-Thrust-Belt and regarded them as indicative resources only. The analytical results of bulk samples of sandstone did not show any anomalous concentration of REEs. However, the ICP-MS results of heavy minerals laminations (black sands) revealed high concentrations (ppm) of LREEs (La: 975, Ce: 2831, Pr: 193, Nd: 746, Sm: 127, Gd: 98.70). We identified monazite-(Ce) [Ce, La, Nd]PO_4 as the primary LREEs-bearing mineral through Electron Probe Micro Analysis (EPMA). The representative quantitative micro-mineral analysis of monazite confirmed promising concentration of Rare Earth Oxides (REOs) maximum (in weight %) - La_2O_3: 16.20, Ce_2O_3: 37.82, Pr_2O_3: 4.77, Nd_2O_3: 21.72, Sm_2O_3: 5.23, Gd_2O_3: 4.88. Considering the thickness, lateral extension and depositional setting of host sediments along-with anomalously high concentrations of LREEs, it has been concluded that these Siwalik sediments host good indicative placer resource potential for low-cost recovery of LREEs.

Keywords: Rare earth elements, LREEs, Placer, Siwalik, Miocene, Himalaya, Pakistan.

Introduction

Rare Earth Elements (REEs) hold great importance due to their extensive utilization in manufacturing strategic/military defense devices, medical diagnostic equipment, hybrid vehicles, clean energy systems and as fluid catalysts. Because of the emergence of high technologies and demand of clean/green energy, the global requirement of REEs is predicted to continually increase in the coming decades (Heikal, 2014; Zhou et al., 2016; Zhou et al., 2017). China and Australia are the leading countries in REEs production with 85% and 10% shares respectively, of the total global REEs production in 2016. The remaining 5% of global REEs production comes from 178 deposits located around the globe (Liu, 2016).

The group of 15 elements in lanthanide group in periodic table along-with scandium and yttrium has been identified as REEs by the International Union of Pure and Applied Chemistry (IUPAC, 2005). The REEs are further sub-divided into light rare earth elements (LREE) and heavy rare earth elements (HREE) on the basis of their atomic radii and electron shell configuration (Cameron, 1973). Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu) and Gadolinium (Gd) are included in LREEs whereas Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu) are documented as HREEs based on United States Geological Survey (USGS) classification (Pagel, 1973; Rudnick and Gao, 2003).

At present more than 200 minerals are well known to host REEs but the major global production is derived from four minerals i.e. bastnasite, monazite, loparite and xenotime (Kanazawa and Kamitani, 2006; Goodenough et al., 2016). China is the principal country in the production of REEs from bastnasite which is followed by Australia and India extracting from monazite, Russia from loparite and Malaysia from xenotime. The major proportion of LREEs comes from these four minerals while HREEs are extracted from ion adsorption clays (Zhou et al., 2017). These REEs-bearing minerals are primarily related to alkaline igneous rocks and carbonatites; however, deeply weathered residual deposits of igneous rocks, marine phosphate, pegmatites, IOCG (iron oxide copper-gold) and placer mineral deposits (sedimentary) may contain economically viable concentrations of REEs.

Presently, there are no well-known REEs deposits located/discovered in Pakistan. The discovery of carnotite uranium mineralization (Azizullah and Khan, 1997) in Siwalik sandstones from the outermost Himalayan foreland Fold-and-Thrust-Belt known as Surghar-Shingar Range (SSR) or Trans-Indus Salt Range has attracted scientists to search placer REEs from Neogene molasses sediments to meet country's own demand. The available/acquired data-base is limited as compared to the economic significance of the rocks exposed in SSR. The published data mainly documented the eastern flank of SSR due to their well-known coal mining from centuries while the western flank of SSR hosting uranium mineralization has relatively remained unaddressed. There is no scientific data available on mid-Siwalik Dhok Pathan Formation of SSR regarding their potential to host placer REEs. This study is aimed at the preliminary placer REEs resource potential assessment of the Himalayan molasses sediments exposed on the western limb of

Surghar-Shingar Range. This will help in further exploration planning, demarcation of prospective areas and identification of undiscovered resources of middle Siwalik sandstones of Dhok Pathan Formation.

Geological Setting

As a consequence of tectonic loading due to the continent-continent collision of India-Eurasia, a flexural depression was developed in the south of emerging mountain ranges (Powell, 1979; Valdiya, 2016, Rehman et al., 2017) known as Himalayan foreland basin. This peripheral basin extends for more than 2000 km from Nepal in the east to Pakistan in the west (Ullah et al., 2009; Fig. 1d). This foreland basin received plenty of detritus produced due to India-Eurasia collision during the Neogene time and emerged as a unique identity called “Siwaliks” (Chuahan, 2003, Najman, 2006). In Pakistan, these Siwalik Group rocks are divided into three sub-groups; Lower, Middle and Upper (Shah, 2009). The Lower Siwaliks include Kamlial and Chinji formations and are comprised of mudstone dominated facies over sandstone. The Nagri and Dhok Pathan formations are mid-Siwalik formations of mainly arenaceous character with typical alternation of sandstone-mudstone facies. The Upper Siwalik Soan Formation is principally conglomeratic in nature. An arcuate mountain belt lying west of the Indus river as a western extension of the Salt Range dislocated by the active strike-slip Kalabagh fault (Fig. 1c) is named as Surghar-Shingar Range (SSR) or Trans-Indus Salt Range which is a part of NW Himalayan foreland basin (Fold-and-Thrust-Belt). The study area lies on the western flank of SSR (Fig. 1a).

The SSR is an overfolded-asymmetrical anticline exposing Mesozoic and Paleocene rocks in the core which are under-laid by Permian rocks (Akhtar, 1983). The SSR is representing the outer-most Himalayan ranges (Powell, 1979; Fig. 1b). The SSR show an EW configuration along the southern fringes of Kohat Plateau and attain NS structural trend while bordering the Bannu basin (Fig. 1c) to the west (Khan and Opdyke, 1987b; Rehman et al., 2017). The Siwaliks are well exposed on the western limb of the anticline (present study area) while older formations are exposed on the eastern limb. The Surghar thrust which is an equivalent of the Salt Range Thrust probably persistent along the axis of Surghar anticline that has brought Punjab foreland alluvium in contact with the Neogene rocks to the south and Permian and Mesozoic rocks in the north (Gee, 1989).

The steep cliffs and rugged topographic expression of SSR have been developed due to head-ward erosion of streams as the range experienced tectonic uplift phases. The eroded material has been laid down in the adjoining Indus and Bannu plains (Danilchik and Shah, 1987). In SSR the marine sedimentation has been brought to an end by the deposition of Siwalik Group rocks. The base of Lower Siwalik can be distinguished by the existence of thick, distinct conglomeratic bed which primarily consists of pebbles and boulders of Eocene formations. The Siwalik Group rocks exposed on the western limb of SSR are 5300 m thick, while the thickness of Dhok Pathan Formation varies from 807-1540 m showing the character of repeated sandstone-shale sequences in fining- upward rhythm (Ali et al., 2018). Khan and Opdyke (1987b) have assigned 7.5-2.5 Ma age to Dhok Pathan Formation of this area based on magneto-stratigraphic studies. The Siwalik Group rocks are also well developed in other parts of the country such as Kohat-Potwar Plateau, the Kirthar and Suleiman Fold-and-Thrust-Belts (Shah and Hafeez, 2009; Ullah et al., 2009).

Materials and Methods

The methods used for this study can be summarized as below:

i. 15 grab samples of sandstone were collected from positions marked as A, B, C on Figure 2 and analyzed for their LREEs concentrations by ICP-MS (Inductively Coupled Plasma Mass Spectrometer).
ii. The quantitative micro-mineral analysis of monazite from selective sandstone samples were carried out by JEOL-JXA-8100-EPMA (Electron Probe Micro Analysis) to evaluate their LREEs resource potential.

These analyses were carried out at Beijing Research Institute of Uranium Geology, Beijing and State Key Laboratory Breeding Base of Nuclear Resources and Environment, East China University of Technology, Nanchang.

Results and Discussion

Bulk Analysis of Sandstone

The values of various LREEs were measured on ICP-MS range from La: 16.3-45.6 ppm, Ce: 31.1-82.9 ppm, Pr: 3.72-9.57 ppm, Nd: 14.3-37.0 ppm, Sm: 2.66-6.83 ppm and Gd: 2.27-5.67 ppm. These values are comparable with the upper crustal concentrations (Rudnick and Gao, 2003). The bulk analysis of sandstone merely shows any anomalous value of LREEs. The results are tabulated in Table 1.

Analysis of Heavy Minerals Laminations

The analysis of heavy mineral concentrates from Dhok Pathan Formation show extremely high content of LREEs. Their LREEs concentration values are up-to La: 975 ppm, Ce: 2831 ppm, Pr: 193 ppm, Nd: 746 ppm, Sm: 127 ppm, Gd: 98.70 ppm (sample # 213-802, Table1).

Micro-mineral Analysis of Monazite

The values of different oxides of LREEs measured through quantitative micro-mineral analysis by EPMA of monazite crystals from selective sandstone or placer deposits thin sections of Dhok Pathan Formation range from La_2O_3: 5.47-16.20 %, Ce_2O_3: 26.64-37.82 %, Pr_2O_3: 2.6-4.77 %, Nd_2O_3: 10.65-21.72 %, Sm_2O_3: 0.92-5.23 %, Gd_2O_3: 3.05-4.88 % (Table 2).

Being lithophile elements, REEs generally occur as oxides, silicates or phosphates in diverse geological environments such as igneous, metamorphic and sedimentary deposits (placer) and never exist as native or in pure metal form. REEs enrich as accessories in minerals due to their ionic radii and cannot be put-up into the crystal structure of common rock-forming elements similar to aluminum, iron, chromium and sulphur etc. Primarily there is an assemblage of LREEs or HREEs in minerals with or without some complex mineral aggregates (USGS, 2015). The REEs enrichment in minerals can be clearly divided into two environments; primary deposits associated with igneous or hydrothermal processes and the secondary deposits developed through the sedimentary or other surface processes of nature such as weathering (British Geological Survey, 2011). In primary REEs deposits the enrichment process is associated with partial melting of crustal rocks or fluids from upper mantle due to their large ionic radius (Möller, 1986) and REEs minerals are often related to skarns, pegmatites, breccia zones and quartz-fluorite veins (Billingsley, 2010). The economic potential is dependent on geological processes and deposit mineralogy. Those deposits having a genetic and spatial association with alkaline igneous rocks can be further divided whether associated with carbonatites or peralkaline igneous rocks (Samson and Wood, 2004).

Placer deposits are the secondary deposits formed due to the accumulation of economic detrital mineral grains under the action of gravity or by the tractional current of flowing water of streams and rivers, deposited as heavy mineral accumulations within sedimentary sequences. Worldwide more than 360 placer REEs deposits have been identified (Orris and Grauch, 2002). Monazite is one of the most important REEs-bearing mineral found in placers along-with certain amounts of allanite, pyrochlore, loparite, xenotime, euxenite, knopite, fergusonite and samarskite (Möller, 1986).

The term occurrence is used for a concentrated mineral in a spatially confined area and it becomes mineral deposit, ore deposit or deposit if that mineral commodity is reasonably exploitable. The LREEs analytical results of bulk sandstones of Dhok Pathan Formation are relatively comparable with the average crustal abundance values (Rudnick and Gao, 2003). However, the sandstone facies of Dhok Pathan Formation frequently contains less than 1 cm to about 1 m thick layers (Fig. 3a, b) of heavy minerals concentrates/black sand whose analytical results gave promising/anomalously high concentrations of LREEs and reveal good potential for LREEs exploration.

Monazite-(Ce) [Ce,La,Nd]PO_4 as concentrated heavy minerals in fluvial sediments has been hosting LREEs deposits in many countries of the world such as Malaysia, India, USA and China (Orris and Grauch, 2002). Similarly, monazite-(Ce) has been identified as the main LREEs-bearing mineral in this study (Fig. 3c, d). The quantitative micro-mineral analysis has also confirmed the potential of monazite mineral for LREEs along with minor amounts of silver (0.024-0.101 %) (Fig. 3e, f).

In our previous study, we concluded that the sediments of Dhok Pathan Formation in this area had been deposited by the Indus river system (Ali et al., 2018b). The catchment areas of Indus river have diverse geological environments and evolutionary history. The placer gold-uraninite-scheelite has already been reported from many hundred miles (1100 miles) down-stream of river Indus (Davidson, 1962) and gold is being actively extracted through primitive methods. Considering the geological diversity of source area, thickness and lateral extension of Siwalik sequence exposed in Surghar-Shingar Range, the present study has confirmed promising concentrations of LREEs through analytical techniques over a strike length of less than 30 km and discloses good indicative LREEs resource potential of Dhok Pathan Formation. Conversely, these anomalously high concentrations of LREEs can be treated as “path finder”, which helps in determining the source of these commodities.

Once the area will have been explored systematically, the REEs-bearing minerals/ore can be up graded by physical beneficiation processes and by further treating them chemically or through metallurgical procedures to extract low-cost individual Rare Earth Element.

Conclusion

The bulk analysis of sandstones did not show any anomalous concentration of LREEs. However, ICP-MS analysis of heavy minerals laminations (black sand) divulged good concentrations of LREEs. Also, the EPMA micro-mineral analysis of LREEs-bearing mineral (monazite) depicted high concentrations. Keeping in view the thickness, lateral extension and depositional setting of Siwalik rocks, our preliminary conclusion is that these Himalayan Neogene molasse sediments hold good resource potential for placer LREEs occurrences/exploration.

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