Chapter – IV

Cerium

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Chapter - IV

Cerium

4.1 Introduction:

Cerium most abundant of all the REEs and forms several minerals including monazite \((\text{Ce},\text{La},\text{Nd},\text{Th})\text{PO}_4\) and Xenotime \((\text{Y},\text{Ce})\text{PO}_4\), and the rarer Bastnaesite \((\text{Ce},\text{La})\text{CO}_3(\text{F},\text{OH})\) and Cerite \((\text{Ce},\text{La})_9(\text{Mg,Fe})\text{Si}_7(\text{O,OH,F})_{28}\)

Cerium differs from other REEs in that it can also occur in the Ce \(^{4+}\) oxidation state, which has a smaller solid-state ionic radius (87 pm). Accessory minerals, such as allanite, apatite, zircon and sphene are important in the enrichment of Cerium in igneous rocks.

Cerium minerals, such as fluocerite \((\text{Ce},\text{La})\text{F}_3\), loparite \((\text{Na},\text{Ce},\text{Ca})\text{TiO}_3\) and monazite \(\text{Ce(PO}_4\)), are primarily associated with alkalic and granitic rocks and their pegmatites, and with hydrothermal mineralisation.

4.2 Cerium in stream water:

Cerium values in stream water range over four orders of magnitude, from <0.002 \(\mu\text{g l}^{-1}\) to 10.1 \(\mu\text{g l}^{-1}\) (excluding an outlier of 36.5 \(\mu\text{g l}^{-1}\)), with a median of 0.055 \(\mu\text{g l}^{-1}\). Cerium stream water data correlate most closely with the other lanthanides. In alkaline stream water, carbonate complexes are important.

4.3 Cerium in stream sediment:

The median Cerium content in stream sediment is 65.1 mg kg\(^{-1}\), with a range from 2.2 to 1080 mg kg\(^{-1}\).
Cerium in stream sediment has a very strong correlation (>0.8) with Y, with the
other REE except Lu and Eu, and with Th (0.90); a strong correlation (>0.6) with
Lu, Eu and U, and a good correlation (>0.4) with Nb, Ta, Ti, Zr, Hf and Rb.

These points to the association of the heavy minerals columbo-tantalite,
monazite, zircon and rutile, which are often enriched together in sediments.

4.4 Biogeochemistry of Cerium:

Cerium is the most abundant (about 30% of the total) of the 16 rare earth (RE)
elements which consist of Y and La-Lu (atomic numbers 39 and 57 to 71).
The large variation and abnormally low concentration of cerium with respect to
other members of the cerium group are the most striking features of the
assemblage in both plant and soil samples.

In cerium earth minerals such as monazite and allanite (VAINSHTEIN et al.,
1975) in igneous rocks (SAHAMA AND VAHATALO, 1941), and in shales
(MINAMI, 1935), cerium is the most abundant element of its group, commonly
equaling or exceeding the combination percentages of La & Nd.

Cerium readily undergoes a valence change from 3+ to 4+ with in the
range of pH prevalent in soils. The chemical properties of quadrivalent cerium
differ markedly from those of trivalent rare earth so that this oxidation reaction
provides a simple way of separating cerium from other.

That the precipitation of cerium hydroxide is rapidly oxidized by air to ceric
hydroxide is a well-known fact in chemical chemistry and forms the basis for
separating cerium on industrial scales (POWELL, 1939).
Quadrivalent cerium could become fixed in a soil by precipitation or coprecipitation as a highly insoluble compound or by being held tenaciously in ion exchanging materials of the soil. The cerium in the soils remains trivalent and maintains its normal abundance among the suite of available rare earth elements only in a reducing environment where the concentration of free oxygen is very low.

The roots of the plants penetrate deeply into the soil, and in regions of deep weathering they extend well into the underlying saprolite, the abnormally low cerium content in six of the seven leaf samples indicates that hickory trees feed mostly in horizons where available cerium is low, namely in the sub soils. Thus the nature of the root system and the proportions of rare earth elements assimilated by the hickory tree both attest to its habit of feed in deep in to the soil profile, especially during summer seasons when the surface soil is dry.

Cerium readily undergoes a valence change from $3^+$ to $4^+$ with in the range of pH prevalent in soils. The chemical properties of quadrivalent cerium differ markedly from those of trivalent rare earth so that this oxidation reaction provides a simple way of separating cerium from other.

In Siri River areas, the cerium is concentrated in plants and shows their absorption capacity. The plant Gangurla and Ambachani among the other plants indicated high concentration and shows their absorption capacity. The analytical results of both up and down Stream of Siri River are as follows.
4.5 Analytical data - Up Stream

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Plant name</th>
<th>Botanical name</th>
<th>Ce ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ganguria (4)</td>
<td>Cypercus cria</td>
<td>421</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>313</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>329</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>106</td>
</tr>
<tr>
<td>2.</td>
<td>Ambachani (4)</td>
<td>Polygonum Sp.</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>178</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>3.</td>
<td>Fern (4)</td>
<td>Glycanea Sp.</td>
<td>155</td>
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<tr>
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<td></td>
<td></td>
<td>43</td>
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<td></td>
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<td>193</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>4.</td>
<td>Chota jamun (2)</td>
<td>Eugenia hyeneaxa</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
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</tbody>
</table>

4.5.1 Comparison of plant to sand

<table>
<thead>
<tr>
<th>Plant</th>
<th>Plant assay</th>
<th>Sand assay</th>
<th>Ratio (plant/sand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gangurla</td>
<td>421 1253 329</td>
<td>106 80 109</td>
<td>-6.58 -15.7 -3.02 +0.71</td>
</tr>
<tr>
<td>Ambachani</td>
<td>70 46 178</td>
<td>3 66 118 87</td>
<td>-1.06 +0.38 -1.44 +0.03</td>
</tr>
</tbody>
</table>
4.5.2 Absorption of plant - Gangurla

Gangurla
Plant assay Sand assay
- 421 60
- 1253 80
- 329 109
- 106 150

4.5.3 Graph -1 Absorption Index

4.5.4 Absorption of plant - Ambachani

Ambachani
Plant assay Sand assay
- 70 66
- 46 118
- 178 123
- 5 87
4.5.5 Graph - 2 Absorption Index

Absorption index - Ambachani

4.6 Down stream - Cerium

4.6.1 Absorption of plants- Gangurla:

Gangurla

<table>
<thead>
<tr>
<th>Plant assay</th>
<th>Sand assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>69</td>
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<tr>
<td>252</td>
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</tr>
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<td>249</td>
<td>62</td>
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<td>312</td>
<td>58</td>
</tr>
</tbody>
</table>
4.6.2 Graph -3 Absorption Index

Absorption Index - Gangurla

4.6.3 Absorption of plants - Ambachani

<table>
<thead>
<tr>
<th>Ambachani</th>
<th>Plant assay</th>
<th>Sand assay</th>
</tr>
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<tbody>
<tr>
<td>1301</td>
<td>76</td>
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<tr>
<td>16</td>
<td>69</td>
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<td>191</td>
<td>103</td>
<td></td>
</tr>
</tbody>
</table>

4.6.4 Graph - 4 Absorption Index

Absorption index Ambachani
4.7 Observations:
The comparisons of plant with their bed soils/sand variation were carried out and the results are shown in the graphs (1-4) above.

1. The concentration of Cerium is higher than Yttrium. In four plant species *Cypercus cria* (Gangurla), *Polygonum sp.* (Ambachani), *Glycanea Sp.* (Fern) and *Cynodon dactylon* (Grass-I), both from up and down stream of Siri River.

2. In the plants, Gangurla - *Cypercus Cria* and Ambachani - *Polygonum Species*, the Adsorption Index of Cerium is very high, these plants are good accumulator of Cerium both in up and down stream of the Siri River.

3. High Cerium of 1253 ppm is analysed in *Cypercus Cria* (Gangurla). The plant has long green stem, fibrous root system, penetrate deeply in the stream sediment and adsorb and concentrate Cerium more as compared to the other plants.

4. The Ambachani - *Polygonum Species* also analysed high Cerium up to 178 ppm and helped to hold the stream sediment deposit along with the other plants.

5. The absorption index suggested that there Cerium concentration is remarkably very high in both Gangurla and Ambachani plants.