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Ree composition of dolostone and its implications on lead mineralization, Bandalamottu, Guntur District, Andhra Pradesh

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Abstract

Bandalamottu Pb-deposit located at the northeastern part of the Cuddapah Basin constitutes potential base metal deposit mainly composed of lead followed by zinc and copper. The host dolostone constitutes part of Cumbum Formation. REE abundances of 12 dolostones (6 mineralized and 6 barren) were analyzed by NAA. The results indicate that the REE content of dolomites were not governed by local sources, but rather from a much bigger reservoir like seawater. Normalizing patterns of dolostone with NASC values show the same general trend for all implying that the REE content is independent of mineralization. The study of REE in dolostones and related hydrotherms appear to be potential sources for both syngenetic and epigenetic Pb-Zn mineralization in suitable litho-structural sites in the equivalent middle Proterozoic sediments which is very well corroborated in Bandalamottu area.

Keywords: Bandalamottu Pb-deposit, mineralized dolostones, barren dolostones, REE abundances

1. Introduction

The Bandalamottu deposit (16°14:'79°43'), near Vinukonda, in the northeastern part of the Cuddapah Basin primarily contain lead mineralization and is potentially the largest in the Agnigundala poly-sulphide deposit. Neutron Activation Analysis has been carried out to estimate the REE content of the both mineralized and barren rock to know the variation in the REE contents and their patterns to comment upon composition of the source material, mode of deposition of rock and effects of weathering. The REE content of sediments reflect the mineral contents of deposits and hence the process by which the minerals formed and were incorporated into the deposits. The comparison of normalized pattern with NASC values will give a better picture about REE enrichment / depletion in the rocks concerned. This paper discusss the implications of REE abundances for 12 samples, both of mineralized and barren dolostone.

2. Geological Setting

The Bandalamottu lead deposit hosts the zones of mineralization mainly confined to the upper dolostone and dolomitic limestone, belonging to the Cumbum Formation of Nallamalai Group which crop out along the southern flank of the Bandalamottu hill, strikin ENE-WSW anddipping 200-350 WNW5 (Fig.1). A detailed account of the geology and mineralization of the area was described earlier (King, 1872; Ziauddin, 1964; Dutt, 1975; Ramana Rao and Reddy, 1976; Nagaraja Rao, *et al*. 1987; Kale, 1991) [5, 11, 2, 8, 6, 4]. Archaeans, represented by biotite-schists and amphibolites, are the oldest rocks in this area. Galena is the main mineral with subordinate In addition, granites and dolerite dykes are also found. Rocks of the Nallamalai Group unconformably overlie the biotite schists/ granitic basement. The Nallamalai Group is represented by Bairankonda and Cumbum Formation. Bairankonda Formation is basically an arenaceous unit and represented by grey sandstones with intercalated shale/slate. These sandstones are predominantly exposed on the hills and ridges surrounding the granite domal structures and except for a few places, they are directly overlie the granitic basement. The Cumbum Formation is an argillaceous unit comprising shale, slaty shale, slate and phyllites interbedded with fine to medium and coarse sandstones, and dolomite/ dolomitic limestones at various levels. In the Bandalamottu area, chloritic and carbonaceous phyllites constitute the main country rock, in which occur a main bed of mineralized dolomite and dolomitic limestone intercalated by calcareous argillite, phyllite and pink arenaceous dolomite. Mostly the mineralization is concordant to bedding, although, it occurs as lodes composed of veins, fracture-fillings and disseminations.

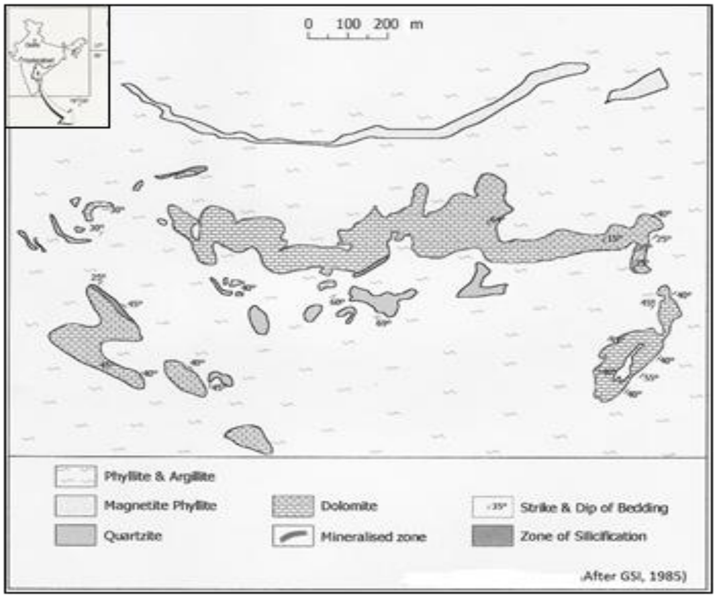


Fig 1: Geological map of Bandalamottu Area (GSI, 1985)

sphalarite, chalcopyrite and pyrite. Apart from Pb, Ag, Zn, Cu and Cd are obtained as co-productsfrom this area (Sivadas *et al*., 1985) [9].

3. Petrography

The dolostone is grey to cream colored on freshly broken surfaces and brown colored on weathered surface. Calcite and quartz occur in the form of veinlets, veins, stringers, lenses and as discontinuous discordant bodies. Chert commonly occurs as nodules, thin beds and irregular replacement bodies. Under the microscope the dolostone predominantly comprises equidimensional mosaic of dolospar, followed by minor quartz and calcite. Chert and argillaceous matter are major constituents in some rocks. The texture is granoblastic represented by medium to coarsely crystalline mosaic and many of the dolomite crystals are subhedral to euhedral, exhibiting the idiotopic fabric of Friedman, 1965. The mineralized dolostone has intermittent segregation of galena, with its associated sulphides in the form of disseminations, veins, stringers and breccia-fillings.

4. Results

REE abundances for 12 samples, both of mineralized and barren dolostone were obtained by Neutron Activation Analysis. The analysis for all the elements is by NAA, except Y, that was analyzed by ICP. The concentrations of the elements are given in ppm**.** All the samples analyze Nd <25ppm; Tm<0.5ppm, by NAA and Pr<10ppm; Gd<10ppm; Dy<5ppm; Ho<8ppm and Er <5ppm by ICP. The Analytical results are given in Table.1 & 2.

Table 1: Rare Earth Element Composition of Mineralized Dolostone

Element	AL/BM/1	AL/BM/3	AL/BM/5	AL/BM/8	AL/BM/9	AL/BM/13	MEAN
La	14.5	13.0	12.0	14.0	11.5	13.2	13.03
Ce	21.0	18.2	17.0	19.0	16.0	18.0	18.2
Sm	6.5	6.2	6.0	6.4	6.2	6.3	6.27
Eu	0.2	0.25	0.3	0.2	0.25	0.3	0.25
Tb	0.3	0.2	0.2	0.4	0.25	0.2	0.26
Yb	0.5	0.65	0.5	0.5	1.0	0.5	0.61
Lu	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Y	7.0	5.0	7.0	4.0	7.0	4.0	6.0
Eu/Sm	0.03	0.04	0.05	0.03	0.04	0.05	0.038
L REE	42.2	37.65	35.3	39.6	33.95	37.8	37.75
H REE	7.9	5.95	7.8	5.0	8.35	4.8	7.00
LREE/HREE	5.34	6.33	4.53	7.92	4.07	7.88	5.84
TOTAL REE	50.1	43.6	43.1	44.6	42.3	42.6	44.74

Table 2: Rare Earth Element Composition of Barren Dolostone

Element	AL/BM/4	AL/BM/6	AL/BM/10	AL/BM/11	AL/BM/12	AL/BM/15	MEAN
La	25	8.5	23	26	21.5	23.5	21.25
Ce	34	12	31	35	29.4	32.5	28.98
Sm	7.5	5.8	8.2	9.4	7.6	8.0	7.75
Eu	0.3	0.2	0.6	0.4	0.45	0.35	0.38
Tb	0.25	0.3	0.35	0.2	0.4	0.2	0.28
Yb	1.5	0.5	1.5	1.6	1.5	1.7	1.38
Lu	0.15	0.1	0.2	0.12	0.15	0.15	0.15
Yb	18	5	12	8	10	23.0	10.6
Eu/Sm	0.04	0.03	0.07	0.04	0.06	0.04	0.048
L REE	66.8	26.5	62.8	70.8	58.95	64.35	58.37
H REE	19.9	5.9	14.05	9.92	12.05	25.05	12.36
LREE/HREE	3.36	4.49	4.47	7.14	4.8	2.570	4.85
TOTAL REE	86.7	32.4	76.85	80.72	71	89.40	69.53

REE are considerably higher in the analyzed samples, in mineralized dolostone, the total REE content ranges from 42.30 to 50.10 with an average of 44.74. The LREE content ranges from 33.95 to 42.2 with an average of 37.75. The HREE content ranges from 4.8 to 7.9 with an average of 7.00. In barren dolostone the total REE content ranges from 32.40 to 89.40 with an average of 69.53. The LREE content ranges from 26.50 to 70.80 with an average of 58.37. The HREE content ranges from 5.9 to 25.05 with an average of 12.36. To arrive at a meaningful relationship correlation coefficient amongst different oxides, Pb, Zn, LREE and HREE were calculated which is given in Table. 3.

Table 3: Correlation of Oxides, Pb, Zn LREE & HREE of Mineralized Dolostone

	SiO_2	TiO_2	Al_2O_3	FeO	MgO	MnO	CaO	Na_2O	K_2O	Zn	Pb	LREE	HREE
SiO_2	1.00												
TiO_2	0.92	1.00											
Al_2O_3	1.00	0.92	1.00										
FeO	-0.17	0.09	-0.17	1.00									
MgO	-0.92	-0.77	-0.92	0.26	1.00								
MnO	-0.38	-0.15	-0.38	-0.16	0.49	1.00							
CaO	-0.94	-0.80	-0.94	0.32	0.99	0.44	1.00						
Na_2O	0.60	0.85	0.61	0.54	-0.47	0.00	-0.46	1.00					
K_2O	0.80	0.97	0.80	0.24	-0.64	0.00	-0.66	0.94	1.00				
Zn	0.39	0.63	0.40	0.31	-0.44	0.23	-0.41	0.83	0.75	1.00			
Pb	0.10	0.26	0.10	0.41	-0.32	-0.08	-0.25	0.53	0.36	0.82	1.00		
LREE	-0.22	-0.24	-0.23	0.65	0.15	-0.46	0.26	0.08	-0.19	-0.07	0.17	1.00	-0.30
HREE	0.28	0.26	0.28	-0.49	-0.17	0.56	-0.21	0.12	0.26	0.17	-0.29	-0.30	1.00

Normalizing factors of the mineralized and barren zone dolostone with North American Shale Composite (NASC) values of Haskin (1985) are shown in Table 4, 5 & 6 and respective normalized patterns in Figures 2 to 6.

Table 4: NASC-Normalized Values of Mineralized Dolostone

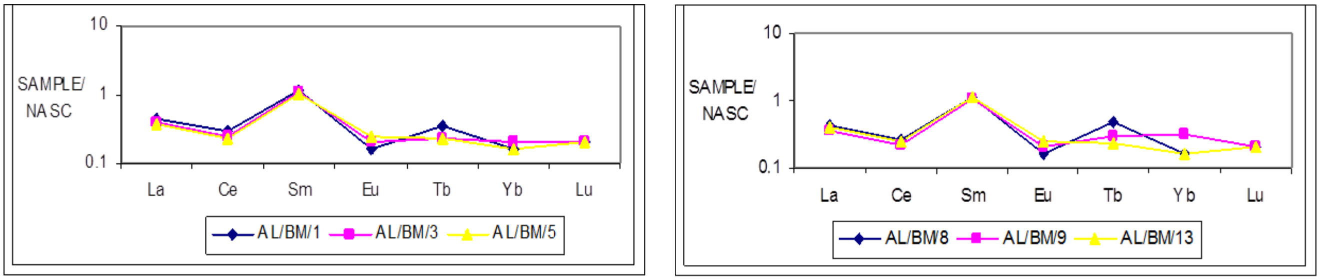
Element	NASC	AL/BM/1	AL/BM/3	AL/BM/5	AL/BM/8	AL/BM/9	AL/BM/13	MEAN
La	32	0.453125	0.40625	0.375	0.4375	0.359375	0.4125	0.407188
Ce	73	0.287671	0.24931507	0.2328767	0.260274	0.219178	0.246575	0.249315
Sm	5.7	1.140351	1.0877193	1.0526316	1.122807	1.087719	1.105263	1.1
Eu	1.24	0.16129	0.2016129	0.2419355	0.16129	0.201613	0.241935	0.201613
Tb	0.85	0.352941	0.23529412	0.2352941	0.470588	0.294118	0.235294	0.305882
Yb	3.1	0.16129	0.20967742	0.1612903	0.16129	0.322581	0.16129	0.196774
Lu	0.48	0.208333	0.20833333	0.2083333	0.208333	0.208333	0.208333	0.208333

Table 5: NASC-Normalized Values of Barren Dolostone

Element	NASC	AL/BM/4	AL/BM/6	AL/BM/10	AL/BM/11	AL/BM/12	AL/BM/15	MEAN
La	32	0.78125	0.265625	0.71875	0.8125	0.671875	0.734375	0.664063
Ce	73	0.465753	0.16438356	0.4246575	0.479452	0.40274	0.445205	0.396986
Sm	5.7	1.315789	1.01754386	1.4385965	1.649123	1.333333	1.403509	1.359649
Eu	1.24	0.241935	0.16129032	0.483871	0.322581	0.362903	0.282258	0.306452
Tb	0.85	0.294118	0.35294118	0.4117647	0.235294	0.470588	0.235294	0.329412
Yb	3.1	0.483871	0.16129032	0.483871	0.516129	0.483871	0.548387	0.445161
Lu	0.48	0.3125	0.20833333	0.4166667	0.25	0.3125	0.3125	0.3125

Table 6: Comparison of Normalized Values of Mineralised & Barren Dolostone with NASC Values

Element	NASC (Haskin, 1968)	Mineralized Dolostone	Barren Dolostone
La	32	0.407188	0.664063
Ce	73	0.249315	0.396986
Sm	5.7	1.1	1.359649
Eu	1.24	0.201613	0.306452
Tb	0.85	0.305882	0.329412
Yb	3.1	0.196774	0.445161
Lu	0.48	0.208333	0.3125



A

B

Fig 2: Normalized Ree Composition of the Mineralized Dolostone

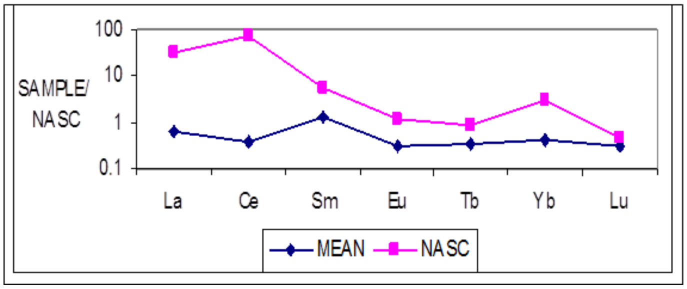


Fig 3: Mean Normalized Ree Plot of the Mineralized Dolostone

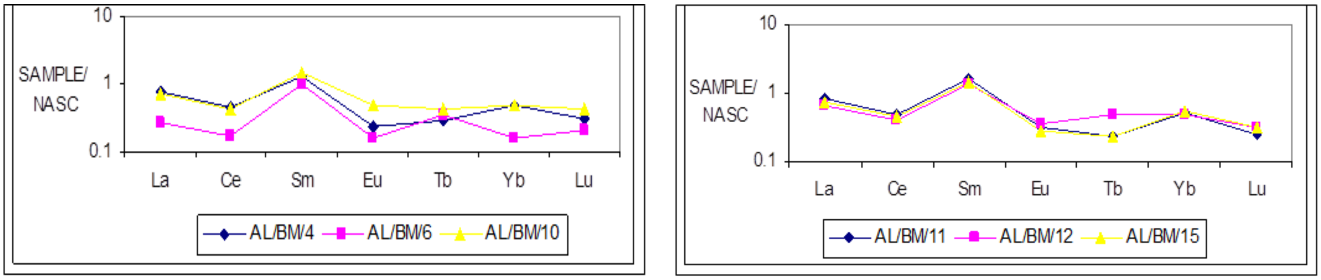


Fig 4: Normalized Ree Composition of Barren Dolostone

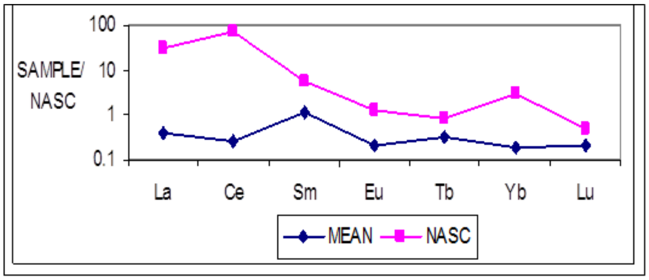


Fig 5: Mean Normalized Ree Plot of Barren Dolostone

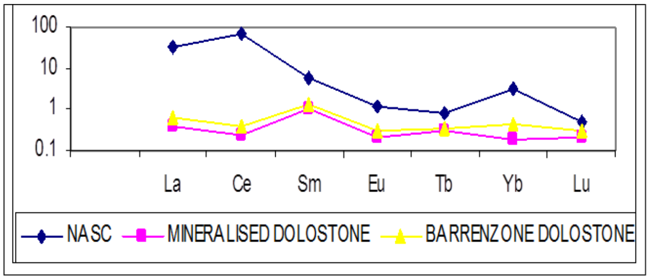


Fig 6: Mean Normalized Ree Plot of Mineralized/ Barren Dolostone Compared To NASC Value

5. Discussion

The LREE contents of the sediments have to be attributed to presence of small amounts of monazite whereas the content of HREE is attributed to the presence of small amounts of zircon and xenotime. A few galena rich samples are slightly enriched in ree. The same samples contain less SiO_2 than other samples. This is because the presence of silica in the form of quartz or chert will dilute the samples in respect of ree, thus, the high content of silica in the dolostone implies less REE. Most natural fluids have very low REE abundance (Zenner *et al*., 1988). Consequently a very high fluid to rock ratio is required to alter the REE in carbonate rocks (Banner and Hanson, 1990; Qing and Mounjoy, 1994) [1, 7]. Also, the dominant portion of the REE in the diagenetic fluids would have been derived from the carbonate rocks themselves. Therefore, diagenesis is unlikely to change REE pattern

A negative correlation between LREE and HREE (r=-0.3) coupled with their relative concentrations suggest that each is independent of their distribution. HREE show positive correlation with SiO_2, TiO_2, Al_2O_3, MnO, Na_2O and K_2O implying its close association with silicate minerals, whereas the LREE show negative correlation with these silicates and are positively correlated with FeO MgO CaO and to some extent with Na_2O (+0.08) implying its primary sedimentary nature and their association with chemically precipitated carbonates. This indicates that the REE contents in the depositional environment of dolomites were not governed by local sources, but rather from a much bigger reservoir. Here it can be suggested that most of the ree are derived from seawater, whereas local sources played a minor role only.

The REE patterns displayed by all the samples show several interesting features, which can be summarized as follow. All the figures show the same general trend implying that the REE content is independent of mineralization and that the mineralization has not influenced the REE content. In all the dolostones, the patterns display significant enrichment of heavy REE (HREE) compared to light REE (LREE). Proterozoic Formations should display negative or no Eu-anomaly, indicating increasing O_2 content in the atmosphere during this period.

The entire set of samples show negative Eu-anomaly in confirmity with the above and most probably it is due to the presence of some feldspar. Negative Ce anomaly has been found in some samples suggesting that weathering process has been effective in mobilizing REEs in this area. Negative Eu- and Ce-anomalies are typical of sea water source of REE. Such dolostones and related hydrotherms appear to be potential sources for both syngenetic and epigenetic Pb-Zn mineralization in suitable litho-structural sites in the equivalent middle Proterozoic sediments.

Preliminary REE data on the Cuddapah carbonate rocks show that they lack a Ce-anomaly but show a negative Eu-anomaly, both indicative of a crustal source for the REE in them. The patterns are broadly similar to those of upper continental crustal rocks. These features together with the evidence for their shallow marine deposition, argue that the REE pattern of the Cuddapah carbonates reflects that of the provenance, without significant REE fractionation between the two (J.K. Zachariah *et al*., 1999) [10]. In the Bandalamottu area the REEs do not appear to have been significantly disturbed by the mineralization. If the REEs were introduced to the rocks by mineralizing solutions, there should be a noticeable variation between the barren and mineralized dolostone, but this was not observed, suggesting that the mineralizing solutions did not transport significant amounts of REE to carbonate rocks.

6. Conclusions

The REE patterns exhibit significant enrichment of HREE compared to LREE.

No significant difference between LREE and HREE content of mineralized and barren dolostone, implies that mineralizing solutions did not transport significant amounts of REE to carbonate rocks.

A negative correlation between LREE and HREE (r=-0.3) coupled with their relative concentrations suggest that each is independent of their distribution and that the REE contents in the depositional environment of dolomites were governed by a much bigger reservoir like seawater.

HREE show positive correlation with SiO2, TiO2, Al2O3, MnO, Na2O and K2O implying its close association with silicate minerals.

LREE show negative correlation with these silicates and are positively correlated with FeO, MgO and CaO implying its association with chemically precipitated carbonates

The study of REE in dolostones and related hydrotherms appear to be potential sources for both syngenetic and epigenetic Pb-Zn mineralization in suitable litho-structural sites in the equivalent middle Proterozoic sediments which is very well corroborated in Bandalamottu.

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