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JOURNAL OF RADIATION, ENVIRONMENT & CLIMATE

Geochemical characterization for REE and Gold mineralization in rhyolites and basic rocks of Dongargarh Kotri belt, Chhattisgarh, India: An Instrumental Neutron Activation Analysis Study

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Abstract—Non-destructive Instrumental Neutron Activation Analysis (INAA) was applied for quantitative multi-elemental analysis to estimate rare earth elements (REE) and other trace elements in surface grab samples of rhyolites (n = 7) and basic rocks (n = 5) from the Bhandaritola-Netamtola area, Rajnandgaon district, Chhattisgarh, India. The study area forms part of a major Paleoproterozoic volcano-plutonic complex represented by a suite of basic to acidic rocks in the Dongargarh-Kotri belt. The technique was utilized for the determination of REE (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu), actinides (U, Th), trace elements (Sc, Cr, Co, Rb, Cs, Ba, Hf, Ta, Sb, Au, Ag), and major elements (Na_2O, K_2O, CaO, Fe_2O_3(T)). Samples were prepared with Certified Reference Materials (CRMs) in aluminium foil and simultaneously irradiated in a thermal neutron flux of 10^{13} n cm^{-2} s^{-1} at the DHRUVA research reactor, BARC, Mumbai, India. Irradiated samples were measured using a gamma-ray spectrometer equipped with a high-purity germanium (HPGe) detector. Chondrite-normalized rare earth element patterns for rhyolites indicated negative europium anomalies (Eu/Eu*) ranging from 0.24 to 0.75, with total REE content (ΣREE) of 256–703 ppm. Basic rocks exhibited ΣREE of 40–158 ppm and Eu/Eu* values of 0.20–0.69. Notably, rhyolites along sheared contacts in the Bhandaritola and Netamtola areas exhibited high gold concentrations (up to 3,139 ppb; average 688 ppb), identifying these formations as promising targets for gold mineralization.

Keywords: *Instrumental Neutron Activation analysis; Rare Earth Element; Chondrite normalization; Dongargarh-Kotri Belt; Gold Mineralization.*

Received 3 July 2026; **Revised** 01 Aug 2026; **Accepted** 12 Aug 2026; **Available online** 15 Aug 2026

1. Introduction

Rare earth elements (REEs) are critical to many modern technologies and, due to their economic importance, have been extensively studied using a variety of techniques over the last several decades [1], [2], [3], [4], [5]. The Dongargarh-Kotri belt has been identified as one of the multi-metal provinces in Central India [6]. Within this belt, the Bhandaritola–Netamtola areas in Rajnandgaon district are located along the sheared, reactivated basement contacts of acidic and basic rocks within the Nandgaon Group of the Dongargarh-Kotri rift zone. These areas exhibit hydrothermal sulphide mineralization and have recently revealed occurrences of gold and other noble metals that were not previously known in this region [7], [8].

Given the precious nature of gold, precise and sensitive analytical procedures are essential for its detection and quantification. Instrumental Neutron Activation Analysis (INAA) has proven to be a highly effective technique for this purpose [9], [10]. Compared to conventional fire assay methods, INAA is cost-effective and offers very low detection limits (approximately 10 ppb) with exceptional sensitivity for Au, platinum group elements (PGE) and REE. The ability to detect gold at such low concentrations is particularly valuable for characterizing geological domains, especially when studied in conjunction with REE distributions. Furthermore, INAA enables the simultaneous determination of multiple elements, providing highly precise and accurate results for a large number of elements across the periodic table, while offering relative freedom from analytical blanks [3], [11]. The advent of high-resolution gamma-ray spectrometry using high-purity germanium (HPGe) detectors has further enhanced the potential of the INAA technique.

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Random representative sampling over ultra-basic rocks (n=5) and quartz porphyry in rhyolites (n=7) along the sheared contacts in the Bhandaritola and Netamtola areas has indicated high concentrations of gold (Au up to 3139 ppb), chromium (Cr up to 1347 ppm), scandium (Sc up to 28 ppm), and hafnium (Hf up to 11 ppm). This research paper presents the application of the INAA technique for the geochemical analysis of these rock samples and discusses the implications of the observed elemental concentrations.

2. Geological setting

Study area (Fig.1) forms part of a major Paleoproterozoic volcano-plutonic complex represented suit of basic to acidic rocks. The main rock types exposed in study area, rhyolite & quartz porphyry of Bijli, amphibolites of Pitepani, Dongargarh granites, gabbros and ultramafic rocks. Small discontinuous hillocks west of these ridges are made up of basic rocks, extending Gaulitola-Arajkund to Netamtola. Further, west hills of rhyolite are seen from Nichekohra in the north to Netamtola in the south. The granites are exposed over a large area in the western flank of surveyed area from Kundertola in the north to Pateli in the south. Granites are coarse grained, porphyritic essentially composed of quartz, potash feldspar, biotite and Fe-oxides. Quartz porphyry and rhyolite are bounded by porphyritic granites on the western side and amphibolites/ gabbroic rocks on the eastern side.

Several, N-S to NNE-SSW trending faults were noticed in the area. One fault is traced near Bhandaritola in the western part of the study area. Quartzite and schists are exposed as inlier between granite and quartz porphyry and extended from south of Tumrikasa to west of Netamtola. They are oldest litho units in the area of investigation. Quartzites are sheared and in filtered by ferruginous stains. Sulphide minerals are seen along the cavities and fractures within the quartzite. Quartz porphyry and rhyolite are bounded by porphyritic granites on the western side and amphibolites / gabbroic rocks on the eastern side. Uranium mineralization is mainly associated with sheared smoky quartz porphyry. Conspicuous occurrence of uranium bearing quartz porphyry was seen all along the Banduka Nala from east of Bhandaritola to south of Tumrikasa.

3. Experimental Procedure

3.1 Methodology of Sample collection

Five (05) representative samples for each geological unit were collected over the exposed rhyolites and ultrabasic rocks. For the rhyolite, two (02) more samples are sampled from Netamtola area, as they are different and showed crypto crystalline nature of the rock with smoky quartz. All the samples showed the presence of sulphide minerals mainly by pyrite which represent the reducing environment of deposition. The samples are drawn from un-weathered and fresh outcrops. The objective of the sampling is intended to check the geological evaluation and economic potentiality.

3.2 Instrumentation

The gamma-ray spectrometer consists of a HPGe detector which is a p - type (PGC 3018) coaxial semiconductor detector (manufactured by DSG detector systems GmbH) with having specifications such as resolution of 1.74 keV at 1332 keV of ^{60}Co source; 57.6 mm diameter, 57.6 mm length and volume 140 cc; relative efficiency of 30%; operating voltage 3000 V. Semiconductor Detector is coupled to the target dMCA-pro-digital Multi-Channel-Analyzer which directly digitizes signals from the semiconductor detector. WinTMCA32 software was used for the analyses of the samples by gamma ray spectrometry.

3.3 Sample Preparation and Irradiations

The collected samples were grinded into powder to -200 mesh (-75 microns) and dried using oven to achieve proper homogeneity. About 10-12 mg of dried powdered samples were wrapped in a aluminum foil. These samples along with elemental synthetic standards and certified reference materials (CRMs) such as G2(USGS), GA (CRPG, France), ORPT-1(UK) and G998-3(Australia) were wrapped in aluminum foil forming a cylindrical shape of 1.6 cm diameter and 3.7 cm length which forms target material [12]. The target material comprising Standards, CRMs and samples of study area were irradiated for three days with thermal neutrons in a thermal flux of 1013 n cm^{-2} s^{-1} in DHRUVA research reactor, at BARC, Mumbai. The irradiated samples and standards are received at Radiation Standards and Analysis Laboratory, Hyderabad after 2 to 3 days from the end of irradiation.

3.4 Analysis and Gamma ray Counting

The elemental analysis was done using INAA by relative standard method. In the relative method, a standard containing a known amount of the element to be determined is irradiated along with the unknown samples. It is assumed that the neutron flux, cross section, irradiation times, and all other variables associated with the count are identical for both the standard and the sample. The concentration/mass of the element of interest were calculated using Eq. (1).

$$W_{std}(e^{-\lambda t})_{std}/W_{sam}(e^{-\lambda t})_{sam} = R_{std}/R_{sam} \qquad (1)$$

where, R is the counting rates of standard (std) and sample (sam), W is the mass of the element, λ is the decay constant, and t is the decay time.

The induced activities were measured after allowing cooling time of 2 to 3 days from the end of irradiation. The determination of all possible REEs namely La, Ce, Nd, Sm, Eu,

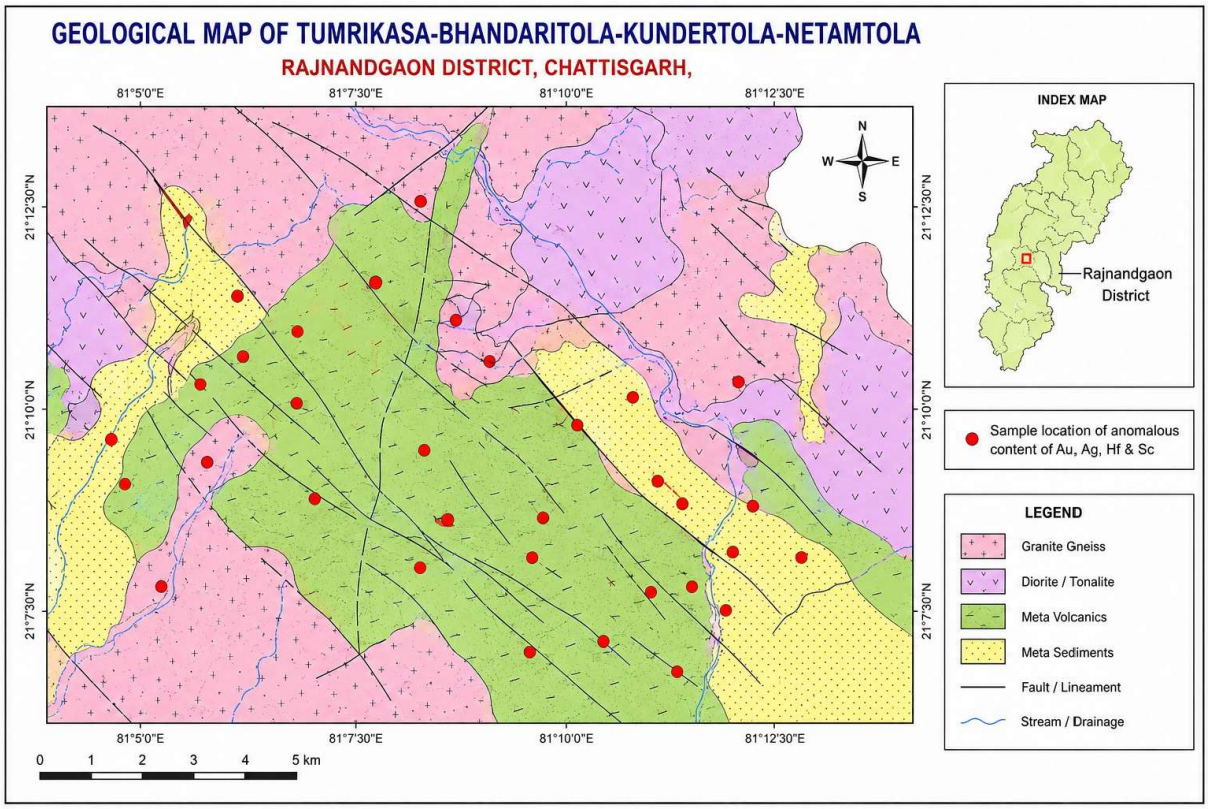

Figure 1: Geological Map of Studied Area.

Tb, Yb, Lu, trace elements Sc, Cr, Co, Rb, Cs, Ba, Hf, Ta, Sb, Au and Ag and major elements Na_2O, K_2O,CaO and Fe_2O_3(T) were made under varying conditions of cooling and counting intervals as different factors, viz. possible interferences, details of radioisotopes and their gamma emission energies, accuracy and sensitivity were described [13], [14], [15].

4. Results and Discussions

The measurements of the gamma emission are carried out in different phases, based on the half-life of the elements of interest. Radio nuclides and their energies used for the estimation of the Rare Earths & Au and photo peaks selected for INAA are shown in Table 1 [4], [11]. Certified Reference Material standards are also analyzed to check the accuracy of the overall analytical procedure and data obtained is shown in Table 2.

Rare Earth pattern from quartz porphyry in rhyolites and basic samples of Bhandaritola - Netamtola areas, Rajnandgaon district, Chhattisgarh were studied. Concentrations of the rare earth elements of quartz porphyry in rhyolites (n=7) and basic rocks (n=5) are shown in table 3 to 4. Rare Earth element concentrations obtained by INAA technique for quartz porphyry in rhyolites and basic rocks are normalized to the

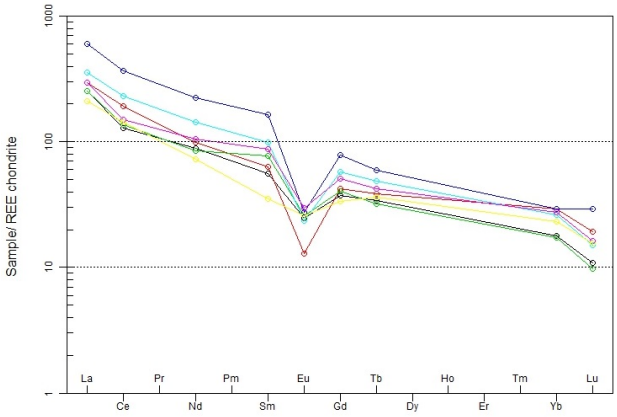

Figure 2: Chondrite-normalize REE pattern in rhyolites.

Chondrite reference value of REE Chondrite [16], [17], [18], [19],[20] and plotted (Fig.2 & 3). The rhyolites are generally characterized by strongly fractionated LREE pattern and nearly flat HREE profiles. The chondrite normalization rare earth pattern obtained on these rock sample indicate Eu/Eu* ranging from 0.24 to 0.75 and a higher range of REE content (Σ REE = 256 - 703 ppm) and for basic rocks Eu/Eu* ranging from 0.2 to 0.69 and REE content (Σ REE = 40 - 158 ppm). The

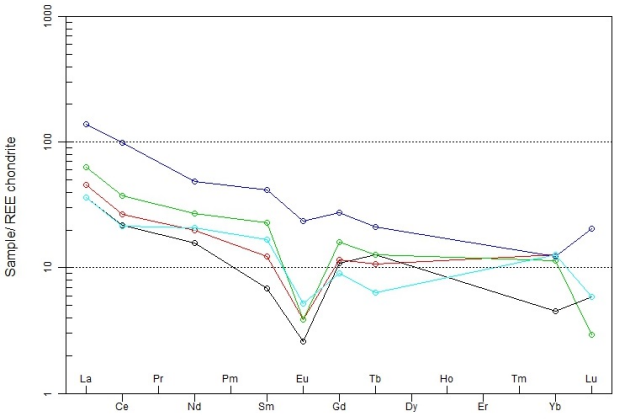

Figure 3: Chondrite-normalize REE pattern in basic rocks.

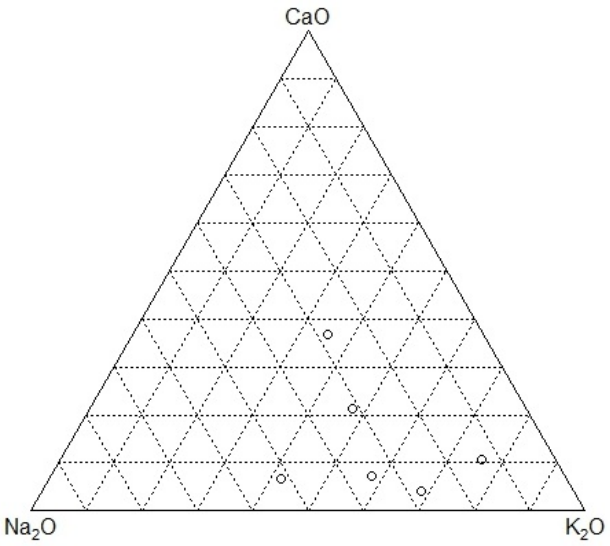

Figure 4: Na_2O - K_2O- CaO ternary diagram of rhyolites.

ratio (CeN/YbN) for rhyolites ranges from 5.6-12.8 indicates that rhyolites hav e LREE enriched crustal origin and have undergone high degree of differentiation involving plagioclase fractionation. In comparison with recent estimates of the abundances of the elements in the earth's crust, [21] ref Table.3, the LREE are enriched by two to four times with respect to average values for rhyolites [16], [22].

The REE slope pattern indicates decreasing values for HREE which is typical for acidic rocks. The negative anomaly of "Eu" indicates oxidizing environment of formation. The reducing environment in geological domains helps in U and REE mineralization in presence of sulphides. Au also concentrates alongside sulphides in the residual silica rich fluids [23]. The Na_2O - K_2O - CaO ternary diagram pertaining to rhyolites (Fig.4) indicates potash rich rocks which are also

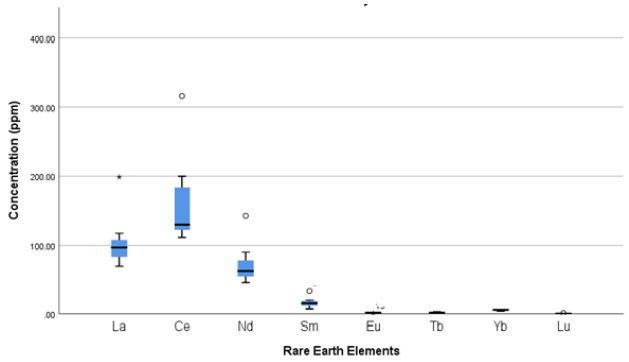

Figure 5: Box Whisker plot of REE concentration in Rhyolites.

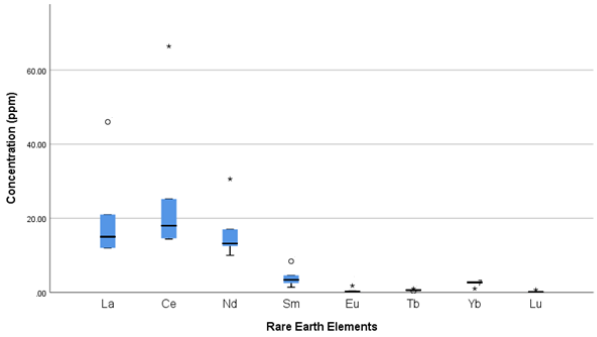

Figure 6: Box Whisker plot of REE concentration in Basic rocks.

differentiated and acidic in nature. Rhyolites are felsic rocks enriched in SiO_2 (>70%) & K_2O (>4.0%) except for sample NR-2 where K_2O is 2.5%. The REE concentrations observed in the rhyolites and basic rocks have been graphically represented by a Box-Whisker plots in Fig 5 & Fig 6. The percent Error due to counting statistics at 2 sigma level for La, Ce, Eu, Yb, Th, U, Sc, Sb, Co, Hf, Ta, Au, Na_2O, CaO, Fe_2O_3(T) and K_2O are within ± 5% for all the samples and Nd, Sm, Tb, Lu, Rb, Cs, Cr, Ba and Ag are within ± 10% for all the samples.

These surface grab samples (n=12) of rhyolites and basic rocks along the sheared contacts from Bhandaritola, Netamtola areas assayed (Au up to 3,139ppb), Cr (up to 1,347ppm) and Sc (up to 28ppm) and moderate to anomalous concentrations of silver (Ag up to 4.6ppm) and Hf (up to 11 ppm).

Geologically the most significant observation is with respect to the gold which is in high concentration especially in the two samples collected from Netamtola (NR-3 & NR-4) assayed 784 and 3139 ppb respectively with an average of 688.68 ppb for rhyolite samples (n=07). Therefore, the average gold content is on par with the mineable gold at different gold mines Eg: Gold is mined at Mt Rawdon mine at an average grade of just 0.60g/t [24], [25]. Therefore, the NAA technique is significant in analyzing such low levels of gold with high accuracy and precision.

Table 1: Radioisotopes used, their half-lives, energies and time of decay before counting.

Element	Radioisotope	Half-life	Energy (keV)	Decay after irradiation (d)
Ba	^{131}Ba	11.5 d	496.3	15–20
Ce	^{141}Ce	32.5 d	145.4	15–20
Co	^{60}Co	5.24 y	1332.2	15–20
Cr	^{51}Cr	27.8 d	320.0	15–20
Cs	^{134}Cs	2.7 y	795.8	15–20
Eu	^{152}Eu	13.5 y	1407.5	15–20
Fe	^{59}Fe	45.1 d	1098.6	15–20
Hf	^{181}Hf	44.6 d	482.2	15–20
La	^{140}La	47.27 h	328.6, 1595.4	5
Lu	^{177}Lu	6.75 d	208.4	5
Nd	^{147}Nd	11.1 d	91.4, 531.0	5, 15–20
Rb	^{86}Rb	18.66 d	1076.6	15–20
Sb	^{122}Sb	2.70 d	564.2	5
	^{124}Sb	60.2 d	1691.0	15–20
Sc	^{46}Sc	83.9 d	889.4	15–20
Sm	^{153}Sm	47.1 h	103.2	5
Ta	^{182}Ta	115.1 d	1188.8, 1221.6	15–20
Tb	^{160}Tb	73 d	879.4	15–20
Th	^{233}Pa	27 d	311.8	15–20
U	^{239}Np	2.35 d	277.5	5
Yb	^{175}Yb	101 h	396.1	5
	^{169}Yb	30.6 d	197.8	15–20
Au	^{198}Au	2.7 d	411.80	5

h = hour; *d* = days; *y* = years.

Table 2: Accuracy and precision for REE analyses by INAA.

Standard	Value	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Au
		ppm								ppb
G2	Estimated	94	146	56	7.3	1.5	0.52	0.83	0.10	–
	Certified	96	150	55	7.2	1.5	0.54	0.80	0.11	–
GA	Estimated	38.3	69	23.2	4.14	1.013	0.64	2.00	0.34	–
	Certified	40	76	27	5.00	1.08	0.60	2.00	0.30	–
ORPT-1	Estimated	31.2	56	35.3	8.4	1.48	1.08	8.33	1.17	–
	Certified	27	62.1	34.8	8.95	1.32	1.8	7.85	1.21	–
G998-3	Estimated					–				784
	Certified					–				785

ppm = 1 mg/kg; ppb = 1 g/kg.

Table 3: Concentrations of REE, U, Th, Au and trace elements for rhyolites.

Element	**Unit**	**BR-1**	**BR-2**	**BR-3**	**NR-1**	**NR-2**	**NR-3**	**NR-4**	**Mean**	**Std. Dev.**	**Abundance** *
La	ppm	83.4	98.3	83.3	199	118	97.2	69.7	106.98	43.3	18
Ce	ppm	112	167	119	316	200	129	124	166.71	72.9	46
Nd	ppm	55.9	62.7	53.7	142	90.4	65.9	45.8	73.77	33.2	24
Sm	ppm	11.4	12.8	15.6	33.4	20	17.7	7.14	16.86	8.4	6.5
Eu	ppm	1.7	0.89	1.8	1.9	1.6	2.1	1.8	1.68	0.38	1.1
Tb	ppm	1.6	1.8	1.5	2.8	2.3	2	1.7	1.95	0.45	0.9
Yb	ppm	3.9	6.4	3.8	6.4	5.8	6	5.1	5.34	1.1	2.7
Lu	ppm	0.37	0.66	0.33	1	0.51	0.55	0.53	0.56	0.22	0.8
U	ppm	7.1	8.1	5.5	17.7	7.1	6.3	4.7	8.0	4.3	4.0
Th	ppm	34	49	33	27.4	36	20	22	31.6	9.7	12
Sc	ppm	2.9	8.3	2.1	1.7	3.3	3.8	4.9	3.85	2.2	5
Cr	ppm	31	17	2.6	72	21	50	31	32.0	22.8	200
Co	ppm	2.7	5.3	2.3	2.4	2.1	5.9	3.3	3.4	1.5	23
Rb	ppm	253	205	237	210	161	149	138	193.2	44.6	310
Cs	ppm	1.8	2.2	1.5	5.9	0.5	2.3	1.6	2.2	1.7	7.0
Ba	ppm	776	261	614	104	546	885	756	563.1	286.0	250
Hf	ppm	9.5	6.7	8.7	10.5	8	11	11	9.3	1.6	45
Ta	ppm	2.1	2.6	1.7	2	2.2	1.6	1.6	1.97	0.36	2.1
Sb	ppm	0.41	0.86	0.31	0.7	0.25	0.42	0.35	0.47	0.22	1.0
Ag	ppm	0.55	0.75	< 0.50	0.5	0.55	0.81	1.2	0.69	0.25	0.1
Au	ppb	316	375	95	23.8	88	784	3139	688.7	1110	0.005
Na_2O	%	2.6	1	2.4	3.5	3.1	3.5	3.9	2.85	0.97	2.83
CaO	%	0.4	0.8	< 1.0	1.2	0.4	2.4	5.1	1.6	1.6	3.63
Fe_2O_3 (T)	%	1.5	6.9	1.4	1.7	1.9	3.3	2.5	2.7	1.9	5.0
K_2O	%	6.5	5.7	4	ND	2.5	5.3	4.9	4.8	1.4	2.59
∑REE (ppm)		270.27	350.6	279.0	703	438.6	320.5	256			
La_N/Sm_N		4.5	4.72	3.28	3.67	3.63	3.38	6.01			
Ce_N/Yb_N		7.3	6.64	7.96	12.56	8.77	5.47	6.18			
Eu/Eu*		0.54	0.25	0.47	0.24	0.31	0.45	0.75			
$(LREE/HREE)_{cn}$		5.1	5.0	5.5	6.8	5.5	4.6	4.2			
K/Rb		0.021	0.022	0.01	0.0001	0.01	0.03	0.03			
Ba/Rb		3.0	1.3	2.6	0.5	3.4	5.9	5.5			

ND: Not Determined., *: Abundance of elements in the earth's crust in ppm [21]

Table 4: Concentrations of REE, U, Th, Au and trace elements for rhyolites.

Element	**Unit**	**NUB-1**	**NUB-2**	**NUB-3**	**NUB-4**	**NUB-5**	**Mean**	**Std. Dev.**	**Abundance***
La	ppm	12	15	21	46	12	21.2	14.3	18
Ce	ppm	14.6	18	25.2	66.4	14.4	27.7	22.0	46
Nd	ppm	10	12.5	17	30.6	13.2	16.6	8.1	24
Sm	ppm	1.4	2.5	4.6	8.4	3.4	4.0	2.6	6.5
Eu	ppm	0.2	0.3	0.3	1.8	0.4	0.6	0.6	1.1
Tb	ppm	0.6	0.5	0.6	1	0.3	0.6	0.25	0.9
Yb	ppm	1	2.8	2.5	2.7	2.8	2.4	0.77	2.7
Lu	ppm	0.18	0.1	0.11	0.69	0.15	0.25	0.25	0.8
U	ppm	3.9	2.4	4.4	6.2	4.2	4.2	1.3	4.0
Th	ppm	0.8	1	1.8	8.9	1.5	2.8	3.4	12.0
Sc	ppm	12.7	11.6	15.5	27.9	17.9	17.1	6.5	5.0
Cr	ppm	1347	852	988	40.3	984	842.2	484.5	200
Co	ppm	77	65	60	23	62	57.4	20.3	23
Rb	ppm	10.7	16.9	29.5	56.2	7.8	24.2	19.7	310
Cs	ppm	1.4	1.3	0.7	9.5	1.3	2.8	3.7	7.0
Ba	ppm	311	296	< 50.0	472	366	299	155.3	250
Hf	ppm	2.4	3	4.2	5.6	2	3.4	1.4	4.5
Ta	ppm	0.2	< 0.10	0.32	0.46	0.33	0.28	0.13	2.1
Sb	ppm	13.8	37	8.3	1.6	3.4	12.8	14.3	1.0
Ag	ppm	2.9	2.8	4.6	4.3	3.5	3.6	0.81	0.1
Au	(ppb)	47.4	99.3	929	164	55.4	259	377	0.005
Na_2O	(%)	0.3	0.9	0.5	2.9	0.6	1.0	1.0	2.83
CaO	(%)	0.6	0.6	3.8	6.2	2.4	2.7	2.3	3.63
Fe_2O_3 (T)	(%)	9.4	10.1	11.7	7.8	8.1	9.4	1.5	5.0
K_2O	(%)	ND	ND	ND	ND	ND	ND	ND	2.59
∑REE (ppm)		40	51.63	71.31	158	46.65			
La_N/Sm_N		5.3	3.7	2.8	3.4	2.2			
Ce_N/Yb_N		4.8	2.1	3.3	8.0	1.7			
Eu/Eu*		0.3	0.33	0.2	0.69	0.42			
$(LREE/HREE)_{cn}$		2.3	2.8	3.3	3.8	2.8			

ND: Not Determined., *: Abundance of elements in the earth's crust in ppm [21]

5. Conclusions

Instrumental Neutron Activation Analysis (INAA) is a non-destructive analytical technique offering high sensitivity, inherent accuracy and precision, and minimal matrix effects for multi-element determination in diverse geological matrices. For rare earth element (REE) analysis, INAA provides distinct advantages due to favourable nuclear properties and simplified sample preparation protocols that minimize contamination risks. This study demonstrates the capability of INAA to determine eight REEs (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) in geological rock samples with high analytical precision, establishing its utility as a reliable tool for REE and Uranium exploration programmes.

The rhyolite samples from the study areas exhibit distinctive geochemical signatures characterized by elevated total REE concentrations (ΣREE = 256 –703 ppm) and pronounced negative europium anomalies (Eu/Eu* = 0.24–0.75). These geochemical features indicate formation under oxidizing conditions, consistent with magmatic differentiation processes involving plagioclase fractionation.

This study confirms that INAA is a reliable, high-precision tool for multi-element determination in complex geological matrices. The geochemical signatures of the rhyolites—significe the LREE enrichment and high gold concentrations—highlight the economic potential of the sheared contacts in the Dongargarh-Kotri belt. The findings suggest a multi-stage evolution where hydrothermal fluids facilitated gold-sulfide co-precipitation.

Authors contributions

Details of authors contribution to the manuscript. Srinivas Yammanur: Concept of work, Methodology, Analysis, Manuscript preparation and revision, writing-review and editing. A. Yugandhara Rao Concept of work, Sample work and Manuscript preparation and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors profusely thank Director, Atomic Minerals Directorate for Exploration and Research, Hyderabad for giving permission to publish this paper and all the officers of the Radiation Standards and Analysis Group for their valuable discussions and suggestions.

Data availability

Data will be made available on request.

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