Rare earth element potential of the felsite dykes of Phulan area, Siwana Ring Complex, Rajasthan, India

The global demand of rare earth elements (REE) is increasing at present due to their unique magnetic, high electrical and thermal conductance, fluorescent, chemical properties and their uses in high-technology applications and in the quest for green energy. China, the largest producer of REE, has largely reduced its export since 2010. As a consequence, all the other countries in the world have intensified their search for REE to meet their demands. The present study may lead to enhancing the REE resources of India.

The Neo-proterozoic Malani Igneous Suite occurring in western Rajasthan, west of the Aravalli Range, covering an area of 20,000 sq. km, is a favourable geological province for the search of REE and rare metals (RM)[1,2] (S. Majumdar; S. K. Rastogi and T. Mukherjee unpublished). The well-studied Siwana Ring Complex (SRC), Rajasthan, India comprises bimodal volcanic sequence of basaltic and rhyolitic flows intruded by different phases of plutonic rocks like peralkaline granite, microgranite, felsite and aplite dykes, which are characterized by significant abundances of REE and RM (Figure 1). Earlier studies of SRC indicated 250 ppm Nb, 500 ppm La, 700 ppm Y and greater than 1000 ppm Zr on an average (S. Majumdar, unpublished). Anomalous concentrations of Rb, Ba, Sr, K, Zr, Nb, REE in granites and microgranites of SRC indicate the potentiality for RM and rare earth mineralization[1]. The anomalous concentration of REE in rhyolites, associated tuffs, granite and microgranite in parts of SRC is reported up to 3719 ppm (S. K. Rastogi and T. Mukherjee, unpublished). Presence of high LREE, Zr, Nb, Th and uranium along with silver in the surface samples of SRC makes it a potential target for volcanogenic multimetal radioactive mineralization[2].

REE mineralization with associated Zr, Nb, Y and Ag was recorded in felsite dykes of Phulan area (25°42′50″N, 72°31′55″E) lying at the northeastern margin of SRC (Figure 2). Detailed studies carried out by the authors have led to the identification and delineation of significant REE mineralization zones of economic interest. Detailed petrological

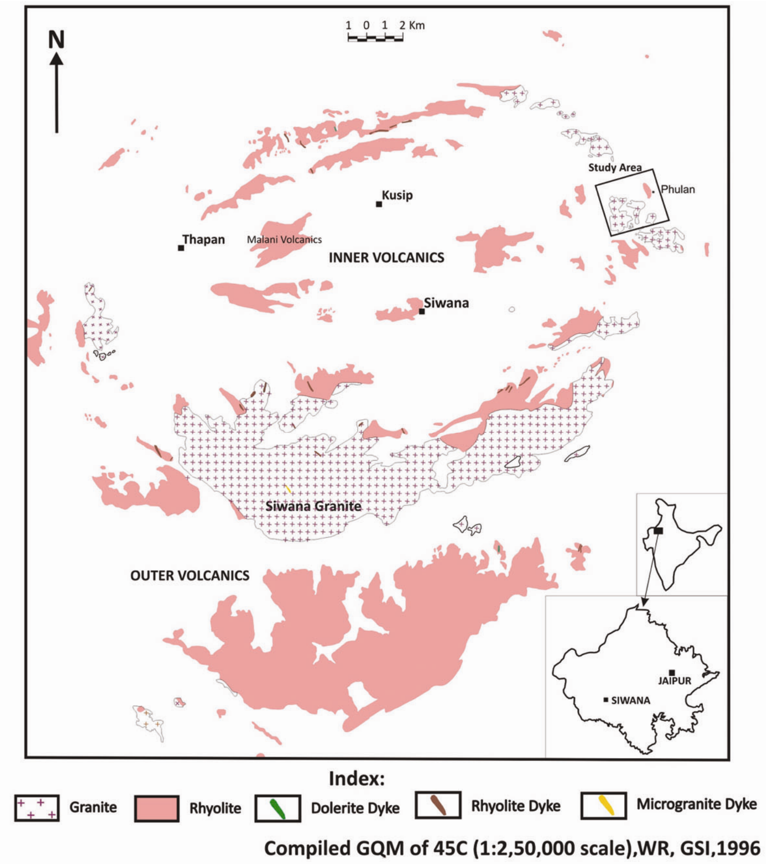

Figure 1. Location map of the study area in Siwana Ring Complex, Barmer district, Rajasthan, India.

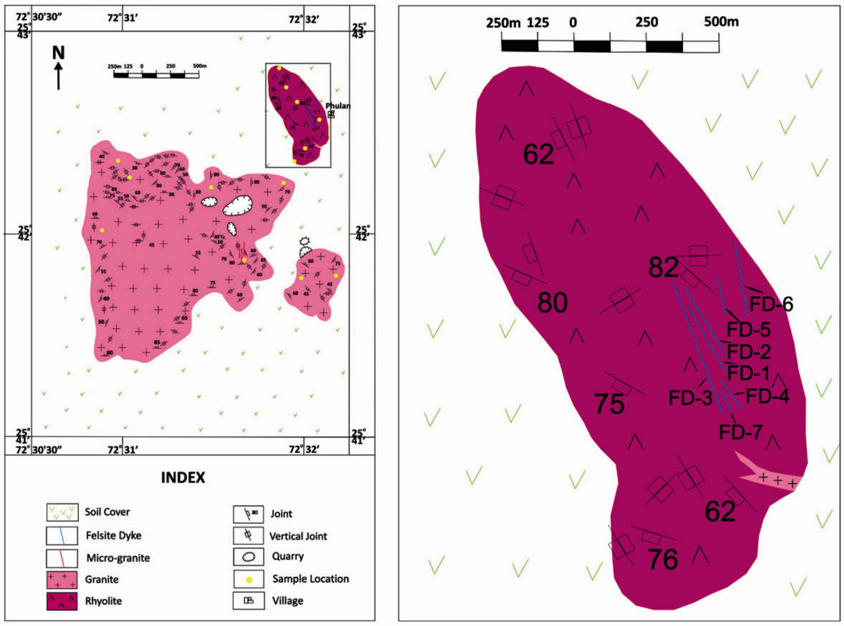

Figure 2. Geological map of Phulan area, SRC.

Table 1. Chemistry of REE and RM-bearing mineral phases identified in felsite dyke samples using EPMA

	All values in wt%											
Mineral	Monazite	Monazite	Eudialyte	Eudialyte	Parisite	Parisite	Perrierite	Perrierite	Tritomite	Tritomite	Zektzerite	Zircon
F	0.56	0.86	0.74	1.09	7.04	6.95	0.31	0.319	4.75	4.21	0.00	0.00
Na_2O	0.00	0.00	2.64	2.06	0.04	0.00	0.183	0.25	0.00	0.04	0.96	0.00
SiO_2	0.72	0.55	48.16	49.78	2.08	0.50	19.105	19.186	10.96	11.32	61.30	32.41
P_2O_5	29.27	28.42	0.00	0.00	0.91	1.61	0.012	0.011	3.10	2.95	0.01	0.13
CaO	0.12	0.00	3.43	3.57	5.56	5.73	1.163	1.33	5.18	4.93	0.08	0.04
TiO_2	0.07	0.08	0.62	0.82	0.28	0.00	17.486	17.862	0.17	0.17	0.02	0.01
MnO	0.00	0.02	5.93	5.04	0.02	0.10	3.41	3.248	0.09	0.00	0.05	0.00
FeO	0.19	0.08	1.53	1.50	0.19	0.14	7.264	7.185	0.46	0.50	0.03	0.32
ZrO_2	0.00	0.03	12.66	13.24	0.31	0.00	0.236	0.704	3.15	2.91	33.36	66.83
SrO	0.00	0.00	0.05	0.03	0.10	0.11	0.069	0	0.11	0.11	0.00	0.00
Y_2O_3	0.00	0.00	5.54	6.43	1.29	1.81	0.258	0.354	10.91	11.64	0.01	0.55
Nb_2O_3	0.00	0.00	1.93	0.63	0.61	0.00	0.861	0.006	0.49	0.74	0.00	0.00
La_2O_3	31.63	26.80	1.03	0.68	14.44	14.25	14.025	12.302	5.13	4.68	0.00	0.23
Pr_2O_3	2.33	2.75	0.59	0.37	3.54	4.03	1.667	1.765	2.46	2.13	0.37	0.20
Nd_2O_3	5.26	6.84	1.43	1.27	13.82	14.87	5.414	7.173	8.71	6.77	0.23	0.09
SmO	0.80	0.13	0.64	0.47	2.11	3.01	0.219	0.716	1.80	2.27	0.00	0.14
Gd_2O_3	0.14	0.10	1.06	1.01	1.07	1.42	0	0.114	2.12	1.44	0.00	0.06
Dy_2O_3	0.00	0.43	0.25	0.07	0.10	0.15	0.024	0	0.72	1.23	0.00	0.03
ThO_2	0.48	0.93	0.00	0.00	0.52	0.58	0	0	20.19	20.32	0.00	0.06
Ce_2O_3	31.62	33.72	2.44	1.85	29.19	29.29	24.901	24.655	11.26	10.43	0.16	0.11

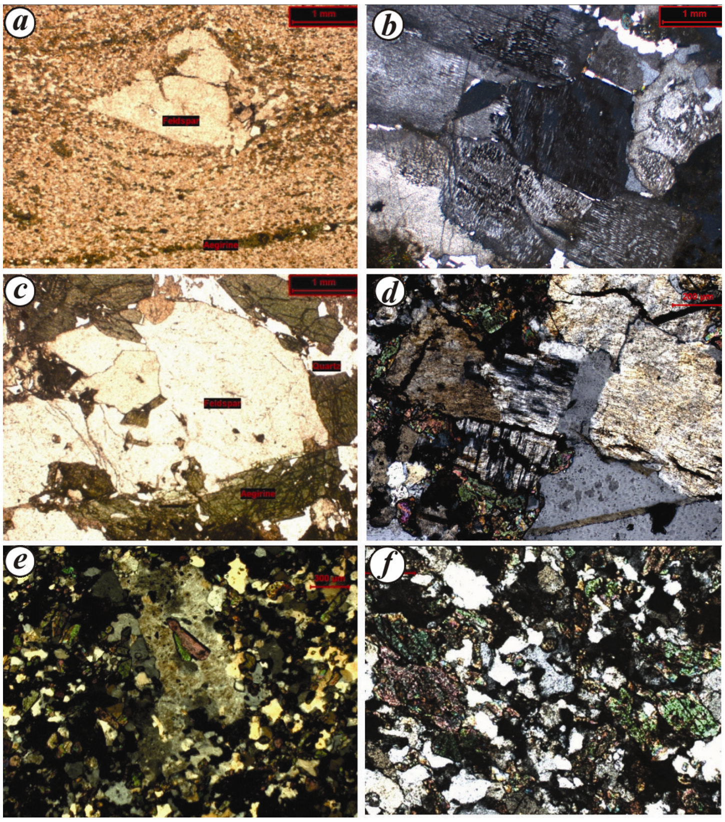

Figure 3 *a*–*f*. Photomicrographs of rhyolite, granite and felsite from Phulan area. ***a***, Embayed alkali feldspar grains and elongated aegirine within a fine-grained matrix in rhyolite (transmitted light, PPL). ***b***, Exsolution lamellae of albite in alkali feldspar showing perthitic texture in Siwana granite (transmitted light, CN). ***c***, Concentration of aegirine along the periphery of subhedral feldspar in Siwana granite (transmitted light, PPL). ***d***, Coarse-grained phenocryst of alkali feldspar with patchy and string albitic exsolution lamellae in felsite (transmitted light, CN). ***e***, Inclusion of aegirine in a subhedral feldspar grain in felsite (transmitted light, CN). ***f***, Subhedral aegirine grains showing two sets of cleavage in a quartzo-feldpathic matix in felsite (transmitted light, CN).

aspects of the host rock for REE and RM, characterization of REE-bearing mineral phases and their mutual textural relations, and the distribution pattern of REE and RM in the felsite dykes and the associated rocks of Phulan area are presented here.

The area is represented by rhyolite porphyry, riebeckite–aegirine-bearing peralkaline granite (Siwana granite) and dykes of micro-granite and felsite. The rhyolite porphyry is exposed as an isolated hill in the eastern part surrounded by dune sand. It is porphyritic with very fine-grained matrix. The phenocrysts consist of K-feldspar (sanidine) and quartz (Figure 3 *a*). The feldspar and quartz grains show embayed margins. Riebeckite and aegirine are invariably present in the groundmass. Vesicles are common in rhyolite and are filled with secondary calcite and quartz in general.

The Siwana granite occupies significant part of the study area and intrudes the rhyolite porphyry east of Phulan village (Figure 2). It is coarse-grained, leucocratic and comprises phenocrysts of alkali feldspar and quartz embedded in a medium-grained groundmass of quartz, feldspar, aegirine and riebeckite. The clustering or lumping together of aegirine and riebeckite is observed near the contact of granite and rhyolite at Phulan village. The intergrowth of microcline and albite manifests as string and braided perthites (Figure 3 *b*). Discrete grains of

Table 2. Major, minor, trace and REE values of felsite dykes 1 and 3

Sample dyke	PCH01-01/01 FD-1	PCH01-01/02 FD-1	PCH03-01/01 FD-3	PCH03-01/02 FD-3	PCH03-01/03 FD-3	PCH03-01/04 FD-3	PCH03-01/05 FD-3
Values (%)							
SiO_2	72.81	71	72.27	74.21	73.25	73.45	72.59
Al_2O_3	4.74	7.88	5.3	5.46	5.3	5.19	5.24
Fe_2O_3	11.45	10.09	11.33	10.21	11.27	12.22	11.16
MnO	0.15	0.18	0.24	0.79	0.32	0.3	0.32
MgO	0.84	0.26	0.51	0.24	0.15	0.22	0.51
CaO	0.74	0.76	0.59	0.52	0.25	0.32	0.3
Na_2O	2.96	4.4	3.64	4.6	3.83	3.43	3.5
K_2O	2.55	3.56	2.57	1.79	3.16	3.55	3.15
TiO_2	0.22	0.4	0.36	0.32	0.2	0.22	0.23
P_2O_5	0.13	0.11	0.17	0.17	0.04	0.02	0.06
Values (ppm)							
Ba	2072	1261	1421	1677	1068	1120	1827
Ga	29	47	53	14	31	25	34
V	43	55	58	50	42	46	44
Th	436	311	571	238	155	174	270
Rb	426	413	294	297	379	550	441
Sr	42	33	42	59	23	34	33
Zr	8669	5836	8885	9373	9944	9031	9683
Nb	1028	732	1156	1385	928	1071	1292
Be	31.8	34.62	52.65	62.85	66.14	63.52	60.85
Ge	6.15	4.65	6.16	5.66	6.65	5.55	6.71
Mo	1.93	2.13	1.25	3.56	1.63	2.62	4.51
Sn	210.35	120.54	230.38	86.28	94.86	137.81	148.52
Hf	350.21	215.27	325.75	351.23	345.54	383.81	352.55
Ta	92.38	55.39	64.86	64.61	73.65	63.54	75.85
U	53.36	38.29	70.53	57.63	63.35	43.65	50.51
La	2535.15	2015.24	2312.63	2895.53	3035.36	1350.23	2259.21
Ce	5015.65	3266.52	3536.56	3915.58	4355.68	2643.36	4001.26
Pr	739.16	514.56	455.64	584.57	532.53	325.61	473.36
Nd	3046.52	2019.65	2080.61	2305.51	2505.68	1395.06	2050.12
Sm	811.21	507.65	670.32	775.58	840.64	366.52	605.52
Eu	76.63	46.54	68.85	79.84	86.56	33.3	56.26
Gd	726.35	425.69	610.34	724.52	790.68	309.85	512.69
Tb	154.57	90.25	141.65	172.62	191.16	68.52	113.32
Dy	927.32	525.67	906.28	1060.62	1235.52	431.63	693.63
Ho	299.74	111.35	202.34	251.15	275.61	95.92	149.31
Er	516.67	290.61	535.12	560.29	730.32	258.54	388.5
Tm	76.54	45.05	85.61	115.19	115.86	41.25	60.69
Yb	450.61	256.69	504.62	576.63	665.52	245.52	349.23
Lu	55.15	31.35	64.81	69.05	82.86	32.56	43.51
Sc	<5	<5	<5	<5	<5	<5	<5
Y	4201.15	3039.68	4220.32	8041.24	7280.57	2482.29	3461.16

Table 3. REE + Y concentration in grab samples of Siwana granite, rhyolite porphyry and felsite

	Analytical results of REE + Y (ppm)		
Litho-variants	Minimum	Maximum	Average
Granite ($n = 16$)	1366	4701	2673.32
Felsite ($n = 5$)	6021	21,937	11774.9
Rhyolite ($n = 4$)	1509	4660	2339.81

plagioclase, mostly albite (Ab_{97-96}), are also present. The intergrowth of quartz and alkali feldspar gives rise to the graphic structure. The aegirine varies from minute needles to well-developed prismatic grains which are subhedral to euhedral; pleochroism in aegirine is marked, but sometimes it is obscured due to cloudy nature of the grains (Figure 3 *c*). The minute needles of aegirine present within the perthite are either pale yellow or pale green in colour. The two varieties of aegirine suggest that they are of different generations. Riebeckite forms the subordinate constituent. Zircon occurs as an accessory mineral. Opaques are generally less in granite.

Seven parallel felsite dykes, varying in strike length from 60 to 200 m and width from 0.10 to 2.50 m, trending NNW–SSE, have been delineated within the rhyolite porphyry near Phulan village.

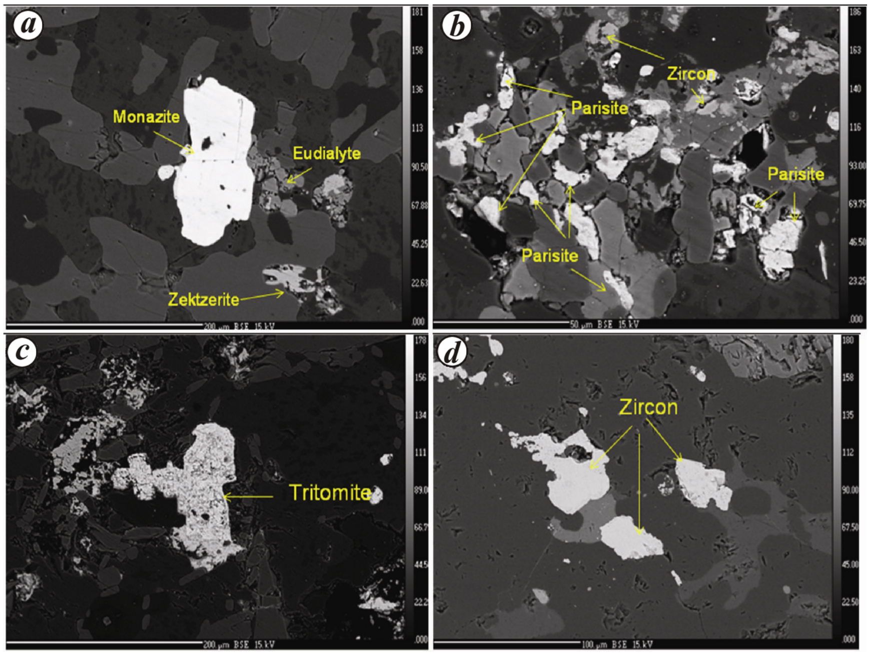

Figure 4 *a*–*d*. BSE images of mineral phases identified in felsite from Phulan area. ***a***, Euhedral monazite in association with eudialyte and zektzerite occurring between the grain boundary of alkali feldspar and aegirine. ***b***, Subhedral to anhedral discrete grains of parisite along with zircon in a groundmass of quartz, feldspar and aegirine. ***c***, Subhedral to anhedral discrete grains of tritomite in a quartzo-feldspathic matrix. ***d***, Zircon as an accessory phase found as inclusion within alkali feldspar.

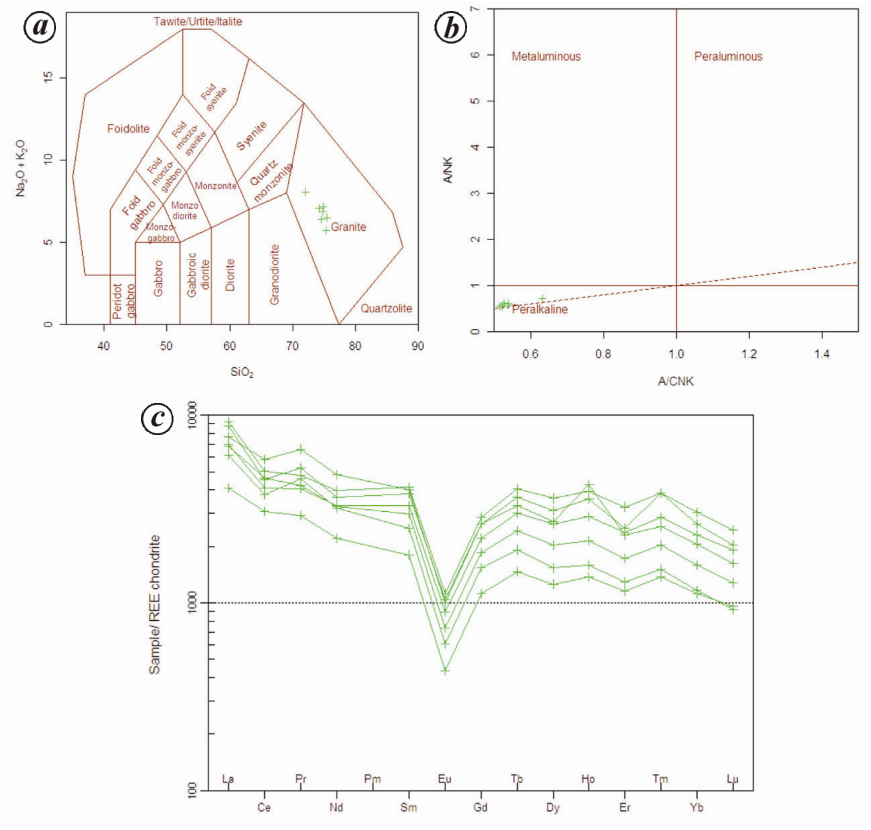

Figure 5 *a*–*c*. Discrimination diagrams of felsite. ***a***, Total alkali versus silica diagram of felsite dyke samples (after ref. 5). ***b***, A/CNK versus A/NK plot of felsite dyke samples (after ref. 6). ***c***, Chondrite normalized pattern of REE of felsite dyke samples (after ref. 7).

These dykes are fine-grained, greenish-grey in colour and composed of quartz, alkali feldspar, aegirine and opaques. The felsites have lower phenocryst density and a finer-grained groundmass compared to the Siwana granite. Quartz grains are anhedral in shape and occur both as megacrysts and fine grains. Alkali feldspar ($Or_{96-56}Ab_{4-44}$) occurs as subhedral to anhedral phenocrysts within the groundmass of quartz, alkali feldspar and aegirine. Perthitic texture is observed in coarse-grained phenocryst of alkali feldspar ($Or_{56}Ab_{2-28}$) with patchy and string perthites of albite ($Ab_{98–97}$). Alkali feldspar shows carlsbad twins (Figure 3 *d*). Both alkali feldspar ($Or_{98–72}Ab_{2–28}$) and plagioclase ($Ab_{98–97}$) are present as inclusions within aegirine. Aegirine constitutes >20% (by mode) in felsites and exhibits two textural relations. The first type is euhedral to subhedral in shape and is commonly present in the groundmass. Aegirine ($Ae_{94.1–93.3}Jd_{1.2–1.4}WEF_{4.7–5.3}$) ranges in size from 50 to 350 µm and appears as long and slender-shaped with two sets of cleavages (Figure 3 *e*). The second type is aegirine ($Ae_{94.2}Jd_{0.7}WEF_{5.1}$) that occurs as inclusion in alkali feldspar grains and the TiO_2 content in aegirine ranges from 0.16 wt% to 2.28 wt% (Figure 3*f*). There is no marked chemical difference between the aegirine present as inclusion and the one present in the groundmass. The aegirine grains are sometimes concentrated along the grain boundaries of alkali feldspar and quartz.

The felsite dykes ($n = 5$) were studied in detail using Electron Probe Micro Analyzer (EPMA) at the EPMA Laboratory, Geological Survey of India (GSI), Faridabad. Chemical composition of minerals was determined on the CAMECA SX-100 probe at 20 kV, a beam current of 30 nA and peak counting time of 30 sec for all elements. The major REE mineral phases identified are monazite (Ce, La, $Nd(PO_4)$), parisite ($Ca(Ce, La, Nd)(CO_3)F_2$), eudialyte (Na, Ca, Ce, Mn, Zr, Y, Si_8O_{22}), perrierite (Ce, La, Pr, Nd, Ca, Fe, Ti, Mn, Si_4O_{22}) and tritomite (Ce, La, Nd, Ca, Y, Th, P, $Si(O,OH,F))_{13}$ in decreasing order of abundance. Zircon, zektzerite, calciohilairite, galena and baryte are also present. Table 1 gives the chemical analyses of the identified REE bearing phases in the felsite dyke samples determined by EPMA. Bastnaesite, monazite and parisite are the three economically significant LREE minerals and account for 95% of LREE currently used.

Table 4. REE concentration in groove samples collected from felsite dykes 1–7

Average dyke	All values in ppm						
	FD-1 (*n* = 6)	FD-2 (*n* = 2)	FD-3 (*n* = 10)	FD-4 (*n* = 1)	FD-5 (*n* = 2)	FD-6 (*n* = 7)	FD-7 (*n* = 2)
La	3061.09	1231.50	2237.13	1423.40	1101.90	2076.80	3127.56
Ce	5499.34	2293.10	3822.41	2653.00	2154.20	3731.00	6695.37
Pr	614.00	296.00	442.39	331.60	272.60	423.20	793.01
Nd	2517.37	1184.30	1891.34	1376.35	1075.70	1760.10	3090.24
Sm	633.01	214.40	511.08	295.00	207.10	422.90	613.27
Eu	59.27	21.90	49.79	27.35	19.60	38.80	64.77
Gd	540.26	213.30	450.74	262.60	148.10	376.60	581.71
Tb	105.13	43.20	97.48	54.00	37.00	73.20	95.73
Dy	589.58	329.90	588.43	319.25	216.10	415.20	521.40
Ho	141.62	57.20	130.99	70.15	42.00	89.10	121.12
Er	330.21	162.10	337.76	194.10	130.40	229.10	323.58
Tm	48.76	25.20	55.33	30.15	20.00	36.20	64.46
Yb	287.35	160.20	314.48	188.25	121.10	214.30	345.58
Lu	34.85	20.70	39.13	24.90	16.30	27.40	49.75
Y	3217.99	1153.90	3467.20	1342.55	1089.80	2538.70	3989.54

Table 5. Distribution of LREE, HREE and ΣREE + Y in felsite dyke samples

	All values in ppm								
	LREE			HREE			ΣREE + Y		
Felsite dyke	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average
FD-1 (*n* = 6)	6,157.6	23,260.8	12,584.82	2,209.23	7,586.22	5,258.49	8,366.83	30,581	17,843.31
FD-2 (*n* = 2)	5,085.7	5,450.65	5,268.17	2,140.15	2,191.85	2,166	7,277.55	7,590.8	7,434.17
FD-3 (*n* = 10)	2,021.55	19,728.25	8,954.13	922.66	11,571.31	5,481.54	2,944.21	25,461.23	14,435.68
FD-4 (*n* = 1)	6,106.7	6,106.7	6,106.7	2,485.95	2,485.95	2,485.95	8,592.65	8,592.65	8,592.65
FD-5 (*n* = 2)	4,158.92	5,503.05	4,830.98	1,587.98	2,053.46	1,820.72	6,212.38	7,091.03	6,651.7
FD-6 (*n* = 7)	1,291.2	21,014.85	8,452.8	477.8715	10,417.36	3,999.73	3,073.81	31,432.21	12,452.54
FD-7 (*n* = 2)	3,879.455	24,889	14,384.22	2,142.009	10,043.73	6,092.87	6,021.464	34,932.73	20,477.09

Monazite and parisite are the most abundant REE-bearing mineral phases in the felsite dykes of the Phulan area. Both Ce and La-bearing monazites are present and the ThO_2 content in monazite varies from as low as zero to as high as 2.381 wt%. Zircon and zektzerite are found as the most abundant accessory minerals in the felsite dykes (Figure 4). The REE mineral phases are in general, euhedral to anhedral in shape with size ranging from 25 to 250 μm. They occur as discrete grains along the grain boundaries of alkali feldspar–aegirine and quartz–aegirine and as inclusions within quartz, alkali feldspar and aegirine.

Whole-rock analysis of felsite dykes 1 and 3 (Table 2) from Phulan area indicates high SiO_2 (72.79%), Fe_2O_3 (11.10%), Na_2O (3.76%), K_2O (2.90%), low to moderate Al_2O_3 (5.58%) and low MnO (0.32%) content. In the total alkali versus silica diagram, the samples of felsite (*n* = 7) indicate granite composition[5]. In A/CNK versus A/NK plot[6], the felsite samples fall in the peralkaline field. The peralkalinity is corroborated by the presence of acmite in the norm. Chondrite-normalized REE diagram of felsite dykes shows moderate fractionation of LREE. HREE are not well fractionated and show flat pattern. Felsites show pronounced negative Eu anomaly, which can be attributed to earlier fractionation of plagioclase in the parent magma (Figure 5).

Bedrock samples of Siwana granite, rhyolite porphyry and felsite exposed in the studied area were analysed in the Chemical Laboratory, GSI, Jaipur using ICP-MS for their REE content (Table 3). The analyses of groove samples from seven felsite dykes indicate significant REE (Table 4) and RM (Table 2) concentration. Among LREE, Ce varies from 0.06% to 1.17%, La from 0.03% to 0.6%, while among HREE, Y varies from 0.03% to 0.8% and Dy from 0.005% to 0.12%. The samples have U up to 169.25 ppm, Th up to 571 ppm, Nb up to 1385 ppm, Zr up to 9944 ppm and Pb + Zn up to 0.18%. Table 5 gives the minimum, maximum and average concentrations of LREE, HREE and ΣREE + Y of felsite dykes. Among the seven felsite dykes studied in the Phulan area, three major dykes, i.e. FD-1, FD-3 and FD-6 have very high average REE content of 1.76%, 1.49% and 1.30% respectively.

Out of 18 advanced projects in the world, only Lynas Corporation (Mt. Weld and Kangankunde, Malawi) and Moly Corporation Inc. (Mountain pass, USA) have the highest average grade of +8% REO, whereas the Matamec Exploration Corporation (Canada) is also exploiting low average grade of 0.23% REO. In view of the high concentration of REE associated with significant Zr, Nb and U contents, with the presence of discrete REE-bearing phases, the felsite dykes of Phulan and the adjoining areas of SRC form a potential area for detailed exploration for REE and RM mineralization.

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Mineral compositional studies of slag from Galla village, Uttarakhand, India

Mineral and chemical compositional studies of ancient iron and its slag for their characterization from various parts of India have been carried out by different workers[1,2]. One of the recent studies from India was on iron slag from Kakching, Manipur[3]. Mineralogical and elemental studies on slags throw light on the prevailing conditions and methods used to extract metals out of enriched rocks by ancient workers. Abundance of iron slags in Kumaon region, Uttarakhand, India might suggest that a close interaction did exist between the Ganga valley and Kumaon in ancient times, and probably metal was one of the main commodities supplied to the Ganga valley for urbanization[4]. Here, we discuss the findings of the compositional studies carried out on the slag samples of Galla village, Nainital district, Uttarakhand and the implications on metallurgical methods adopted by ancient workers of Kumaon Himalaya.

Slags are found strewn along the slope of the terrace of Galla village (Survey of India Toposheet No. 53 O/11). The geological setting of the area comprises Proterozoic Lesser Himalayan sequence with metamorphosed siliceous limestone and phyllites of Betalghat Formation (Jaunsar Group) underlain by Palaeoproterozoic quartzites of Ramgarh Group[5]. Iron mineralization in the rocks of the area occurs as occasional and minor magnetite-rich layers in phyllites and siliceous limestone of Betalghat Formation. Few old workings were noticed in the vicinity of the rock exposures in the higher reaches of the terrace of Galla village, which indicate mining activities by local villagers in the past. Perhaps they used to extract iron metal from these rocks. Mineralogical studies were performed through optical microscopy and electron probe micro analysis (EPMA), whereas chemical analyses of the slag were carried out using X-ray fluorescence (XRF) and atomic absorption spectra (AAS) methods for major oxides and trace elements respectively. EPMA of the slag was carried out in the EPMA Laboratory of Geological Survey of India (GSI), Faridabad using CAMECA SX 100 Electron Microprobe. The thin section to be probed was coated with carbon to conduct away charges on the surface caused by electron bombardment during analysis. The analyses of silicate and oxide phases were done at 15 and 20 kV respectively. Prior to analysis, the calibration was done using natural mineral and pure metal standards. The diameter of the electron beam was kept at 1 μm.

Physically, these slags are brownish to black in colour (Figure 1) with numerous angular to sub-rounded pits. Microscopically, the slag consists dominantly of

Figure 1. Slags collected from Galla village, Uttarakhand, India.