Calcrete Geochemistry in identifying Kimberlite / Lamproite Exploration Targets -A case study from Nalgonda district, Telangana, southern India

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ABSTRACT

The pedogenic carbonates, found mainly in arid and semi-arid regions of the world, are commonly referred to as *calcretes or caliche or kankar*. These are authigenic carbonate products which occur in association with soil, forming the residual regolith. Many rock types can produce calcretes upon weathering and denudation, but calcrete derived from certain rocks like kimberlite/lamproite acts as an exploration guide. Calcrete is a prominent sampling medium in diamond-rich countries like Australia and South Africa whereas it has not received popularity in the Indian context. Kimberlites being ultrapotassic in nature and owing to the enrichment of olivine and serpentine often produce calcrete duricrust as a capping. Recently more than twenty lamproites have been discovered in the Telangana state by the Geological Survey of India. These occurrences unravel a new panorama that the state has a substantial potential for occurrence of more kimberlite/lamproite clan rocks. An attempt has been made here to test the geochemical affinity of calcretes from various locations within Nalgonda district. The geochemical data of calcrete samples of this study has been compared with published geochemical data of lamproites of Ramadugu Field, to understand their geochemical association to kimberlite/lamproite. The calcretes are low in SiO_2 (33.92-45.1 wt %), high in K_2O (1.07-2.21 wt %) and CaO (0.78-13.61 wt %). When compared to other major elements, MgO displays low concentration. The trace elements are found to be enriched in some of the samples collected in close vicinity of known lamproite occurrences. The samples show high degree of chemical weathering, alteration and compositional variation indices. It is observed that enrichment of elements like Cr, Nb, Ba, Ti, Zr etc. indicates, similar to parent kimberlite/lamproite rock, favourable targets for further ground exploration in virgin areas. In the present study, two samples, towards five kilometers northeast of Vattikodu Lamproite Field, possess higher concentrations of Nb (>25ppm), Ba (>400 ppm), Zr (>650 ppm) and Ti (>3500 ppm) which stand out as plausible explorable targets for further ground investigations. Further investigations on these two locations are suggested to ascertain whether or not these two targets unveil new kimberlites/lamproite occurrences in the area.

Keywords: Kimberlite, Lamproite, Geochemistry, Exploration, Calcrete, Regolith, Target selection, Nalgonda, India.

1. Introduction

Calcic horizons are formed where the net moisture is deficient, such that carbonate produced in the dry season is not leached away during the wet season, leading to the formation of authigenic carbonates known as calcretes. Many terms are in use for terrestrial authigenic carbonates, like *caliche, kankar*

and travertine (e.g. Aristarain, 1971, Goudie, 1972a, 1973, 1983, Milnes and Hutton, 1983). The calcrete was coined by Lamplugh (1902) to describe carbonate-cemented gravels, along with the terms like silcrete and ferricrete for weathered products cemented by silica and iron oxide respectively. Based on Netterberg (1980), Watts (1980) and Goudie (1973, 1983), Wright and Tucker (1991) have defined the calcrete as *"A near surface, terrestrial, accumulation of predominantly calcium carbonate, which occurs in a variety of forms from powdery to nodular to highly indurated. It results from the cementation and displacive and replacive introduction of calcium carbonate into soil profiles, bedrock and sediments, in areas where vadose and shallow phreatic groundwaters become saturated with respect to calcium carbonate. .....The term is not used to describe tufas, travertines, beach rock and lake carbonates."*

Hill et al. (1999) used the general term 'regolith carbonate' synonymously covering all types of authigenic calcretes. The regolith carbonate is defined as 'secondary carbonate minerals within the regolith.

Almost every rock type can produce calcrete depending upon the enrichment of calcium in its mineral constituents. The provenance of calcretes is depictable by the presence of mineral constituents of the parent rock type. Owing to the enrichment of minerals like olivine, serpentine, calcretes derived from kimberlites contain pseudomorphs of these minerals along with other kimberlitic xenocrystic minerals like ilmenite, Cr-diopside, phlogopite, garnet etc. and hence kimberlitic calcretes are enriched in elements like Nb, Ni, Cr, Co, Ti and Zr (e.g. Phani and Srinivas, 2016). On the other hand, calcretes produced out of granitoid rocks significantly contain recognisable fragments of quartz, semi-weathered feldspar, chert etc. This particular feature readily distinguishes from kimberlitic calcrete and those derived from other rock types. Calcretes originated from sedimentary rocks like limestone and dolomite contain enriched carbonate material and absence of siliceous component.

In India, calcretes are not popular sampling media in mineral exploration except recent exercises in case of uranium exploration (Misra et al., 2011) and kimberlites (Roy, 2002 and Roy et al., 2009).

However, in the western world, the utility of surface geochemistry pertaining in particular to calcrete, is being utilised as an effective tool in mineral exploration (e.g. Anand et al., 1989, 1993, 1997). In this paper, an attempt is made to utilize the calcrete geochemistry to decipher the provenance and in identifying target locations for kimberlite/lamproite occurrences in Nalgonda district. The study resulted in identifying two prospectable locations where further ground investigations are suggested.

1.1 Kimberlites and Lamproites in Nalgonda district

The recent discoveries of kimberlite/lamproites in Nalgonda district opened up a new panorama for the exploration of kimberlites/lamproites in the district which stand out as a bench mark to state that the district has further potential for kimberlite/lamproite exploration. Owing to the occurrence of residual/ *in-situ* regolith, the area offers congenial ground for kimberlite/lamproite exploration by surface geochemical methods. Different kinds of surface exploration methods are in practice in kimberlite prospecting; out of which geochemical techniques are of prime importance in deciphering the targets for further exploration in conjunction with other methods.

Kimberlite/lamproite bodies occur as clusters of occurrences. A group of individual intrusions is known as cluster and more than one cluster together is called a field. Recently more than 20 lamproite occurrences have been discovered at Ramadugu, Vattikodu, Chintalpalle, Marepalle and Gundrapalli villages in Nalonda district by the Geological Survey of India (Sridhar and Rau, 2005, Alok Kumar et al., 2013, Alok Kumar et al., 2016), which are grouped as Ramdugu Field (RLF) and Vattikodu Field (VLF). The RLF contains a cluster of ten dykes situated at Ramadugu village and Somavarigudem (Sridhar and Rau, 2005) while the VLF contains ten small dykes at Vattikodu and additionally one dyke each at Gudrapalli and Marepalli villages occur (Alok Kumar et al., 2013). The lamproite outcrops possess the calcrete duricrust with relict lamproitic mineral assemblages and textures. The hand specimens of calcretes in the present study display mottled structure; however macroscopically they are rich in chert/silica content (Fig.1).
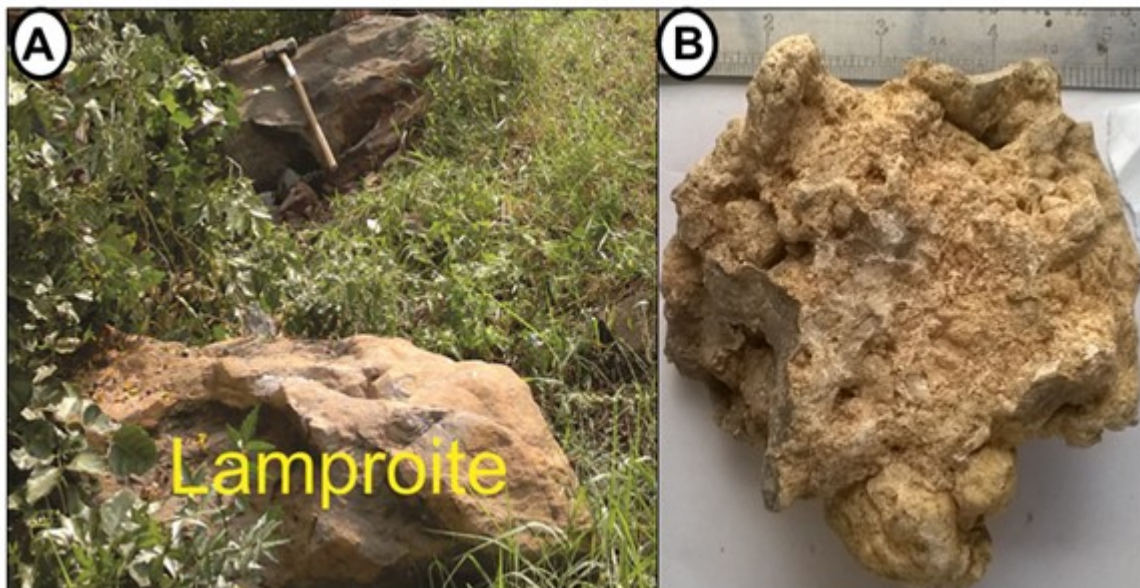
Figure 1. A-Field photograph showing calcrete duricrust over lamproite outcrop, Chintalapalle, Nalgonda district, Telangana (Source: Alok Kumar et al., 2016). Hand specimen of calcrete at Koppole village within the study area.

2. Study Area

The study area in the present investigation is bounded by latitudes 16°50' and 17°12'N and longitudes 79°00' and 79°30'E (Fig.2). Geomorphologically, the study area forms a pediment- pediplain complex with linear structural hills and valeys that are moderately dissected. Physiographically, the highest altitude (475m above msl) is at Chamalapalli where residual hills made up of granitoid rocks are present. The lowest elevation is ~150m above msl south of Ramadugu village in the Krishna river valley portion. The area possesses well-developed dendritic drainage from first to 5th order (Kongal River).
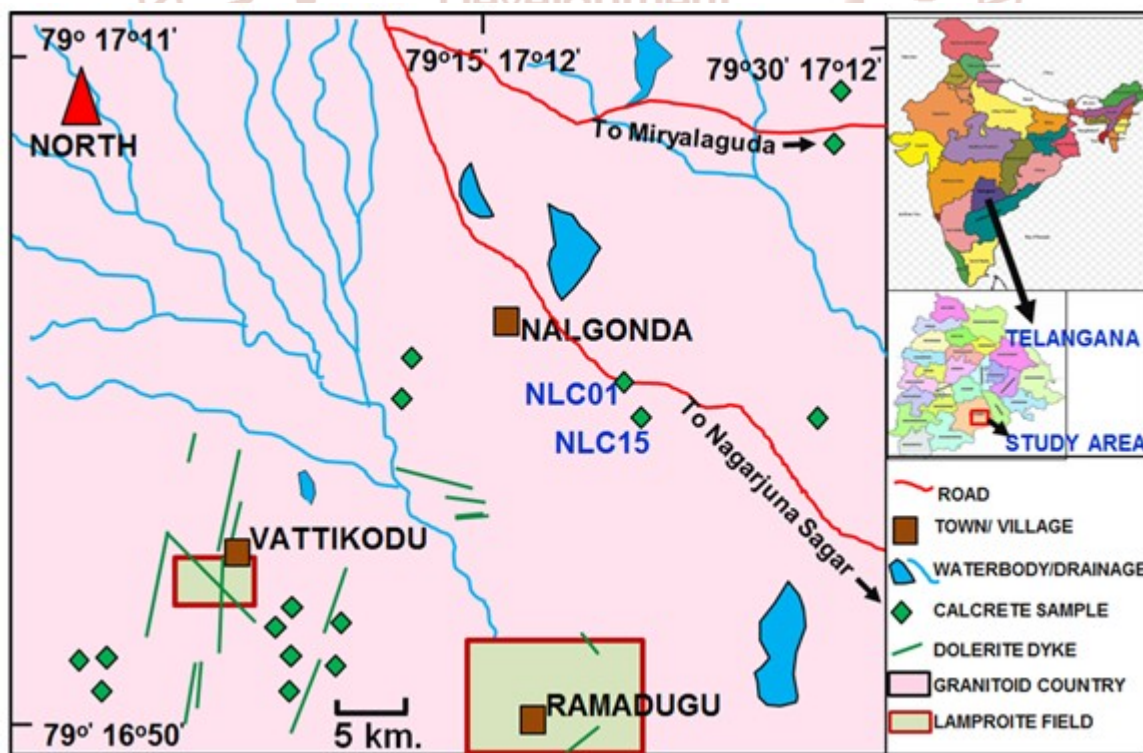
Figure 2. Map showing the location of the study area and sample points.

3. Sampling and Analysis

In total, sixteen calcrete samples from *in-situ* regolith have been collected, with each sample weighing 500 grams (Fig.1). The calcretes occurring in association with transported black cotton soil and those with clearly identifiable granitic fragments are omitted in this study. The samples were ground, pulverized and reduced to 50 grams by coning and quartering and pellets were prepared. Preliminary geochemical analysis has been conducted in a private laboratory, well-versed with kimberlite geochemistry, accredited by NABL (National Accreditation Board for Testing and Calibration Laboratories) at Bangalore. Major elements were analysed by XRF and trace elements by ICP-MS with ICP-OES finish. The major and trace element data is shown in Table 1. Geochemical data of RLF average (Chalapathi Rao et al., 2014) has been used as reference to compare the geochemistry of calcretes of this study.

4. Results and Discussion

The major oxide analysis shows that the calcretes are low in silica (SiO_2: 33.92- 45.1 wt%), K_2O (1.07- 2.21 wt%) content is higher than Na_2O (0.08- 0.89 wt%), high in CaO (0.78- 13.61 wt%), P_2O_5 (0.49- 1.64 wt%) and TiO_2 (0.29- 0.91 wt%). The trace element concentrations also are observed to exhibit wide variations- Ba (271.73- 441.29 ppm), Cr (0- 93.73 ppm), Nb (5.35- 36.71 ppm), Ti (1708.24- 5401.20 ppm), V (120.73- 249.94 ppm) and Zr (198.61- 687.16 ppm). Since the calcrete is a weathering product, the various geochemical diagrams commonly used in the interpretation of sedimentary provenance hold good in understanding their provenance. Using the geochemical data, provenance of the calcretes of the present study has been interpreted involving three parameters viz., alteration, weathering and compositional variations. The chemical composition of any secondary rock depends considerably on the composition and weathering conditions of the source rock areas (Nesbitt and Young, 1989: Nesbitt et al., 1996). The formulae used calculate these parameters are shown below.

$$CIA=[Al_2O_3/(Al_2O_3+CaO*+Na_2O+K_2O)]\times100[molar];$$

$$CIW=[Al_2O_3/(Al_2O_3+CaO*+Na_2O)]\times100 \text{ [molar] and}$$

$$ICV= (Fe_2O_3 + K_2O + Na_2O + CaO + MgO + TiO_2)/ Al_2O_3 \text{ (wt \%).}$$

*CaO in silicate fraction.

The chemical index of alteration (CIA) values, for the calcretes of study area, range from 19.97 to 61.73, indicating low intensity of silicate weathering (Nesbitt and Young, 1982). This index expresses well in case of decreasing concentrations of Ca, Na and K while weathering intensity increases (Duzgoren et al., 2002). If the CIA values are 50 or less, it reflects a cool and/or arid conditions and when CIA is >50 it indicates a high degree of weathering (Fedo et al., 1995). The chemical index of weathering (CIW) values range from 21.15 to 78.19 implying a higher degree of weathering and denudation (Harnois, 1988). Yet another parameter, the index of compositional variation (ICV) ranges from 1.46 to 5.23 indicating a closer composition to that of parent granitoid rock forming the basement rock in the study area (Cox and Lowe, 1995).

Table 1.Major and trace element analyses of calcretes in the study area.

| Sample ID		NLC01	NLC02	NLC03	NLC04	NLC05	NLC06	NLC07	NLC08	NLC09	NLC10	NLC11	NLC12	NLC13	NLC14	NLC15	NLC16	MIN.	MAX.
SiO_2	(XRF - wt.%)	42.12	43.96	42.84	38.05	37.39	39.12	42.84	45.1	44.67	39.17	43.49	38.16	33.92	36.83	41.36	34.47	33.92	45.1
Al_2O_3		5.25	6	5.43	4.43	5.8	4.35	5.12	5.46	5.82	4.65	4.93	5.09	3.85	4.49	4.93	6.09	3.85	6.09
CaO		5.32	0.78	2.86	8.74	8.01	3.7	6.18	2.8	3.29	7.65	2.03	6.3	13.61	8.43	8.1	9.27	0.78	13.61
MgO		4.2	3.7	2.8	4.1	3.8	2.3	4.5	3.8	2.9	5.6	3.4	2.8	4.1	2.8	5.1	4.3	2.3	5.6
K_2O		2.21	2.04	1.64	1.64	1.73	2.21	1.42	2.02	1.94	1.84	1.92	1.56	1.1	1.47	2.2	1.7	1.07	2.21
Na_2O		0.72	0.89	0.68	0.76	0.81	0.08	0.72	0.83	0.45	0.74	0.77	0.87	0.76	0.65	0.88	0.67	0.08	0.89
Fe_2O_3		5.13	4.59	4.35	5.04	4.03	4.04	4.03	4.1	4.29	2.91	3.17	4.56	4.31	3.47	3.38	6.38	2.91	6.38
MnO		0.03	0.01	0.04	0.04	0.01	0.00	0.03	0.02	0.03	0.00	0.00	0.03	0.04	0.02	0.01	0.05	0.00	0.05
P_2O_5		1.29	0.6	0.66	0.68	0.58	0.51	0.71	0.85	0.8	0.54	0.63	0.49	0.5	0.51	1.64	1.21	0.49	1.64
TiO_2		0.91	0.46	0.42	0.68	0.36	0.48	0.44	0.37	0.4	0.29	0.32	0.39	0.41	0.32	0.63	0.48	0.29	0.91
Ba	ICP-MS with ICP-OES finish-ppm	441.29	271.73	393.71	402.15	380.91	357.52	293.33	358.57	363.34	302.87	306.6	306.96	273.85	346.44	429.05	381.78	271.73	441.29
Bi		32.4	35.08	22.63	28.21	25.68	52.51	12.65	15.65	10.34	11.76	10.73	10.72	12.00	20.32	35.54	15.54	10.34	52.51
Cr		0	49.16	93.73	63.37	55.45	46.9	67.54	63.64	87.27	44.93	34.05	66.89	69.51	40.77	37.14	73.31	0	93.73
Mn		175.3	0	224.58	237.13	0	0	154.72	93.68	199.28	0	0	197.31	277.41	87.78	0.00	354.23	0	354.23
Nb		36.71	8.63	8.68	21.32	11.74	11.55	6.94	5.35	8.51	6.1	5.55	7.4	6.2	8.04	27.11	6.07	5.35	36.71
Pb		2.6	5.54	2.72	2.27	3.82	3.02	1.54	2.27	2.97	0.00	3.09	4.66	1.39	1.87	2.51	3.23	0	5.54
Rb		60.38	47.28	44.53	45.37	61.24	62.42	41.25	47.7	50.77	49.64	46.18	37.82	36.47	40.81	50.76	40.93	36.47	62.42
Sr		111.99	81.24	86.58	116.37	136.86	61.34	147.17	112.8	127.1	77.88	126.27	165.89	96.45	154.38	113.69	89.09	61.34	165.89
Ti		5401.2	2704.2	2478.11	4009.90	2143.81	2822.16	2585.38	2207.86	2382.67	1708.24	1888.3	2301.35	2429.86	1911.06	3722.08	2806.13	1708.24	5401.2
V		236.72	205.1	200.02	228.75	200.48	189.3	173.9	155.31	188.3	126.02	120.73	182.64	157.5	152.03	212.18	249.94	120.73	249.94
Zn		27.72	18.16	24.52	23.18	28.16	14.45	25.58	21.96	23.55	9.13	11.88	30.75	19.89	34.83	8.79	28.9	8.79	34.83
Zr		687.16	295.91	404.8	434.73	360.99	456.12	280.3	233.87	298.98	241.84	240.48	275.28	198.61	285.40	662.61	532.76	198.61	687.16
CIA		38.87	61.73	51.2	28.44	35.45	42.07	38.09	49.12	50.61	31.22	51.1	36.84	19.97	29.84	30.61	34.35	19.97	61.73
CIW		46.48	78.19	60.55	31.79	39.66	53.51	42.57	60.04	60.88	35.63	63.81	41.51	21.15	33.07	35.45	38	21.15	78.19
ICV		2.72	1.46	1.83	3.81	2.58	2.42	2.5	1.85	1.78	2.89	1.66	2.69	5.23	3.2	3.08	3.04	1.46	5.23

The UCC normalized (Taylor and McLennan, 1985) diagram of major elements shows that the calcrete samples have paucity in the MgO content. This is probably due to derivation of majority of the samples from granitic sources (Fig.3A). Also, from this diagram, it can be noticed that K_2O content is more than Na_2O. Among trace elements, Zr appears to be elevated in its concentrations which is also observed in kimberlite/lamproite and although Nb content is moderate, in few samples it is higher (Fig. 3B). The wide variation in the major and trace element concentrations is observed in the calcrete samples of present study which may be attributed to the local lithological variation represented by granites, granodiorites, gneisses intruded by mafic dykes.
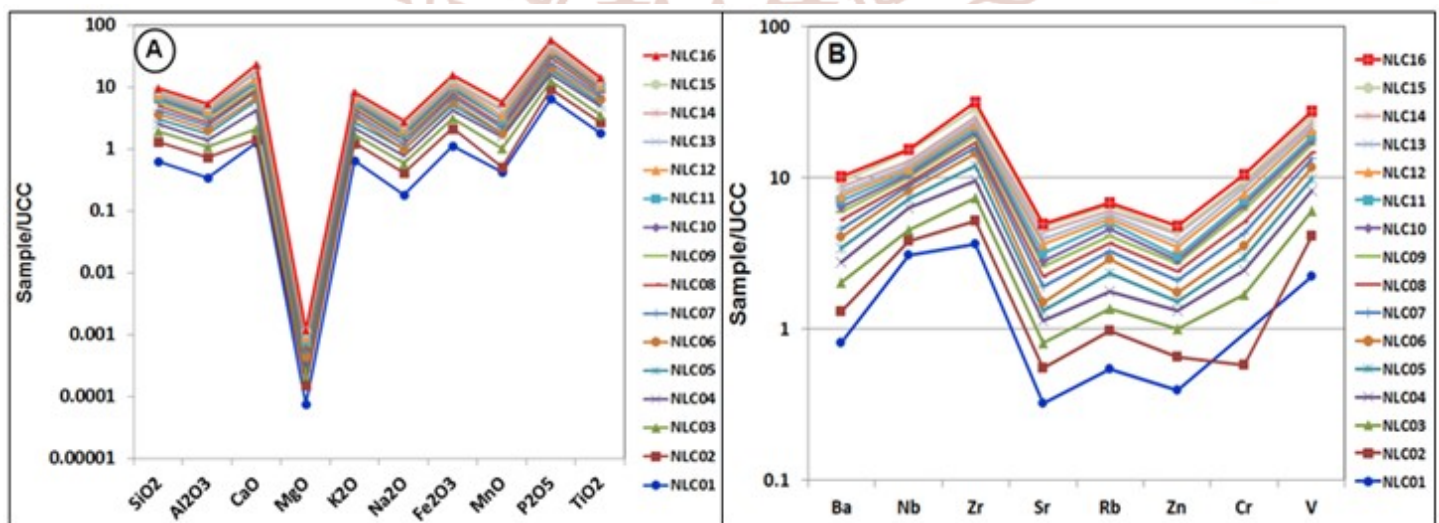

Figure 3. UCC (Upper Continental Crust, Taylor and McLennan, 1985) normalized plot of (A). Major elements. (B). Trace elements in calcretes of Nalgonda.

In the southern part of Nalgonda district, there exist Proeterozoic litho-untis represented by Srisailam quartzites and Palnad limestones. As there can be a possibility that the calcrete might have been derived not only from igneous rock but also from carbonate sedimentary sources from the south, the data has been plotted in the ternary diagram between Al_2O_3 and $CaO-Na_2O+K_2O$ to distinguish their origin. It is observed that all samples are derived from igneous rocks except one sample (NLC02), which appears to be derived from sedimentary rocks (Fig. 4 A and B).
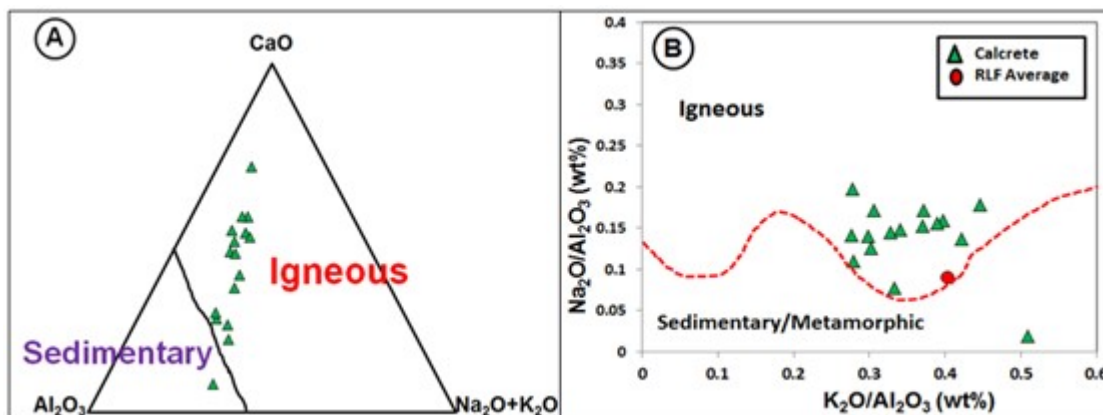
Figure 4. (A). Ternary plot of Al_2O_3-CaO-Na_2O+K_2O (Werner, 1987) and (B). K_2O/Al_2O_3 versus Na_2O/Al_2O_3 (Garrels and McKenzie, 1971) proportions for the calcretes of present study.

All the calcrete samples appear to have formed in an active continental margin setting (Fig.5) (Roser and Korsch, 1986). In the binary diagram between Fe_2O_3+MgO versus TiO_2 also, the samples plot close to active continental margin setting.
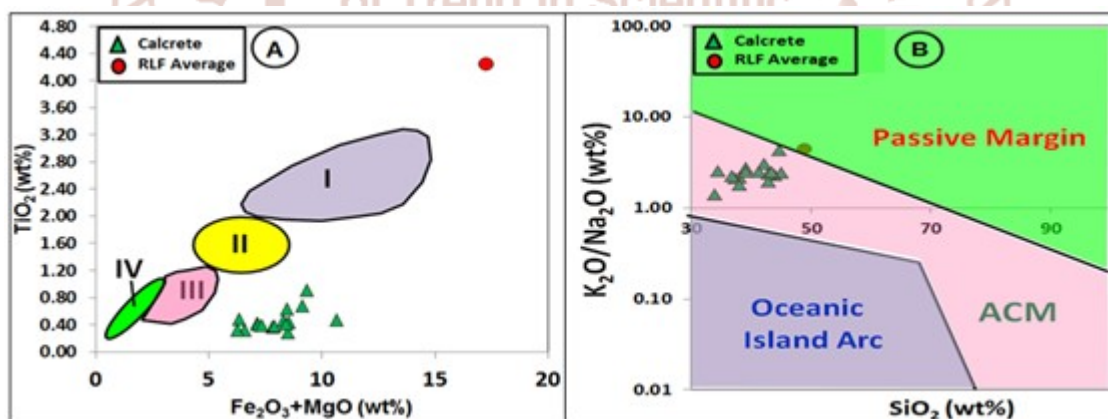

Figure 5 (A) and (B). Plots of major element compositions of calcretes of Nalgonda showing tectonic discrimination (A-Bhatia, 1983, b- Bhatia and Crook, 1986). I- oceanic island arc, II- continental island arc, III- active continental margin (ACM), IV- passive margin.

The calcrete samples of this study macroscopically are rich in clay content giving feeble effervescence upon acid test. Geochemically, the calcrete samples are found to be rich in illite (Fig.6A) and the calcrete as a whole appears to be dolomitic in nature (Fig. 6B), (Deer et al., 1978, McQueen, 2006).
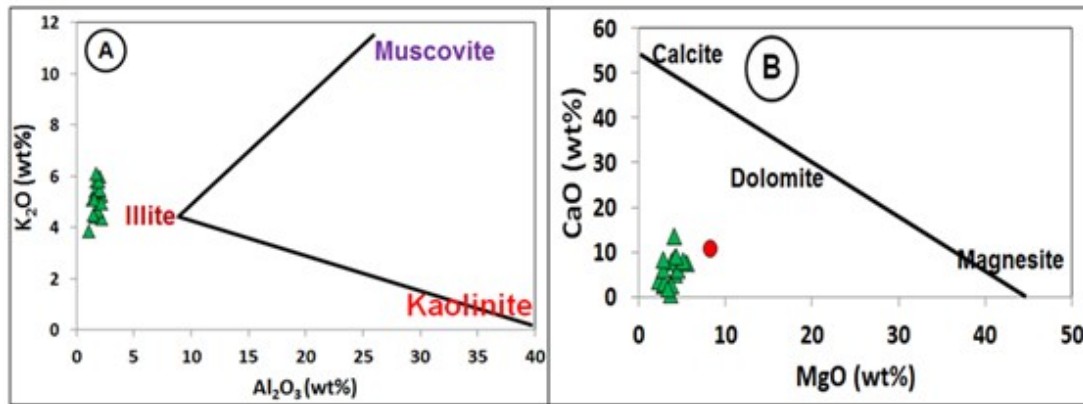
Figure 6. (A) and (B). Major element discriminatory plot showing mineralogical proportion of calcretes of Nalgonda under present study (Deer et al., 1978 and McQueen, 2006). Symbols as in previous figures.

In the binary plot of K_2O versus Na_2O, the samples show enrichment in quartz; however two samples have lesser amount of silica (Fig.7A). The samples appear to be rich in silica content indicating silicification and in turn that the majority of the samples are derived from a granitic source. However one ample shows affinity towards kaolinisation (Fig.7B).
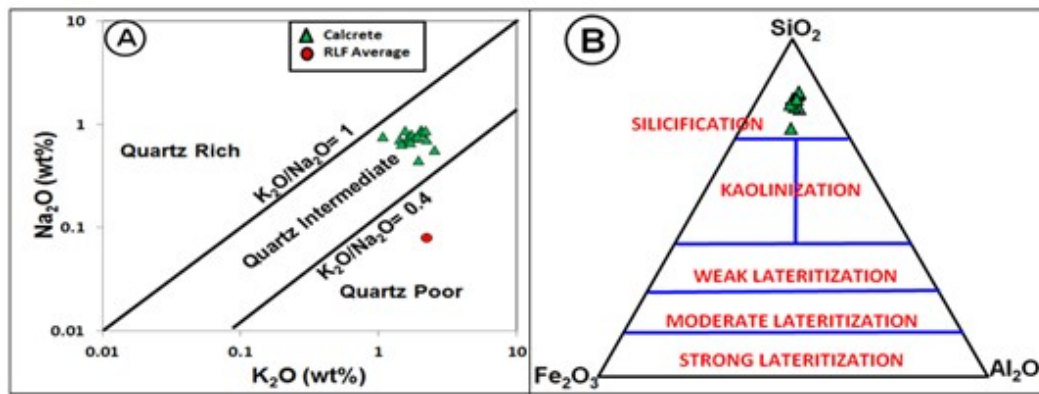

Figure 7. (A). Binary plot between K_2O and Na_2O (Bhatia, 1983) and (B). Ternary diagram showing Silicification in majority of the calcretes of present study. Limits of kaolinisation are determined according to the calculation of Schellmann (1986).

The binary plot between $Al_2O_3+K_2O+Na_2O$ versus SiO_2 has been used to understand the depositional environment of the calcrete samples. It is noticed that the samples plot in the field of semi-arid climatic conditions (Fig.8A). This is also supported by the SiO_2-K_2O/Na_2O diagram (Jaques et al., 1985) wherein it is observed that two samples plot within the ultrapotassic field (Fig.8B).
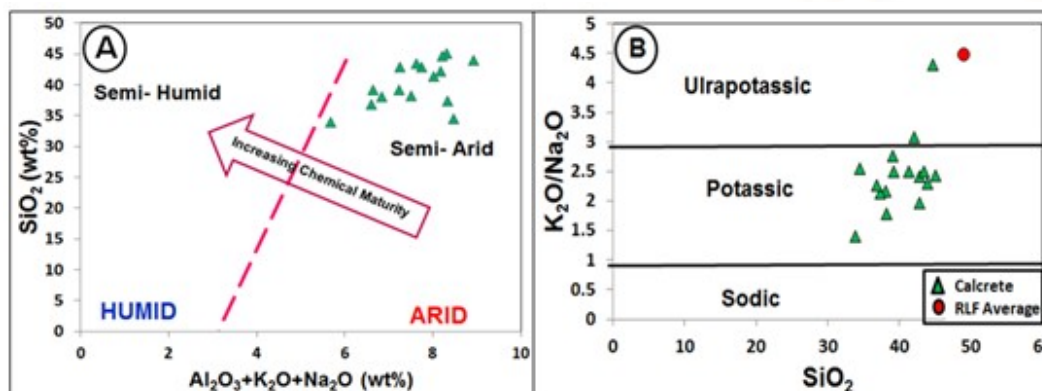
Figure 8. Binary plots showing (A). $Al_2O_3+K_2O+Na_2O$ versus SiO_2 (Suttner and Dutta, 1986) and (B). Variations in SiO_2- K_2O/Na_2O compositions (Jaques eta l., 1985) of the calcretes of the study area.

In the binary diagram between Zr and TiO$_2$, majority of the calcrete samples plot in the felsic igneous rock source whereas two samples (NLC01 and NLC15) plot in the mafic, ultramafic and intermediate igneous rock source (Fig.9A). At the same time, it is important to note that, in the Zr/Nb versus Cr/V binary diagram, one sample shows affinity towards derivation from an ultramafic source which deserve further scrutiny (Fig. 9B).
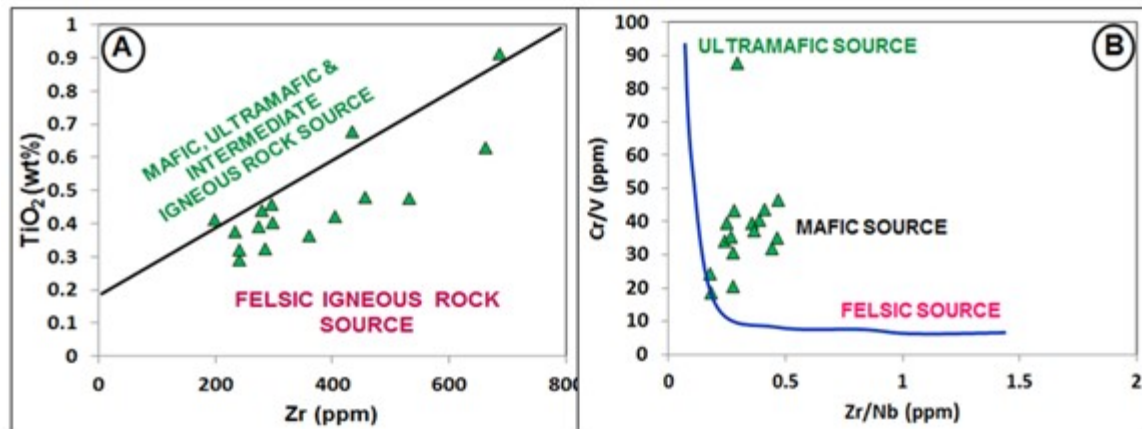
Figure 9.Binary diagrams showing (A).variations of Zr-TiO$_2$ and (B). Zr/Nb- Cr/V ratios for the calcretes of the study area.

Thus, owing to the geochemical behaviour, majority of the calcrete samples studied in this investigation, indicate that they might have been derived from granitic and/or mafic sources in a semi-arid environment. However, the two sample locations (NLC01 and NLC15) possess high concentrations of Nb (36.71 and 27.11 ppm), Ba (441.29 and 429.05 ppm), Zr (687.16 and 662.61 ppm) and Ti (5401.2 and 3722.08 ppm) might have possibly been derived from an ultramafic source.

5. Conclusions

The investigated calcrete samples show high degree of alteration, weathering and compositional variation indices. The calcretes in majority appear to have derived from weathering of granitoid and mafic rocks supported by paucity in MgO content, in a semi-arid environment. As kimberlites/lamproites possess higher concentrations of elements like Cr, Ni, Nb, Co, out of which a concentration (>25 ppm of Nb in this case) probably brings out an explorable target for further ground investigations based on the background values in the study area. The concentrations of these elements remain unchanged in the calcretes, by virtue of presence and preservance of mantle derived kimberlitic xenocrystic minerals, if at all the calcretes are derived from kimberlitic/lamproitic source. Further ground exploration is suggested at the selected targets to

confirm whether they emerge as fruitful targets in tracing out a probable ultramafic rock or kimberlite/lamproite. However, it is vital to note that calcrete geochemistry alone cannot provide targets for kimberlite/lamproite search, but selection of targets in integration and with a thorough synthesis aided by other methods like geophysics and additional geochemistry is inevitable. Thus this study highlights the application and additional impetus of using calcrete geochemistry in identifying targets for further ground investigations in search of kimberlites/lamproites.

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