

Trace Element Geochemistry of Carbonatites and Associated Alkaline Rocks of Mundwara Igneous Complex, Sirohi District, Rajasthan, India

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Abstract

Carbonatites are widely recognized for their potential to host significant deposits of rare earth elements (REEs) and other rare metals. These igneous rocks, characterized by their high carbonate mineral content, are often rich in REEs, niobium, tantalum, and other valuable elements. This makes carbonatites key targets for mining and exploration. Carbonatites are believed to form from either primary carbonate magma derived directly from the mantle or from secondary melts. These secondary melts can originate from carbonated silicate magmas through liquid immiscibility or from the residual melts resulting from the fractional crystallization of silicate magmas. The coexistence of carbonatites and alkaline silicate rocks in most complexes, their coeval emplacement in many, and overlapping initial ⁸⁷Sr/⁸⁶Sr ratios supports the theory of their cogenesis. In this study, we aim to investigate the trace element geochemistry of carbonatites and coeval alkaline silicate rocks from the Mundwara Igneous Complex, Sirohi district, Rajasthan in India. Our trace element data indicate that the carbonatites and alkaline silicate rocks in this complex are products of fractional crystallization from two separate parental melts, formed through liquid immiscibility of a carbonated alkaline silicate magma.

Keywords: carbonatite, alkaline rocks, trace elements, REE, fractional crystallization, liquid immiscibility.

Introduction

Carbonatites are a distinctive type of magmatic rocks known for their low silica content and high concentrations of incompatible trace elements, making them unique among igneous rocks (Bell, 1989). Despite their rarity compared to other magmatic rocks, carbonatites have garnered significant scientific interest due to their unusual physicochemical properties. Studies of carbonatites have greatly enhanced our understanding of various mantle processes such as mantle metasomatism, melt extraction, crustal material recycling into the mantle, and mantle degassing (Bell and Tilton, 2002). Their wide age distribution from the Archean to the present makes them valuable for studying the long-term evolution of the Earth's mantle. However, fundamental aspects of the origin and evolution of carbonatites remain unresolved. There is ongoing debate regarding the nature of primary carbonatite melts, their mantle sources, and the magmatic processes leading to their emplacement in the Earth's crust. Some hypotheses propose that carbonatites originate directly from silica-undersaturated magmas derived from the mantle

(Harmer and Gittins, 1998), while others suggest they result from magmatic differentiation, such as fractional crystallization (Petibon et al., 1998) or immiscibility of carbonate-silicate melts (LeBas, 1989). Experimental studies support all three scenarios (Sweeney, 1994; Lee and Wyllie, 1997; Veksler et al., 1998a). However, the observed coexistence of carbonatites and alkaline silicate rocks in most complexes; experimental results suggesting existence of silicate-carbonate liquid immiscibility at crustal and mantle depths; their overlapping initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and above all the absence of high magnesium number, primary melts suggest that carbonate-silicate melt immiscibility is a significant factor in many cases. Therefore, it is essential to develop a robust method to test this possibility using a variety of geochemical tracers.

Trace elements, including rare earth elements (REEs), have been extensively and successfully used as tracers of magmatic processes. Carbonatites are noted for their unusually high concentrations of incompatible trace elements (Woolley and Kempe, 1989). Interestingly, many traditionally incompatible elements often exhibit compatibility within the carbonatite system (Dunworth and Bell, 2001), which adds complexity to their study. The investigation of trace elements in carbonatites is thus highly stimulating. While previous studies have utilized trace element variations in carbonatites to unravel their evolutionary complexities (Keller and Spettel, 1995), quantitative methods to identify major processes such as liquid immiscibility in their genesis have been relatively scarce. In this study, we endeavour to enhance understanding of the origin and evolution of carbonatites and associated alkaline silicate rocks within the Mundwara Igneous Complex in western India using trace element data.

Geological background

The Late Cretaceous to Early Eocene Deccan Volcanic Province (DVP) in central and western India spans nearly 500,000 sq. km. It exhibits tholeiitic compositions in the east and southeast but varies towards tholeiitic to alkaline compositions in the west and northwest (Vandamme et al., 1991). Within the DVP, numerous volcano-plutonic complexes are found in its northern and northwestern regions (Fig. 1). These complexes host a wide range of intrusive rocks with diverse compositions, including ultramafic rocks, gabbros, syenites, highly silicic rocks like granophyres, silica-undersaturated alkaline rocks, as well as lamprophyres and carbonatites (Sukheswala and Sethna, 1973). The post-Deccan basalt alkaline-lamprophyre-carbonatite magmatism in the DVP is notable for its richness and variety of rock types and minerals. This alkaline magmatism is predominantly observed in parts of Rajasthan and Gujarat states in India (Bose, 1980; Leelanandam, 1989; Rao, 1971; Srivastava, 1989).

Geology of Mundwara Igneous complex

The Mundwara Igneous complex, located 40 km WSW of Sirohi town in southwestern Rajasthan, covers an area of approximately 12 sq. km. It consists of three distinct plutons that are remnants of laccolith-like bodies extensively intruded by radial and concentric dykes of basic and syenitic compositions (Pascoe, 1950; Sharma, 1968). The largest pluton Mer, forms a ring intrusion rising about 300 m above the surrounding flat plains of basement granite, occupying around 2 sq. km. It exhibits a diverse suite of rocks including gabbro, essexite and nepheline syenite. The Tua pluton, located north of the Mer pluton, is a partial ring structure dominated by cumulate gabbros and pyroxenites with minor nepheline syenite. The Musala pluton, situated near Mundwara village, is a circular hill approximately 800 m in diameter. It shows essexite at its base transitioning to nepheline syenite towards the top. Each pluton comprises

numerous constituent intrusions, and the complex is characterized by a chilled basanite composition at its margin (Subrahmanyam and Leelanandam, 1989). The three plutons are intersected by numerous dykes and veins composed of basanites, nepheline syenites, lamprophyres, tephriphonolites and carbonatites (Viswanathan, 1977; Subrahmanyam and Leelanandam, 1989) (Fig.2).

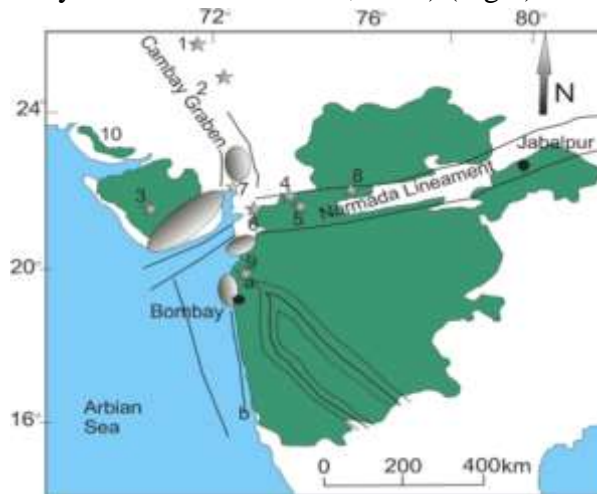


Fig.1: Distribution of the Deccan Volcanic Province in central and north-west India (Modified after Basu et al., 1993) showing the locations of associated silicic-alkaline igneous complexes in western and northwestern India. Its major tectonic framework includes the Narmada Lineament, Cambay Graben, Panvel Flexure (a), West Coast fault (b). The current extent of Deccan traps is shown in green colour. Areas of positive gravity anomalies are shown in grey ellipses. Alkali complexes marked with stars: 1. Sarnu-Dandali, Barmer District, Rajasthan; 2. Mundwara, Sirohi District, Rajasthan; 3. Mount Girnar, Gujarat; 4. Phenai Mata, Gujarat; 5. Ambadongar, Gujarat; 6. Netrang, Gujarat; 7. Kadi, Gujarat; 8. Barwaha, Madhya Pradesh; 9. Jawhar Nepheline Syenite Dyke, near Bombay, and associated alkalic rocks of Bassein and Trombay; and 10, alkali olivine basalt lava flows and plugs of central Kutch.

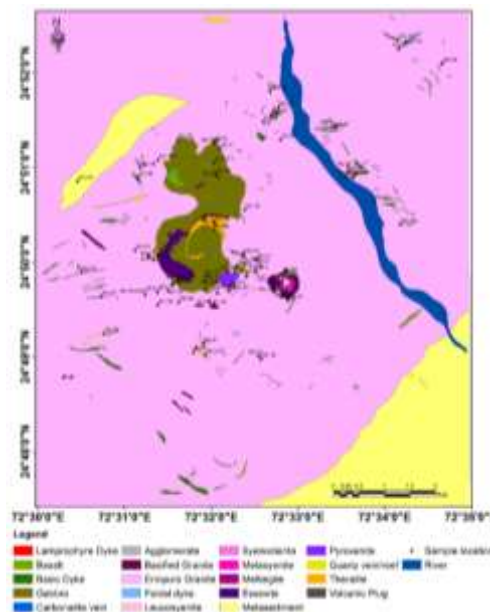


Fig.2: Geological map of Mundwara Igneous Complex (modified after Kamble *et.al.* 2015).

Analytical Techniques and Methodology

In order to understand the geochemical signatures, classification scheme and petrogenetic history of the

different rock types, fresh petrochemical samples were collected from the different rock types. For XRF studies, 5 gm (approximate) of finely powdered sample (-200mesh) was thoroughly mixed with the solution of a suitable binder. The mixing was carried out with the help of agate pestle mortar. This sample was spread uniformly over boric acid bed in an aluminium cup and it was then pelletized using the automatic pelletizer machine. The pressed pellet of sample thus prepared was analysed for major oxides and trace elements using WD-XRF (BRUKER S8 TIGER) Machine at Chemical Division, GSI, NCEGR, Faridabad. For ICP-MS (Inductive Coupled Plasma Mass Spectrometer) studies, accurately weighed finely powdered geological sample was thoroughly mixed with tetra borate and metaborate flux. It was then fused properly (at 1100⁰C) and the melted mass was allowed to cool overnight. Next day, the fused mass was dissolved in dilute HNO₃ (8% V/V). It was then transferred quantitatively in 250 ml volumetric flask containing suitable internal standard (usually Indium solution) and the solution was made up to the mark in such a way so that the final concentration of HNO₃ in the stock solution became 4%. Finally, it was measured by ICP-MS instrument at Chemical Division, GSI, NCEGR, Faridabad.

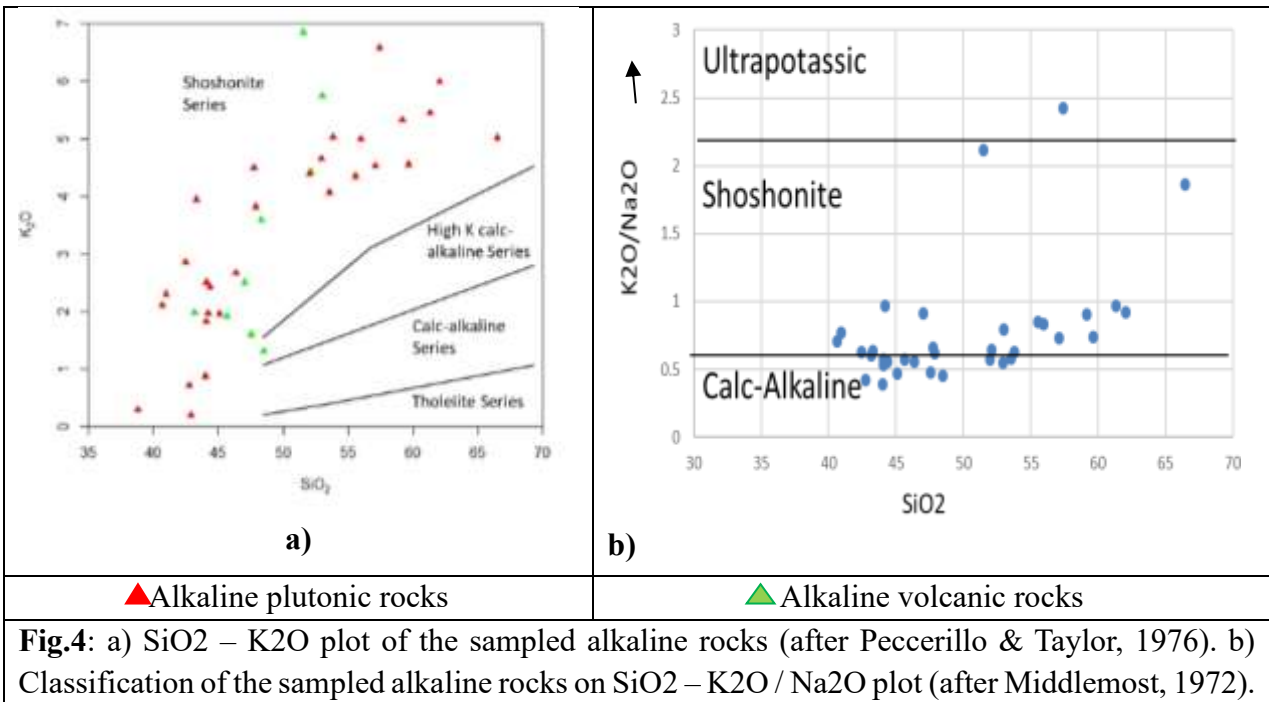
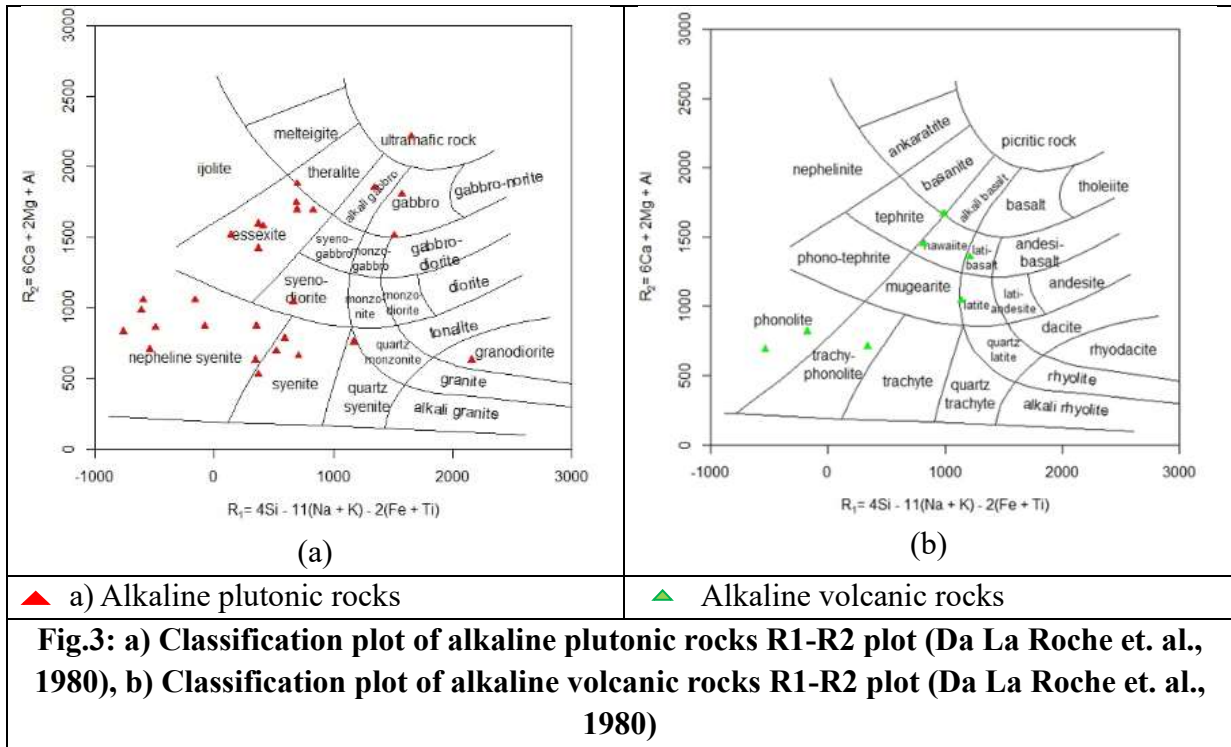
Trace element geochemistry

The alkaline silicate rocks found within the Mundwara Igneous Complex are categorized on the R1-R2 plot (De La Roche et al., 1980). Plutonic under-saturated rocks are spanning from ultramafic compositions to alkali gabbro-essexite and up to felsic under-saturated rocks such as nepheline syenite to syenite (Fig.3a) while basic undersaturated rocks aligning with fields like lati-basalt, trachy phonolite, and phonolite (Fig.3b).

The alkaline rocks such as essexite, alkali gabbro, and alkali syenite, were also analyzed using the SiO₂ – K₂O plot (Peccerillo & Taylor, 1976) and SiO₂ – K₂O / Na₂O plot (Middlemost 1972) exhibiting predominantly shoshonite affinities, with a few more evolved variants transitioning towards a High-K calc-alkaline and calc-alkaline series (Fig. 4a & 4b). Therefore, the parental melts of these rocks are suggested to show affinities ranging from calc-alkaline to shoshonitic (ultrapotassic) compositions.

Carbonatites exhibit a range of compositions from predominantly calcite-carbonatites to ferro-carbonatites, as shown in the Gittins and Harmer (1997) plot (Fig.5a). In this classification, CaO content varies widely from 31.0% to 51.1%, MnO ranges from 0.2% to 1.5%, and MgO varies from 0.5% to 2.6%. These carbonatites are notable for their high concentrations of Ba (up to 6%) and Sr (up to 1.9%). Late-stage carbonatites that have not been altered by subsequent hydrothermal silicification are characterized by elevated iron content, reaching up to 14.98% as Fe₂O₃ and very low levels of SiO₂ (< 18.3%). The P₂O₅ content varies widely from 0.1% to 5.1%, likely influenced by the distribution of apatite within these rocks.

Carbonatites and their associated rocks were analyzed using the ternary variation diagram by Le Bas (1981) to observe their differentiation trends and understand whether they originated from natrocarbonatite magma. The rocks exhibit a range spanning from CaO-rich to MgO + FeO-rich domains on the diagram. This suggests that fractional crystallization likely played a significant role in the genesis of these carbonatites. Alternatively, it's possible that processes resembling crustal-level fractionation, as described by Le Bas (1981), contributed to their formation. These findings imply complex differentiation processes influencing the composition and evolution of carbonatite melts (Fig.5b).



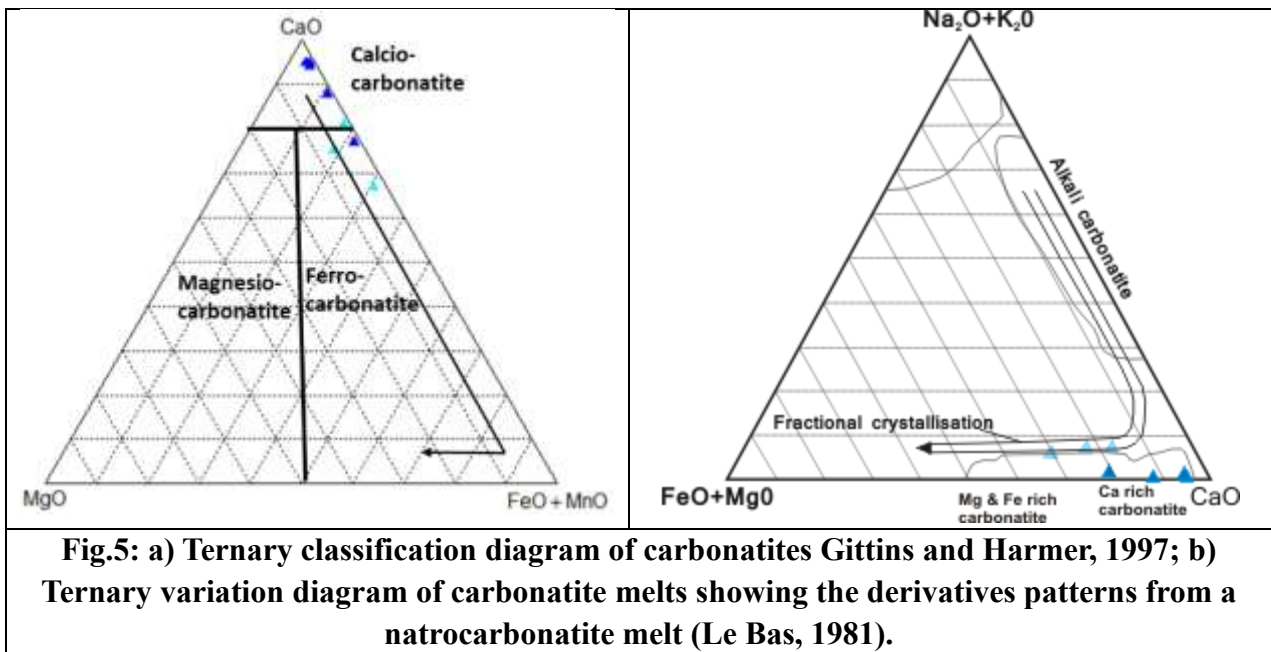
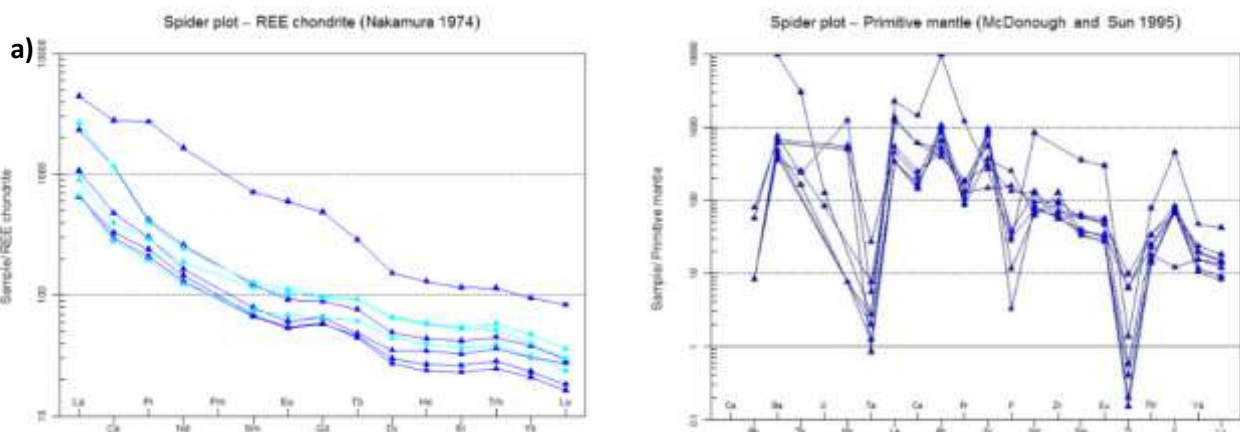


Fig.5: a) Ternary classification diagram of carbonatites Gittins and Harmer, 1997; b) Ternary variation diagram of carbonatite melts showing the derivatives patterns from a natrocarbonatite melt (Le Bas, 1981).

Rare Earth Elements

The chondrite normalized REE patterns (Nakamura, 1974) shows almost similar trend for carbonatites and alkaline rocks i.e., enrichment in LREE and depletion in HREE (Fig.6 a & b). The Σ REE and Σ REE+Y+Sc concentrations of Mundwara carbonatites varies from 638 to 5678 ppm (average composition of 1725 ppm) and 961 to 7669 ppm (average composition of 2243 ppm) respectively. High Ba concentrations (2332-64773 ppm) and Sr content (2924-18839 ppm) is characteristic of Mundwara carbonatites. The Mundwara carbonatites show a strong positive trend in the variation diagrams of La vs Y, Yb vs Y, Y vs Ce and Yb vs Ce, moderate to weak positive correlation in Yb vs Nb, moderate to weak negative correlation in Y vs Nb & Zr vs Nb and negative correlation of CaO vs. MgO, Ba vs. Sr, Nb vs Sr and Nb vs Ce. While the samples of the alkaline rocks show a positive trend in the variation plots of CaO vs MgO, Ba vs Sr, Zr vs Nb, Yb vs Ce and Nb vs Ce, a moderate to weak positive correlation in La vs. Y, Y vs. Nb, Yb vs. Nb and Y/Ce and a moderate negative correlation of Yb vs. Y and Nb vs Sr (Fig.8). Tectonic discrimination diagrams, based on trace elements, shows that Mundwara Igneous complex belongs to the within-plate magmatism area (Fig.7a & 7b).



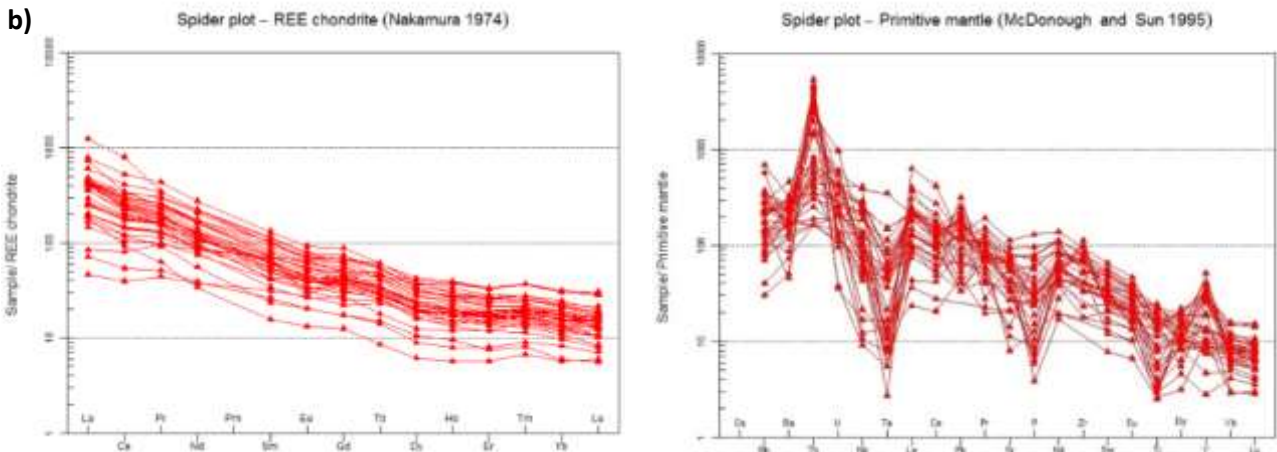


Fig.6: a) Chondrite normalized REE plots (Nakamura, 1974) and primitive mantle normalized plots (McDonough and Sun, 1995) of Mundwara carbonatitic rocks. b) Chondrite normalized REE plots (Nakamura, 1974) and primitive mantle normalized plots (McDonough and Sun, 1995) of alkaline rocks.

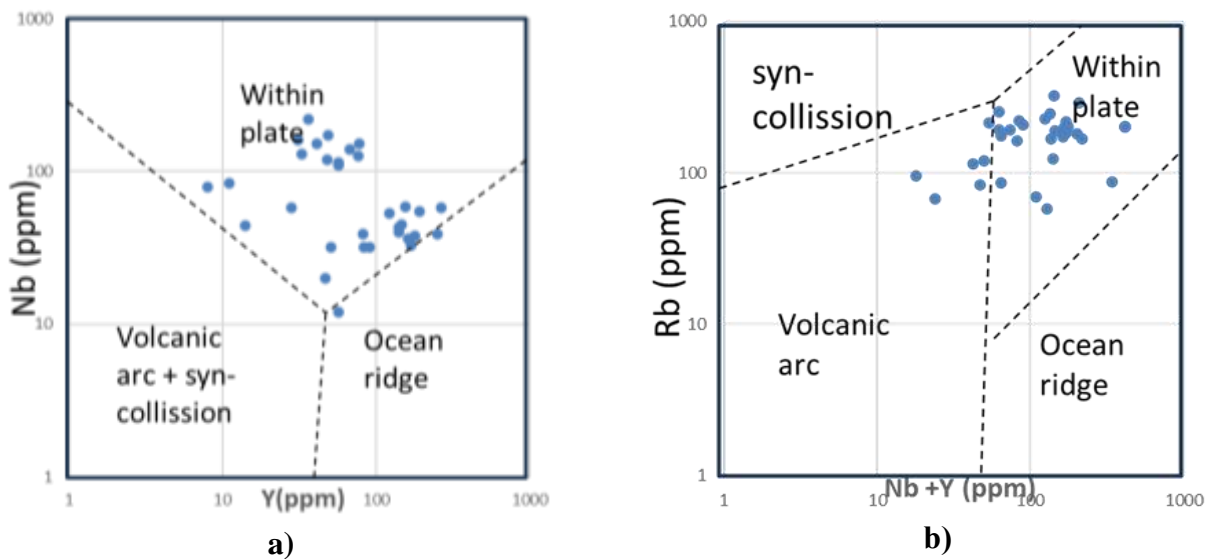


Fig.7: a) Tectonic setting discrimination diagram for alkaline rocks after Pearce et al. (1984), Pearce (1996) b) Batchelor and Bowden (1985)

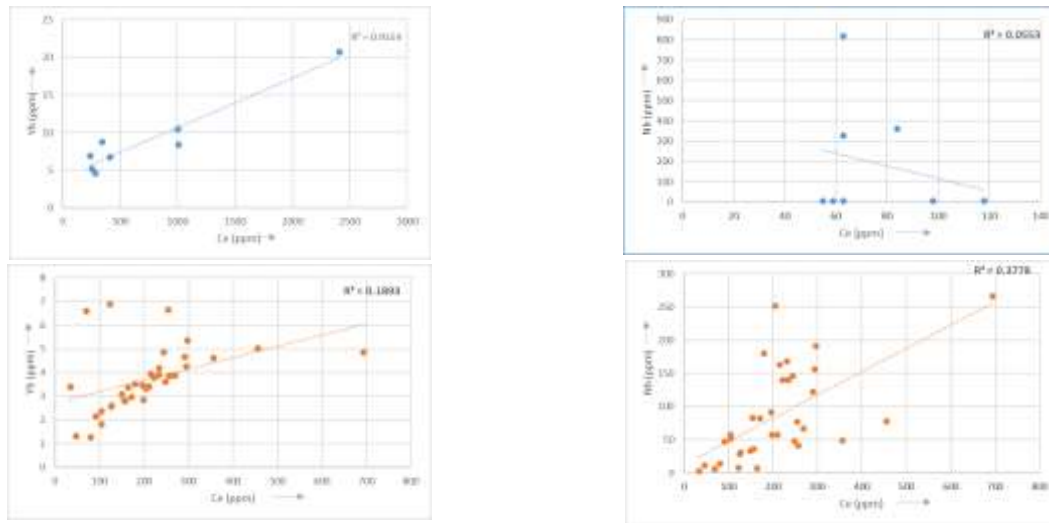


Fig. 8: Variation diagram of MgO vs CaO, Sr vs Ba, La vs Y, Y vs Nb, Zr vs Nb, Yb vs Y, Yb vs Nb, Sr vs Nb, Ce vs Y, Yb vs Ce and Nb vs Ce for carbonatites and associated alkaline rocks.

Fractional crystallization in Mundwara Igneous complex

The increase in LREE and Ba contents from calcio-carbonatite to ferro-carbonatites in Mundwara like many carbonatite complexes worldwide (LeBas 1989), is indicative of fractional crystallization of parental carbonated melt for Mundwara carbonatites. The effect of fractional crystallization is more pronounced in the chondrite-normalized $(La/Yb)_{CN}$ vs. La_{CN} plot (Fig. 9a), where it can be clearly seen that La being highly incompatible, has partitioned more into the late crystallized ferro-carbonatites. The overlapping distribution of $(La/Yb)_{CN}$ versus $(La)_{CN}$ in calcite carbonatites and ferro carbonatites can also be considered as an evidence for their derivation from one single melt by fractional crystallization. A fractionation trend is also observed for the associated alkaline silicate rocks. Generation of carbonatites as a result of fractional crystallization of carbonated silicate magma is a known possibility (Korobeinikov et al 1998; Veksler et al 1998a). This would mean that crystallization trends in alkaline rocks and carbonatites should have identical slopes. However, the trends observed in $(La/Yb)_{CN}$ vs $(La)_{CN}$ plot (Fig. 9a) rule out such a possibility.

The confirmation that silicate rocks and carbonatites of Mundwara Igneous Complex evolved independently comes from the plot of chondrite-normalized Nd/Sr vs Sr plot (Ray and Shukla 2004). Nd is incompatible in both silicate and carbonate systems, but more so in alkaline rocks and therefore, the slope of the fractional crystallization trend in alkaline rock is higher (Fig. 9b).

To determine whether the calcio-carbonatites and ferro-carbonatites of Mundwara Igneous Complex belong to a single crystallization sequence and do not represent two separate parental magmas, we took the help of Ba/Sr_{CN} versus Ba_{CN} plot (Fig.9c). Ba is believed to be highly incompatible during the crystallization of carbonatite minerals (Ionov and Harmer 2002; Klemme and Dalp'e 2003), whereas Sr abundance appears to remain constant (Ionov and Harmer 2002). Therefore, in the above plot as it is expected, the data from both types of carbonatites plot in a straight line which confirms our view that the calcite carbonatites and ferro-carbonatites of the complex have fractionally crystallized from a single parental melt. From the above discussion it is confirmed that two independent crystal fractionation processes, involving two separate parental melts (a silicate melt and a carbonate melt) by liquid

immiscibility were responsible for the formation of the alkaline silicate rocks and carbonatites of Mundwara Alkaline Complex.

Some LILE contents such as Ba and Sr also provide the information of the crustal assimilation process (Motoki et.al. 2015). The Sr and Ba contents tend to increase according to the silica saturation index (SSI). That could explain by increase of continental crust assimilation. Their upper limits elevate linearly by SSI. However, the concentrations of these elements are distributed randomly in the area beneath the upper limit, The SSI vs. Ba/Sr diagram (Fig. 9d) shows distinct trends of fractional crystallization and continental crustal assimilation. In the field of $SSI < -200$, negative correlation trend is observed because of fractional crystallization. In the domain of $SSI > -200$, positive trend is found due to continental crustal assimilation.

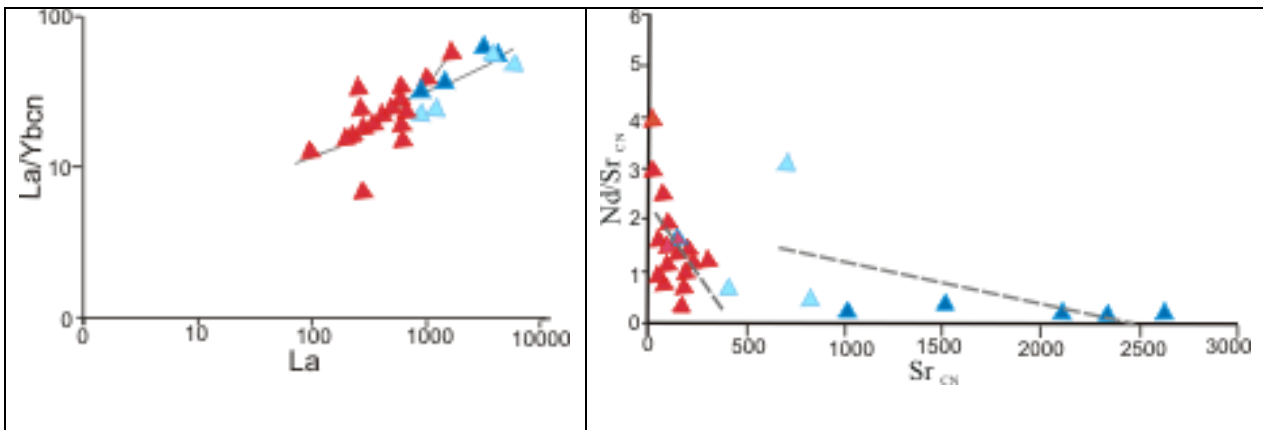


Fig.9: a) Plot of chondrite-normalized La/Yb_{CN} ratios versus La concentrations of alkaline silicate rocks and coexisting carbonatites of Mundwara Igneous Complex. Dashed lines are linear regressions on silicate rocks and carbonatites (Ray and Shukla 2004). b) Plot of chondrite-normalized Nd/Sr_{CN} ratios versus Sr concentrations. Dashed lines are linear regressions showing the trends of fractional crystallization (Ray and Shukla 2004).

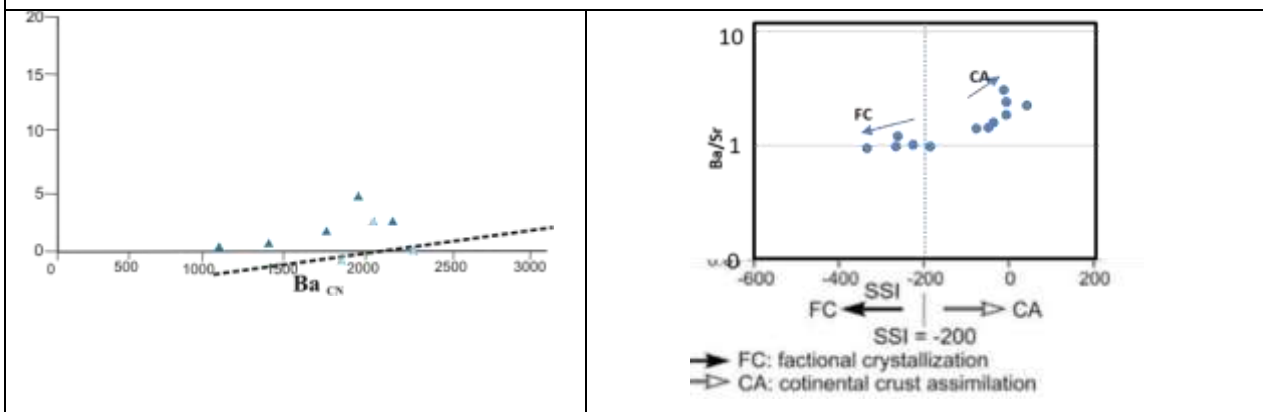


Fig.10: a) Plot of chondrite-normalized Ba/Sr_{CN} ratios versus Ba concentrations of Mundwara calciocarbonatites and ferrocarbonatites (Ray and Shukla 2004). b) Variation of alkali earth elements according to silica saturation index (SSI): SSI vs. Ba/Sr (ppm ratio). Motoki et.al. 2015.

8. Conclusions

Trace and rare earth element contents and their normalized patterns of Mundwara carbonatites are akin to those observed elsewhere. The incompatible trace element concentrations show a general increasing trend:

alkaline silicate rocks < calcite carbonatites < ferrocarbonatites. The contents and ratios of various trace elements clearly show that the calcite carbonatites and ferrocarbonatites of Mundwara have fractionally crystallized from a parental carbonate melt. We also find that the alkaline silicate rocks do not belong to the same crystallization sequence as the carbonatites, instead they represent products of fractional crystallization of a parental silicate melt. Our work brings us to the conclusion that a silicate-carbonate melt system yield results that are consistent with the suggestion that the parental carbonate and silicate melts for the complex have been derived from a mantle derived primary magma as a result of liquid immiscibility. The rocks of Mundwara Alkaline Complex have also undergone fractional crystallization as well as crustal assimilation.

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