Significant variability in the δ44/40Ca of global carbonatites: implications for carbonate recycling, magma differentiation and source-mantle mineralogy

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Abstract

Stable Ca isotopic composition (δ44/40Ca) of crustal carbonates are typically lighter than that of the bulk silicate Earth value (~1.05 potentially trace recycled crustal carbonates into the mantle. We report the Ca isotopic compositions of globally distributed carbonatites (n = 46), which are unique igneous rocks with more than 50% modal carbonate minerals, with eruption ages ranging from Precambrian until recent. The δ44/40Ca (w.r.t. SRM915a) of these carbonatites show a large range (0.35 uncertainty (0.08IISc. These samples are well-characterized in terms of their major and trace element geochemistry as well as Nd, Sr, B, C, and O isotopic compositions for selected samples. No systematic trend is observed between δ44/40Ca of the carbonatites and their eruption ages. Significant variability is observed in δ44/40Ca values in samples from individual provinces including those from the Oka complex in Canada (0.44 Newania complexes (0.44 South Indian carbonatites (0.65 the Palabora complex in South Africa (0.35 δ44/40Ca of carbonatites from Oka, Newania and the Ambadongar show strong correlations with Ca/Mg, Ca/Fe as well as CaO and MgO contents. The δ44/40Ca of the Oka and Ambadongar carbonatites show correlated variations with their Mg# and K/Rb ratios, respectively. The large variability in δ44/40Ca of global carbonatites is explained in terms of: (1) presence of isotopically lighter ancient subducted carbonates in the mantle-source regions and carbonate metasomatism of the mantle, (2) partial melting and differentiation of the carbonatite magma and (3) heterogeneity in the source-mantle mineralogy of carbonatites.

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Introduction

Stable Ca isotopic compositions ($\delta^{44/40}Ca_{SRM915a}$) of crustal carbonates are typically lighter (typically 0.2 ‰ or lower, *Huang et al., 2011; DePaolo, 2004*) than the bulk silicate Earth (BSE) or upper mantle compositions (0.94-1.05 ‰) (*Huang et al., 2010, Kang et al., 2017, DePaolo, 2004*). Carbonatites are unique igneous rocks with more than 50% modal carbonate minerals. Hence, these unique igneous rocks provides ideal opportunity to study the role of recycled carbonates in their mantle sources. In this study, we report major, trace element concentrations and Ca-Sr isotopic compositions of WR-carbonatites of different ages (from the Precambrian to recent) and exposed in different geographical locations of the world to understand their origin as well as explaining the reason of variability of $\delta^{44/40}Ca$ in such unique igneous rock types.

Sampling of carbonatites: location and ages

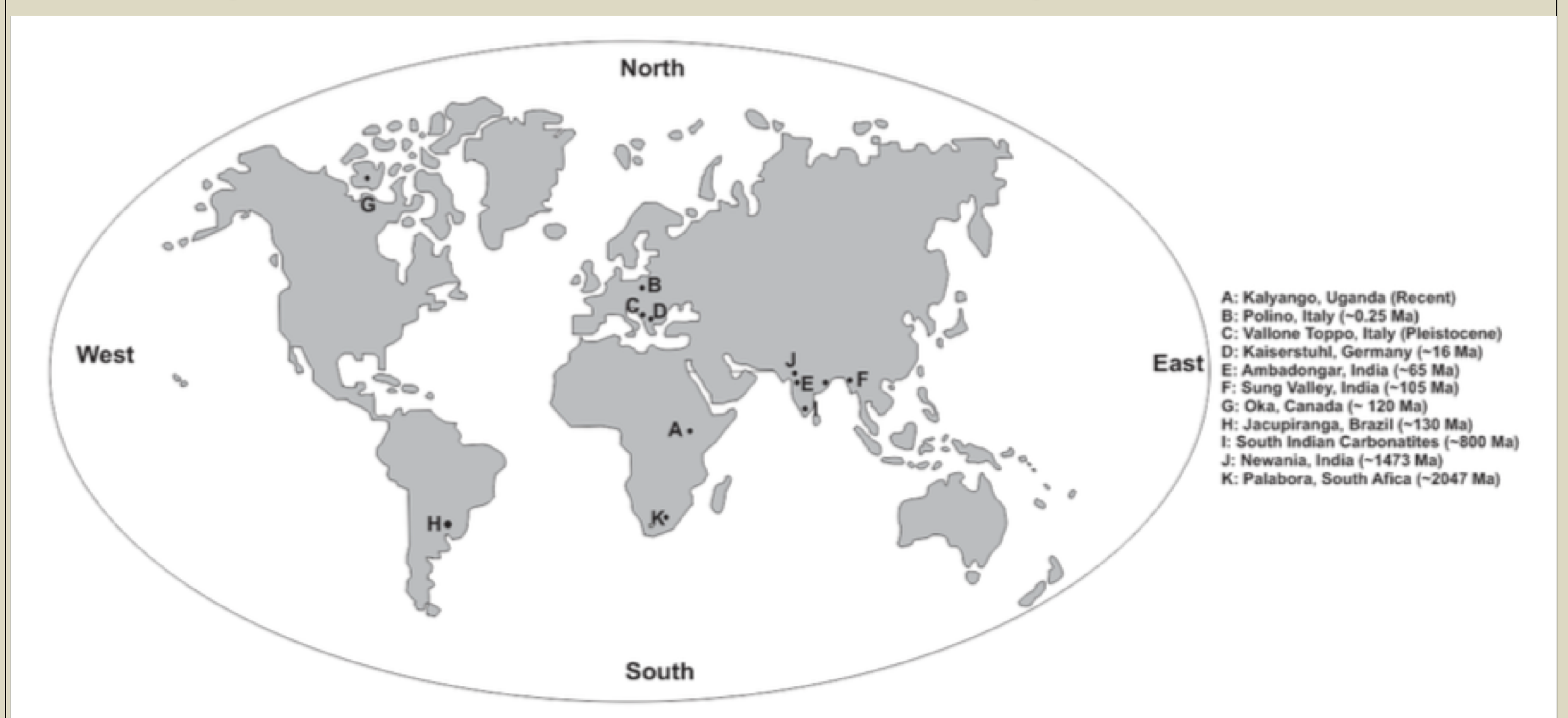

Figure 1. Geographic locations of the carbonatites (n = 46) analysed in the present study with their eruption ages.

Classification of carbonatites

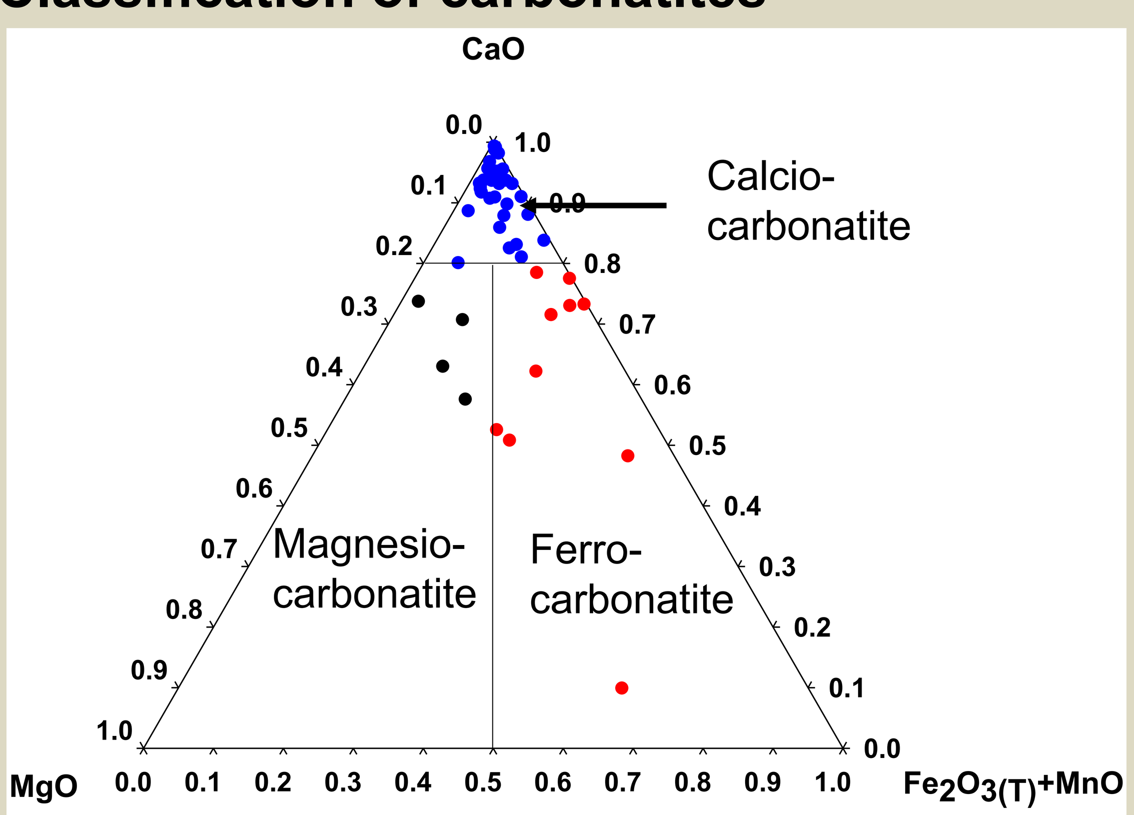

Figure 2. Most of the studied global carbonatites analysed are calcio-carbonatites while few carbonatites plot in the ferro-carbonatite and magnesio-carbonatite domains.

Mass-dependent isotopic fractionation

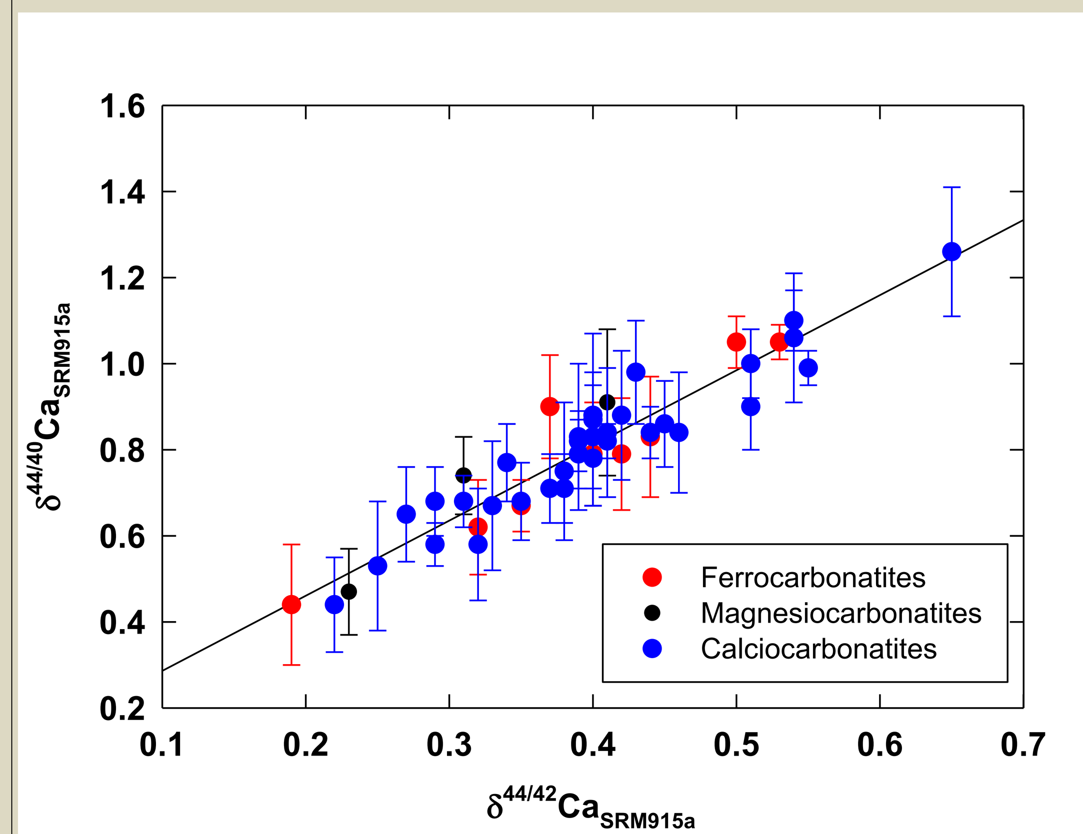

Figure 3. Plot of $\delta^{44/40}Ca$ versus $\delta^{44/42}Ca$ of global WR carbonatites. All the carbonatites plot on the theoretical mass dependant fractionation line. External precision for $\delta^{44/40}Ca$ is better than 0.08‰ (*Mondal and Chakrabarti, 2018*).

$\delta^{44/40}Ca_{SRM915a}$ of global carbonatites

Average $\delta^{44/40}Ca$ from a complex

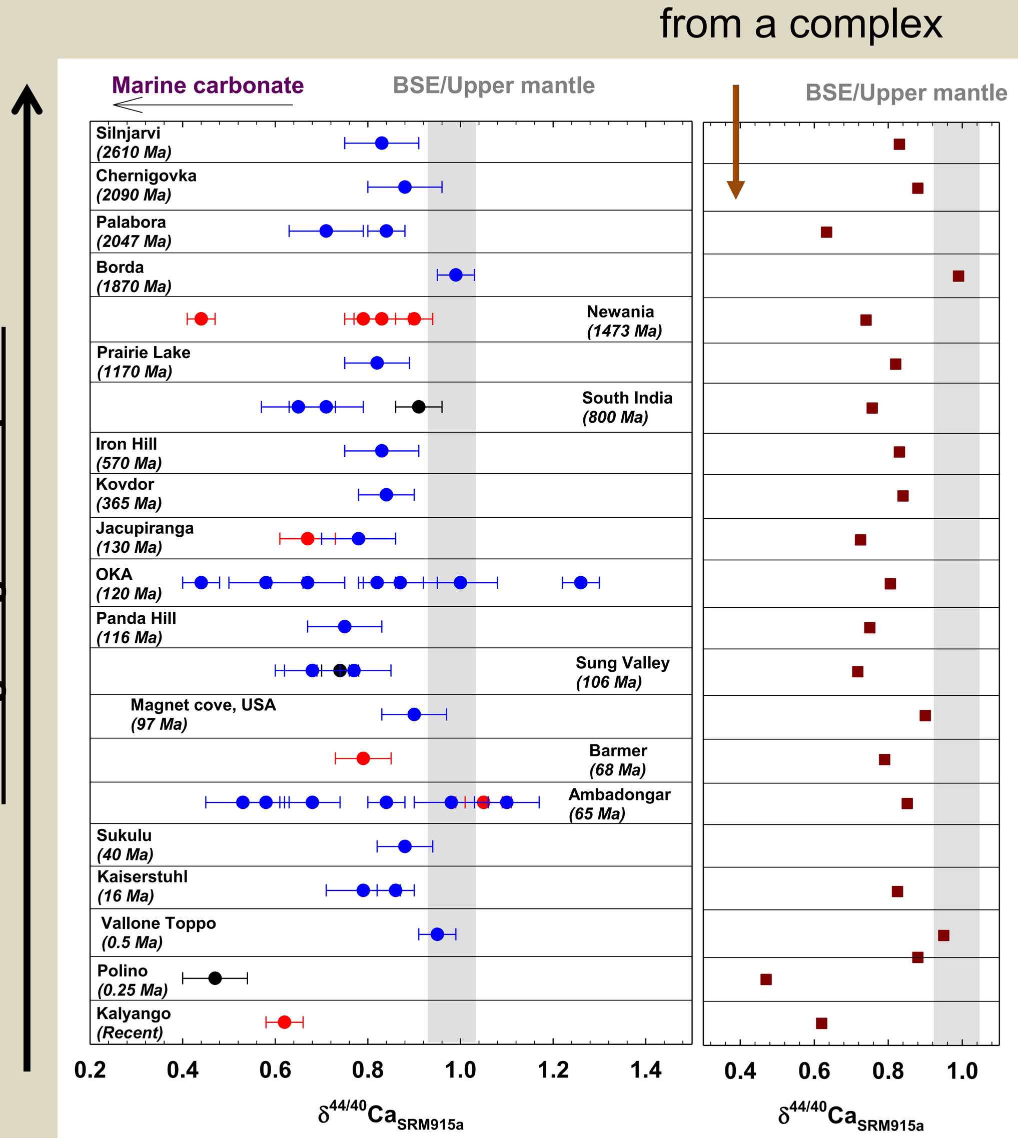

Figure 4. **(a)** Plot of $\delta^{44/40}Ca$ (**0.35-1.26 ‰, n= 46**) of global carbonatites. No apparent variation in $\delta^{44/40}Ca$ has been observed with their corresponding eruption ages.

$\delta^{44/40}Ca$, $\delta^{11}B$ and $^{87}Sr/^{86}Sr_{(t)}$ of global carbonatites

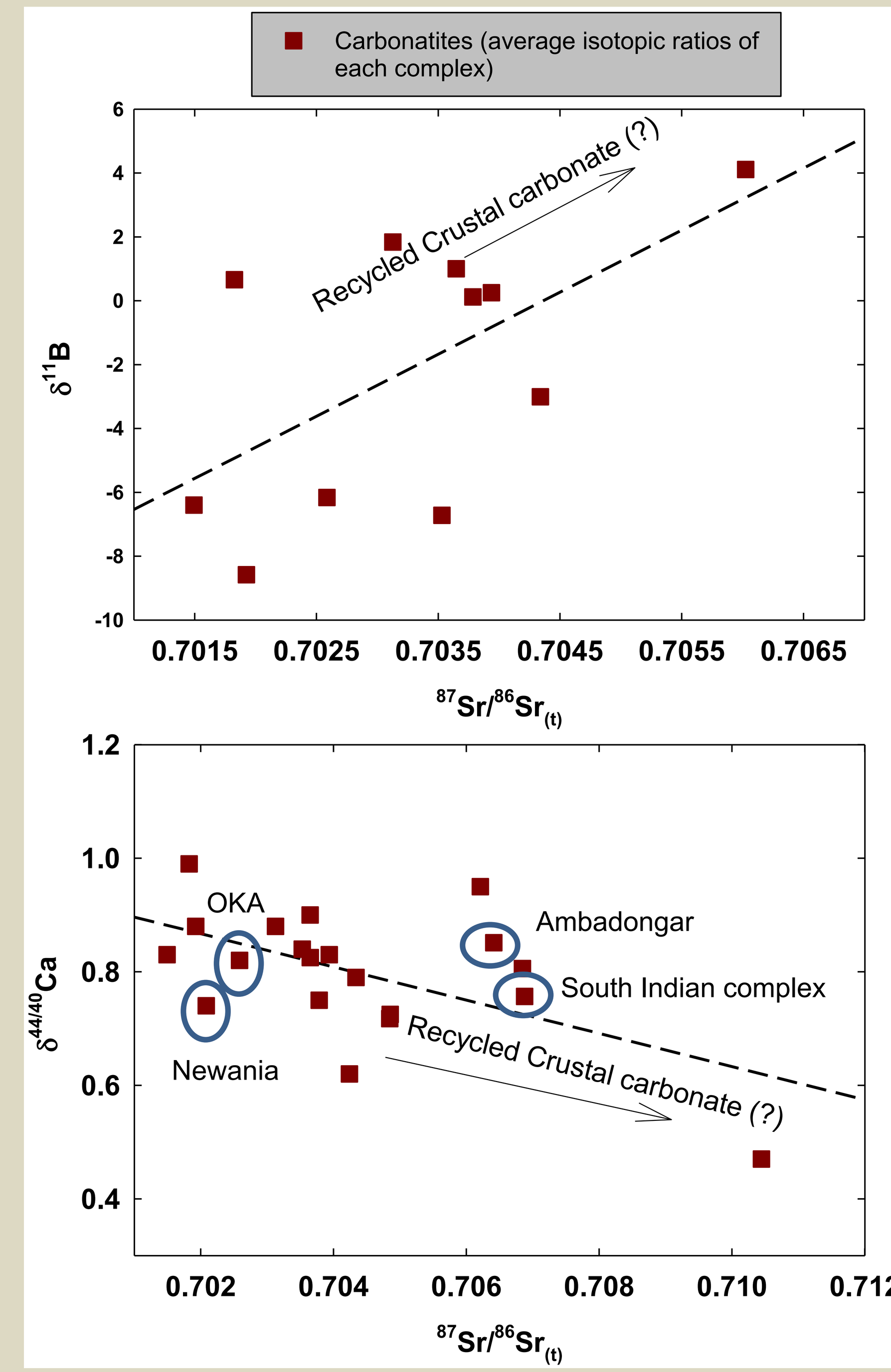

Figure 5. Plot of $^{87}Sr/^{86}Sr_{(t)}$ versus $\delta^{11}B$ (top panel) and $\delta^{44/40}Ca$ of whole rock carbonatites from multiple carbonatite complexes. Average values are plotted for carbonatites complexes reporting multiple whole rock analyses. B isotopic compositions (n = 17) are reported in *Hulett et al., 2016.*

Newania carbonatite complex

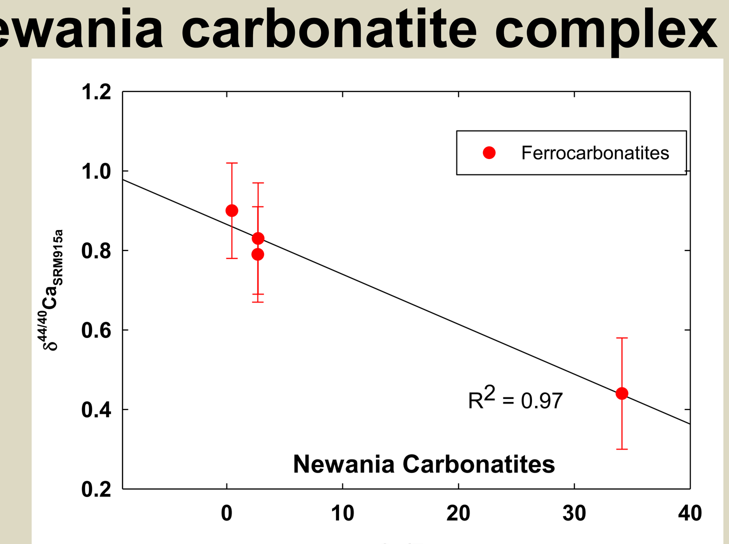

Figure 6. $\delta^{44/40}Ca$ of Newania carbonatites (n= 4) varies with Ca/Fe content. This could indicate that $\delta^{44/40}Ca$ of carbonatites can vary with **mineralogical compositions.**

OKA carbonatite complex, Canada (~120 Ma)

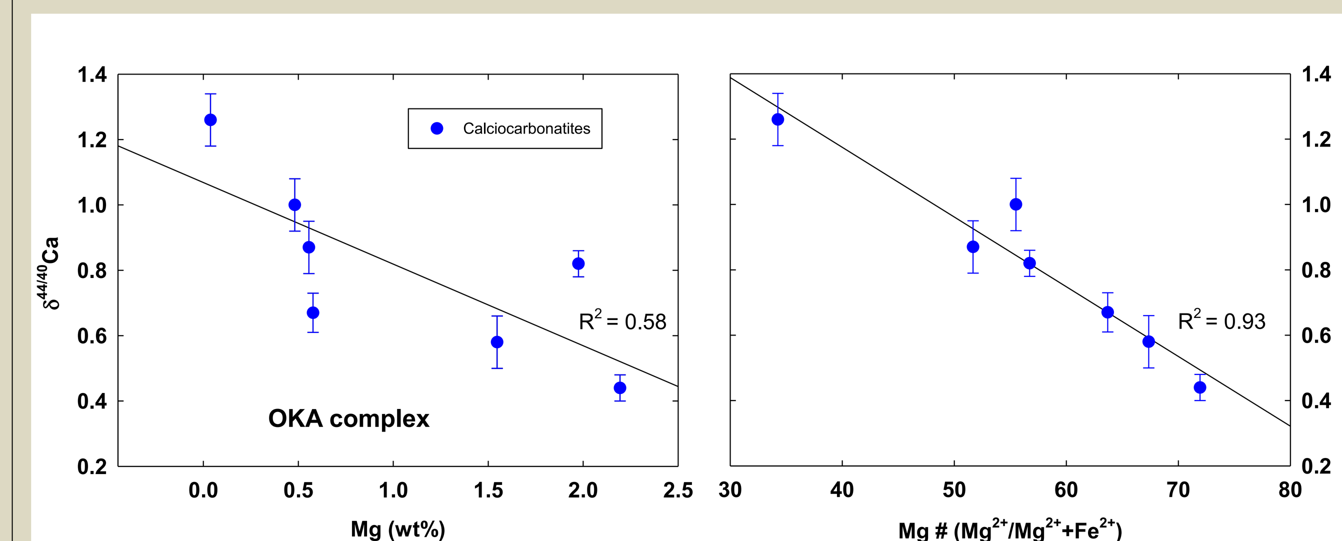

Figure 7. $\delta^{44/40}Ca$ of carbonatites (n = 7) from the OKA complex shows strong correlation with their Mg concentration and Mg# , thus indicating $\delta^{44/40}Ca$ can vary depending on the **nature and degree of differentiation of the magma**

South Indian Carbonatites (~800 Ma)

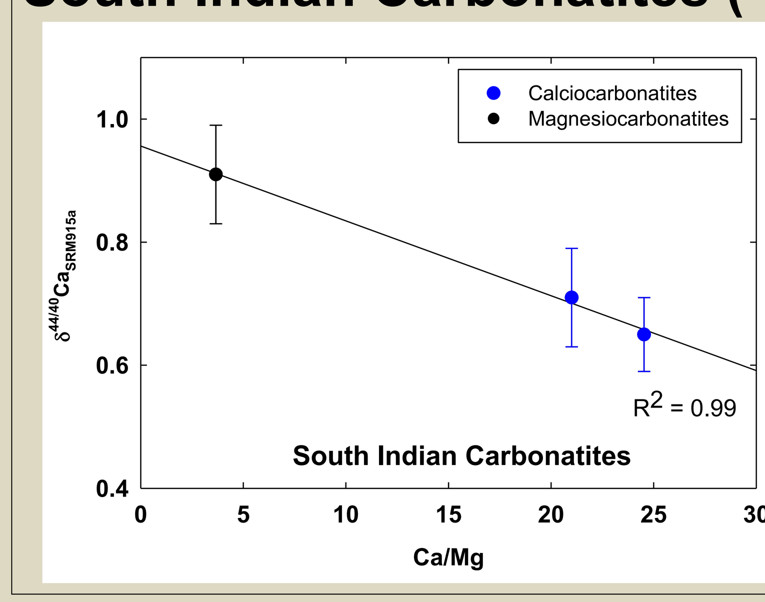

Figure 8. $\delta^{44/40}Ca$ of carbonatites from the South Indian occurrences (n = 3) shows strong correlation with their corresponding Ca/Mg ratios, which apparently indicates that $\delta^{44/40}Ca$ of these carbonatites might be a function of their **mineralogical compositions**

Ambadongar carbonatite complex, India (~65 Ma)

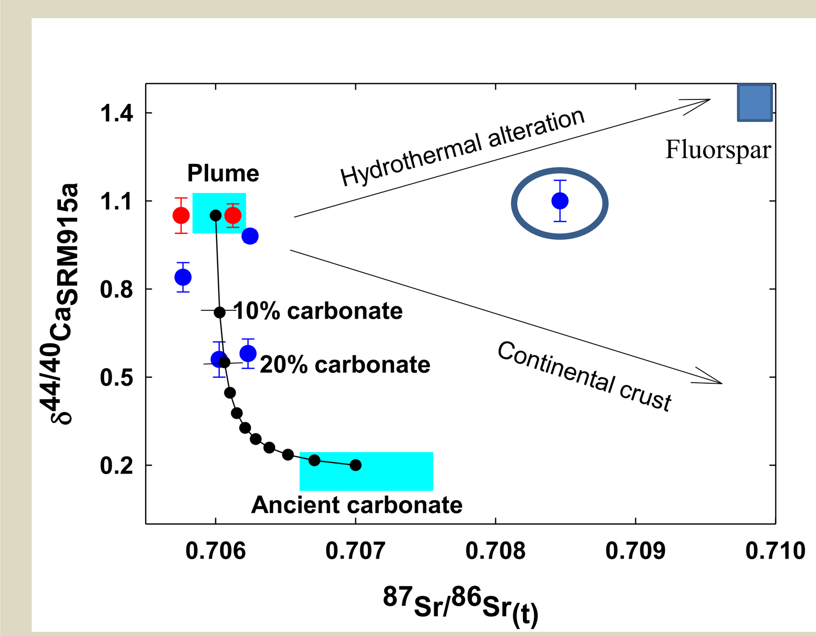

Figure 9. Large range of $\delta^{44/40}Ca$ values of carbonatites (*n*= 6)from the Ambadongar complex, India and their co-variation with $^{87}Sr/^{86}Sr_{(t)}$ can be explained by **role of recycled carbonates** in the Reunion plume source. One carbonatite (*n*= 1)shows effect of **hydrothermal alteration**

Conclusions

(1) No variability of $\delta^{44/40}Ca$ of global carbonatites with their age of eruption.
(2) Variability in $\delta^{44/40}Ca$ of carbonatites from a particular complex can vary as a result of (i) *presence of isotopically lighter ancient subducted carbonates in the mantle-source regions*, (2) *degree of differentiation of magma* and (3) *mineralogical compositions.*
Hence, a comprehensive study of carbonatites from a particular complex is required to explain the variability in $\delta^{44/40}Ca$ of these rocks