Isotopic evidence for late-stage processes in carbonatites: rare earth mineralization in carbonatites and quartz rocks at Kangankunde, Malawi

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Introduction

The characteristic enrichment of carbonatites in the rare earth elements often results in the formation of significant rock-forming quantities of *REE* minerals in the final stages of emplacement. Processes at this stage are poorly understood and can involve quartz rocks as well as carbonates.

The Kangankunde carbonatite, part of the Chilwa Alkaline Province, Malawi, has no associated silicate rocks nor calcite carbonatite but consists almost entirely of 'late' magnesio- and ferrocarbonatites which host major monazite-(Ce)-strontianite-baryte mineralization. A similar assemblage, of monazite-(Ce)-baryte- florencite-(Ce)-quartz occurs within the main 1.6 by 0.8 km area of carbonatite and also within the 2 km fenite aureole and beyond. This study aims (1) to test the relationship between minerals in the carbonatites and quartz rocks using Sm-Nd isotopes and (2) to use C, O and Sr isotopes to determine the final stage evolution of the carbonatite and possible interaction with externally-derived fluids and country rock.



FIG. 1. Sm/Nd isochrons for Kangankunde rocks.

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On the basis of textural evidence such as the presence of pseudomorphs containing the *REE* mineral assemblage, veinlets and drusy cavities it is thought that much of the *REE* mineralization replaces earlier carbonatite and so mineral separates and concentrates were used where possible.

All isotopic analysis was carried out at NIGL using standard bulk chemical techniques. Normalization factors used are 0.7219 for ¹⁴⁶Nd/¹⁴⁴Nd and 0.1194 for ⁸⁶Sr/⁸⁸ Sr. Fourteen radiogenic and 80 stable isotope determinations were made

Relationship between quartz rocks and carbonatites

Most, but not all, the quartz rocks are directly related to the carbonatite. An isochron (Fig. 1) links monazite-(Ce) and secondary apatite from carbonatites with monazite-(Ce), florencite-(Ce) and *REE*-rich apatite from quartz rocks. Fenite itself also plots on the isochron. However, a quartz-fluorite rock, 1.5 km from the carbonatite, does not relate to the same carbonatitic source and is considerably younger (Fig. 1).

Source of rare earths

Neodymium and Sr isotope results for Kangankunde minerals are compatible with values previously obtained for mantle-derived East African carbonatites and would plot at the most depleted end of the 'East African carbonatite line' (Bell and Blenkinsop, 1989).

Carbonates from the *REE* mineralization and host carbonatites

Having said that the carbonatite is mantle-derived, none of the carbonates from the *REE*-rich rocks



FIG. 2. Carbon and oxygen isotopes in Kangankunde carbonates.

plot in the mantle-derived primary igneous carbonate box (PIC, values used here are from Keller and Hoefs, in press). Only *REE*-poor, apatite-rich dolomite carbonatites ('beforsites') which predate the *REE* carbonatites plot in the PIC range. When affected by *REE* mineralization, this dolomite (d* on Fig. 2) re-equilibrates to C and O values close to that of the carbonate in the *REE*-rich rocks.

Strontianite, representative of the REE mineralization, has a narrow range of δ^{18} O and δ^{13} C values in a variety of carbonatites. It is close to isotopic equilibrium with associated light-coloured ferroan dolomite, (fractionation factors from the compilation in Deines (1989)), at temperatures of about 400°C obtained from preliminary fluid inclusion data. This rules out mineralization by a CO₂ phase which would have produced heavier O and C and places the REE mineralization very close to magmatic carbonatite, although the mineralizing fluid appears to have behaved metasomatically.

In contrast, the strontianite is clearly not in equilibrium with associated dark-coloured ankeritedolomite carbonates (Fig. 2). This is explained best by a subsequent re-equilbration and recrystallization of much of the carbonate which left the strontianite unaffected. Magnetic separates demonstrate that the ankerite and ferroan dolomite recrystallized to lower Fe contents, higher $\delta^{18}O$ and lower $\delta^{13}C$, in a trend (A on Fig. 2) towards secondary calcite, probably in response to low temperature interaction with groundwater, possibly as a result of deep weathering.

A second less common trend to high δ^{18} O with little change in δ^{13} C (B) is likely to correspond to re-equilibration of the Fe-containing carbonates with carbonatite-derived fluid as the intrusion cooled. Again the strontianite was unaffected and the *REE* mineralization is not related to this process.

Formation of REE-rich quartz rocks

REE-rich quartz rocks have a distinct range of quartz δ^{18} O values from 12.5 to 17.6 per mil (SMOW) which are higher than the 8.3 to 9.0 measured in quartz from low grade fenite and the younger quartz-fluorite and compatible with crystallization from carbonatitic fluid at temperatures 200°C below that of the carbonates. There is no evidence of groundwater interaction and δ^{18} O quartz values are too low for the quartz to have been formed during the late carbonate interaction with groundwater (trend A) which produced the secondary calcite. Successively higher quartz δ^{18} O values indicate lower temperatures in the outer rocks.

Interaction of mineralizing fluids with country rock

Only florencite in the outermost quartz-florencite rock has higher initial 87 Sr/ 86 Sr ratios than the main carbonatite (0.703423, similar to high grade fenite, and compared with 0.7030 for minerals in the main carbonatite) suggesting that only in this outermost mineralization is there a significant interaction with the country rock.

References

- Bell, K. and Blenkinsop, J. (1989) Neodymium and strontium isotope geochemistry of carbonatites.
 In: Bell, K. (ed.) Carbonatites: genesis and evolution. 278-300, Unwin Hyman, London
- Deines, P. (1989) Stable isotope variations in carbonatites. In: Bell, K. (ed.) Carbonatites: genesis and evolution. 301-59, Unwin Hyman, London
- Keller, J. and Hoefs, J. (in press) Stable isotope characteristics of recent natrocarbonatites from Oldoinyo Lengai. In: Bell, K. and Keller, J. (eds) Oldoinyo Lengai and the petrogenesis of natrocarbonatites. IAVCEI Proceedings in Volcanol.