Late-stage apatite: a potential HREE-enriched co-product of LREE minerals in carbonatites

Sam Broom-Fendley
Camborne School of Mines, University of Exeter, UK

Frances Wall  Gus Gunn  Aoife Brady  Will Dawes  Jens Andersen
• Chilwa Alkaline Province, Malawi
• Late Jurassic/Early Cretaceous
• Mkango Resources Ltd.
• REE-resource, 13.2 Mt @ 1.62 % TREO, 18.6 Mt @ 1.38 % TREO. (Cut-off, 1 %)
Drill core results show Y–P$_2$O$_5$ correlation

- Higher REE concentration in the later-stage ferruginous-calcite-carbonatite (as could be expected)

- Correlation between P$_2$O$_5$ and Y in all lithologies

- Evidence apatite (Ca$_5$(PO$_4$)$_3$F) is the control on the HREE concentration
LA-ICPMS of apatite confirms M/HREE-enrichment

- Y concentration of fluorapatite from Songwe is higher than data from other carbonatites and granites

Typical carbonatite

Data compiled from 24 different published studies

Granite data

Carbonatite data

Songwe data (Ap-3)
Why is apatite M/HREE-enriched?

Questions:
• What is the **paragenesis** of the apatite at Songwe?
• At which **temperature** did crystallisation take place?
• What is the **source of the crystallising fluid**? Is it meteoric or magmatic?

Techniques:
• Detailed **mineralogy**, coupled with laser ablation data
• Fluid inclusion analyses
• **O and C** isotope analyses of **carbonates** and **apatite**

Also see talk by Safaa Al-Ali, next...
Songwe Paragenesis

- 3 main carbonatite stages
  - **Magmatic**
  - **Hydrothermal**
  - **Alteration**

- Hydrothermal stage subdivided into
  - Calcite rich
    - apatite
  - Ankerite rich
    - synchysite

- Apatite occurs in 4 stages
  - Ap 1, 2 – magmatic
  - Ap 3, 4 hydrothermal

How does the apatite vary with the paragenesis?...
Earliest Songwe Apatite (Ap-1)

Medium-grained, calcite carbonatite

Isolated occurrences in breccia

Apatite habit

lozenge shaped, eu-subhedral

Similar to typical carbonatite apatite

Apatite chemistry

LREE Rich, around 3 % REO substituting

High Sr, low Mn

Normal for igneous apatite

Calcite

500 μm
Earliest Songwe Apatite (Ap-2)

Apatite habit: **Zoned** and **fractured**

Inclusions are rare

Closer look at an ovoid grain (BSE)

Laser ablation data, compared with data from other carbonatite-apatite

50 μm

First signs of HREE enrichment at Songwe

:REE distribution

Slight **Dy enrichment** on rim
Magmatic—Hydrothermal apatite

(Ap1,2—Ap-3)

Early ovoid apatite (Ap-1,2)

Later anhedral apatite (Ap-3)

Transition to non-magmatic textures
Magmatic—Hydrothermal apatite
(Ap1,2—Ap-3)

Early ovoid apatite (Ap-1,2)
Later anhedral apatite (Ap-3)

Later apatite is more Y-rich

Later apatite is more Y-rich
Cathodoluminescence images

Hydrothermal apatite (Ap-3)

- Most common apatite type at Songwe
- Stringers, anhedral, banded
- Same apatite habit in all carbonatite types
- Different REE distributions
Hydrothermal apatite Ap-4

- Found outside the main carbonatite body
- Abundant fluorite
- Very HREE-rich
- Xenotime overgrowths
Apatite crystallisation temperature

Increasing inclusion abundance
Decreasing T
Decreasing CO₂ (?)

– Mostly LV inclusions
– Lower T
– Many open, hard to analyse
– Small data set, wide spread of Th
Fluorite – post apatite

Fluorite provides a more reliable T constraint on apatite crystallisation.

Incorporation of fenite
Ferroan-calcite
Apatite
Calcite
Fluorite
Baryte
Quartz
Xenotime

Homogenisation temperature
Stable isotope evidence for hydrothermal alteration - carbonates

Carbonate isotope data indicates a hydrothermal influence --- meteoric or deuteritic?
Stable isotope evidence for hydrothermal alteration - apatite

New isotope data – in collaboration with NIGL, UK

Apatite:

Not influenced by diffusion

Records conditions during REE mineralisation

Apatite isotope data suggests a meteoric influence

Apatite isotope data

Summary

Ap-1,2

Ap-3

Ap-4

More meteoric values

$\delta^{18}O_{\text{PO}_4}$ (%o, VSMOW)

Sample number

Paragenesis

1 sd analytical uncertainty
Trends in REE concentration

Magmatic:
- Calcite
- Zircon
- Apatite

Early carbonatite
- δ¹⁸Oₐp: 2–3‰
- ~300 °C?

Transitional/hydrothermal:
- Ovoid and anhedral apatite
- Synchysite-(Ce)
- Florencite
- Ferroan calcites
- CO₂-bearing inclusions

δ¹⁸Oₐp: 1–2‰

Late carbonatite
- 180 °C
- 160 °C
- Sm/Dy
- Fluorite, baryte calcite
- Xenotime formation
- No CO₂ inclusions found

δ¹⁸Oₐp: 0–1‰

Summary

Conclusions

Questions:
• What is the **paragenesis** of the apatite at Songwe?
• At which **temperature** did crystallisation take place?
• What is the **source of the crystallising fluid**? Is it meteoric or magmatic?

Answers:
• Complicated! But dominantly **anhedral and hydrothermal**. Varied REE distribution
• Uncertain, but limited FI data suggests low-T, but above **160 °C**
• Isotope data suggest interaction with **meteoric water** caused crystallisation