The Petrogenesis and Geochemistry of the Zandkopsdrift Carbonatite Complex, Namaqualand, South Africa

Abstract 259134

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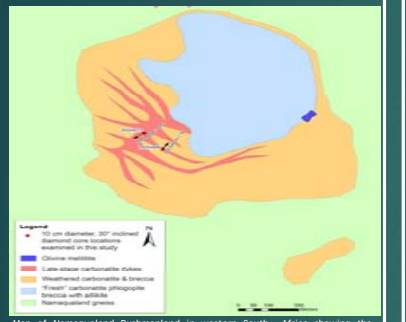
INTRODUCTION

Carbonatites are igneous rocks composed mainly of carbonate minerals and are typically associated with alkaline magmatic activity. They may be intrusive or extrusive, with or without associated alkaline silicate rocks (e.g. Woolley & Kjarsgaard, 2008). Carbonatite varieties are named on the basis of the dominant carbonate minerals present: Calciocarbonatite ($CaCO_3$, Calcite), Magnesiocarbonatite ($(Ca\,Mg(CO_3)_2$, Dolomite), Ferrocarbonatite ($(Fe,Mg,Mn)_2(CO_3)_2$) and Natrocarbonatite ($Na.K(CO_{3)2}$) .

GEOLOGICAL SETTING

Simplified geological map of the Zandkopsdrift Carbonatite Complex, modified from Harper et al., (2015) and Venter et al., (2010).



Map of Namaqualand Bushmanland in western South Africa showing the regional geology and distribution of diatremes of the southern NBW province. The main southern portions of the Namaqualand and Bushmanland diatreme clusters are outlined. The circled locality marked "Zand." is the Zandkopsdrift complex. Modified from Viola et al. (2012)

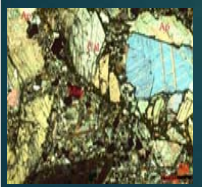
Zandkopsdrift is a 55Ma (Venter et al., 2010) ≈1km diameter intrusive complex containing carbonatite breccias and dykes with subsidiary quantities of aillikikite (potassic ultramafic lamprophyre) and olvine melilitite. It is part of the NE-SW-oriented, age progressive (50-80 Ma) "Namaqualand-Bushmanland-Warmbad" swarm of melilitite & kimberlite diatremes extending 400 km from the west coast of Namaqualand to SE Namibia (Moore & Verwoerd, 1985). The Zankopsdrift complex includes a weathered cap zone that contains economic quantites of rare earths (up to 17 wt.% total RE oxides; Venter et al. 2010).

SAMPLE COLLECTION

The freshest available samples were used. Most are core samples from >100 m below the altered cap zone at 2 locations (courtesy Frontier Rare Earths). A few additional samples were obtained by surface sampling. Carbonatite samples range in colour from off-white to dark grey, and all of the silicate rock samples (aillikite and melilitite) are medium to dark gray

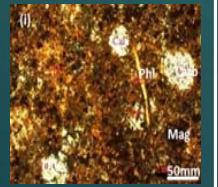
Photo of fresh cored carbonatites from Zandkopsdrift sampled for this study

PETROGRAPHY



Photomicrograph of **calciocarbonatite** (sövite) dominated by calcite and apatite (under XPL)

Photomicrograph of **olivine melilitite**: Olivine phenocrysts in groundmass (under PPL)

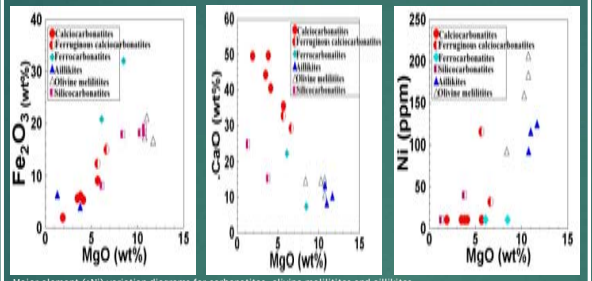


Photomicrograph of aillikite: Colorless calcite is set in a phlogopite-rich groundmass (under PPL)

GEOCHEMISTRY

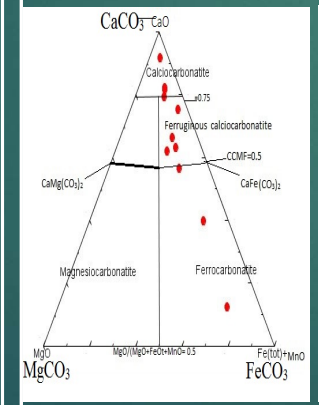
Major Elements were analysed by XRF Spectrometry and Trace Elements by ICP-MS at UCT

Carbonatites have low to moderate Mg-numbers (35-65), variable MgO contents (1.2-8.50 wt.%) and high Ca/Ca+Mg (0.73-0.97 in atomic units) indicating that they are not likely simple mantle melts. Aillikite and olivine melilitite constitute a significant proportion of Zandkopsdrift. These rocks have relatively low SiO_2 (25 - 31 wt.%) and Al_2O_3 (5.3 - 6.1 wt.%), high K_2O (6 - 6.3 wt.%) and TiO_2 (5.6 - 9.5 wt.%) and moderate Mg numbers (51 - 58).



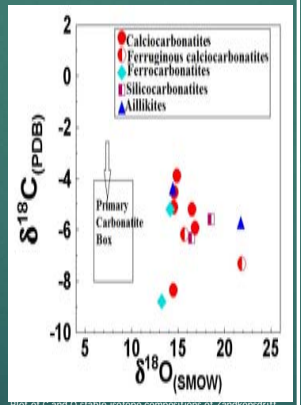
Major element (+Ni) variation diagrams for carbonatites, olivine melilitites and aillikites

CLASSIFICATION OF CARBONATITES



Model classification for compositions of Zandkopsdrift carbonatites (molar proportion) After Gittins and Harmer (1997).

$\delta^{18}O$ AND $\delta^{13}C$ ISOTOPES

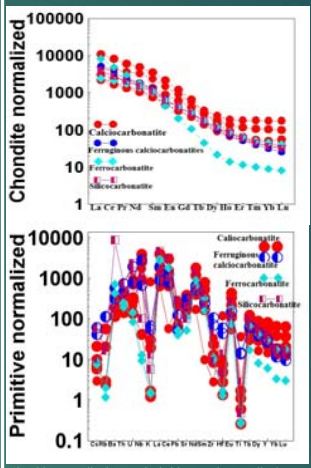


Plot of C and O stable isotope compositions of Zandkopsdrift carbonatites and aillikite $\delta^{18}O$‰ values +6 to +8‰$_{(SMOW)}$ and $\delta^{13}C$ -8 to -4‰$_{(PDB)}$ 'Primary carbonatite field' After Taylor 1967 and Keller & Hoefs 1995

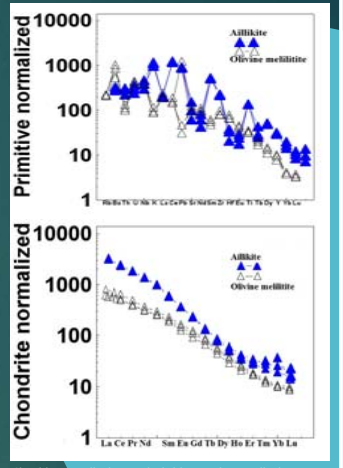
Zadkopsdrift carbonatites are classified as calciocarbonatites, ferruginous calciocarbonatites and ferrocarbonatites on the basis of mineralogy and mineral chemistry using molar proportion Gittins and Harmer (1998). Our sample set also includes a few silicocarbonatites, with SiO_2 enrichment due to secondary processes. Some calciocarbonatites display relatively high Fe and Mn contents and are classified as ferruginous carbonatites

Carbonate stable isotopes were analysed by conventional fluorination and gas source mass spectrometry at UCT. $\delta^{18}O$ and $\delta^{13}C$ isotope values were measured for carbonatites and aillikites. The $\delta^{13}C_{PDB}$ values are close to those expected for mantle-derived carbonatites (-3.9 to -8.83‰), whereas the $\delta^{18}O_{SMOW}$ values are significantly higher (+13. 25 to 21.84‰), likely due to low temperature aqueous alteration.

TRACE ELEMENT PATTERNS



Chondrite-normalised REE and Primitive mantle-normalised trace element diagrams for Zandkopsdrift **carbonatites (normalising values from Sun & McDonough, 1995)**

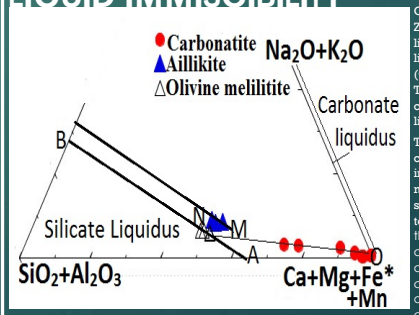


Chondrite-normalised REE and Primitive mantle-normalised trace element diagrams for **aillikites** and **olivine melilitites**

LREE are enriched relative to HREE in all Zandkopsdrift samples, with $(La/Yb)_N$ ratios of 27 to 901. Total rare earth oxide contents of the carbonatites range between 0.3 and 1.3 wt.%. The REE contents of the carbonatites are, in some cases, more than an order of magnitude higher than the olivine melilitite. Aillikites also have higher REE contents than in olivine melilitites but typically less than those in carbonatites. The carbonatites (and to a lesser extent, the aillikites) also display strong negative anomalies in K, Zr, Hf and Ti on their primitive mantle-normalised trace element patterns, typical of most mantle-derived carbonatites.

Some ratios of incompatible elements are indicative of metasomatic processes in the sources of carbonatites and related alkaline igneous rocks. Zr is variably depleted relative to Hf (Zr/Hf =60-278) and Nb is strongly enriched relative to Ta (Nb/Ta =52-946). Both of these element pairs have identical incompatibility during mantle melting and so likely represent elemental fractionations due to metasomatism.

LIQUID IMMISCIBILITY



Liquid immiscibility phase relation plot of the Zandkopsdrift carbonatite, olivine melilitite and aillikite. After Kjarsgaard and Hamilton 1988)

On the phase diagram at left, the Zandkopsdrift carbonatites plot on a tie line between the carbonate and silicate liquidi toward the lower right corner (Ca+MgO+FeO+MnO end-member). The olivine melilitites lie at the conjugate position very near the silicate liquidus.

This indicates that the Zandkopsdrift carbonatites either (a) were derived by immiscible separation from a moderately differentiated hybrid silicate-carbonate magma very similar to the olivine melilitites (point M) or (b) that they are derived from a more alkali-rich hybrid magma, such as the aillikites (point N), but that the carbonatites experienced alkali-loss due to diffusion into the surrounding country rocks during ascent.

Experimental studies suggest that such immiscible separation occurs at roughly 1250°C and between 15 and 24 km depth.

Further crystallization of the carbonatite magmas drove the compositional evolution from calciocarbonatite toward ferrocarbonatite

CONCLUSIONS

- MgO contents, Mg numbers and Ni & Cr contents are below those of primary mantle melts. High Fe and Mn suggest that Zandkopsdrift carbonatite and the silicate rocks are variably evolved. Phase diagram($Cafemics-SiO_2+Al_2O_3-Na_2O+K_2O$) indicate that Zandkopsdrift carbonatite separated out immiscibly from a enriched carbonate silicate magma with further fractional crystallization.
- Primary REE enrichment in Zandkopsdrift carbonatites and silicate magmas is likely due to derivation from one or more differentiated carbonate-rich source magmas derived from metasomatised mantle sources. Radiogenic isotope work (in progress) will allow us to constrain when this metasomatic source enrichment took place
- Zandkopsdrift carbonates have primary mantle carbon isotope signatures but heavy oxygen isotope signatures. The high $\delta^{18}O$ values observed in carbonatites and aillikites is most likely attributable to secondary alteration by groundwater
- Zandkopsdrift carbonatite is magmatic in origin but was later affected by secondary alteration which resulted in the elevated O stable isotopes. The 'mantle-like' C isotope composition is inconsistent with significant assimilation of C-bearing crustal rocks.
- The high overall REE contents of the Zandkopsdrift carbonatites (0.3 to 1.3 wt.%) are the result of (1) a LREE-enriched metasomatised mantle source and (2) significant fractional crystallization prior to emplacement.
- Zandkopsdrift carbonatites were most likely formed by immiscible liquid separation from a moderately fractionated carbonate-rich silicate parental magma, followed by further fractional crystallization

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