Electronic supplement material (ESM1) -Analytical techniques for the paper:

Neoproterozoic kimberlite and lamproite magmatism of the Man Craton, Liberia, from a common sub-lithospheric source

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To be submitted to: ***IKC2024 Special Issue – Mineralogy and Petrology***

Analytical techniques

Electron microprobe

Phlogopite analyses

The Camp Alpha phlogopite analyses were performed at the University of Johannesburg using a CAMECA SX 100 Electron Microprobe that is equipped with four wavelength dispersive spectrometers. Calibration standards are jadeite (Na), olivine (Mg), almandine (Al), diopside (Si), orthoclase (K), TiO_2 (Ti), Cr_2O_3 (Cr), rhodonite (Mn), hematite (Fe), wollastonite (Ca), and the beam accelerating voltage was 15 kV for both mica and spinel analysis. The beam current for the phlogopite analysis was 15 nA, with a beam diameter of 2-5 µm and an on-peak counting time per element of 10 – 50 s, depending on the element. The elements, F (Kα, fluorite), Cl (Kα, NaCl), Ca (Kα, wollastonite) and Ba (Lα, barite), were quantified in addition to the elements mentioned above.

Perovskite analyses

Perovskite analysis was performed for Camp Alpha dike samples (SC11-A1 n=5 grains and SC11-B1 n=5 grains) and two Weasua rock samples. Analysis of perovskite major elements was conducted at the University of Cape Town using a JEOL Superprobe JXA-8100 Electron Microprobe that is equipped with four wavelength dispersive spectrometers, a range of crystals (LDE1, LDE2, PETJ, PETH, TAP, LIF, LIFH), fitted with two gas-flow proportional and two sealed Xenon detectors. The electron beam was set to an accelerating potential of 15 kV, a beam current of 20 nA, and a diameter of 1-3 µm. Measurements were performed with counting times of 10 seconds on peak and 2 x 5 seconds on the background. The following standards were used for calibration: Pyrope (Si, Al, Fe), Ce Metal (Ce), La Metal (La), Rhodonite (Mg), Rutile (Ti), Clinopyroxene (Ca), Chromite (Ni), Hornblende (Na).

Bulk-rock major element analysis

The whole-rock samples were measured for their major and trace element compositions by the X-ray fluorescence technique in the Department of Geological Sciences, UCT. Major elements were determined on fused disks. These were prepared by first weighing out 2 grams of powder into a ceramic crucible, which was dried in an oven at 110ºC overnight and then weighed again. These weights were used to calculate the adsorbed water content (wt.% H_2O^-). The dried powders were placed into a furnace at 900 º C for at least four hours, removing for all the

structural volatiles such as H_2O and CO_2. This also oxidised all of the ferrous iron oxidized to ferric iron. After cooling in a desiccator, the crucibles with the ignited powder were weighed again to determine wt.% loss on ignition.

Fused disks were prepared from 0.7 grams of ignited sample powder added to 6 grams of Claisse XRF flux (composed of 57% Li tetraborate + 43% Li metaborate) and the flux-powder mixture was melted and homogenised in platinum crucibles using an automated Claisse M4 Fluxer. This device melted and mixed the flux-powder mixture for fourteen minutes to form a homogeneous melt. The melt was then poured into a heated Pt mould to create the fused disk, which was removed from the mould after cooling, ready for XRF analysis.

Pressed powder pellets for XRF trace element measurements were prepared from 10 grams of rock powder mixed with 2.5 grams of Hoescht tabletting wax (used as a binder). These were prepared as a homogeneous mixture and poured into a die, compacted and placed into a manual hydraulic press under 10 tonnes pressure.

Major oxide and trace element concentrations were obtained using the Panalytical Axios XRF spectrometer in the department of Geological Sciences at the University of Cape Town. The instrument was calibrated using well-known natural rock standards (issued by agencies such as MINTEK, the USGS and the Geological Survey of Japan) and prepared identically as samples for analysis. Calibration curves were generated by plotting the known concentrations against with the corrected peak – background intensities in order to determine elemental concentrations of the unknown. The correction procedure employed mass attenuation coefficients to correct for enhancement and absorption effects, and spectral overlap corrections (e.g., the overlap of RbK_β on YK_α).

XRF major and trace element analysis employed a wide array of approximately 50 international natural rock standards, of widely varying composition for calibration, prepared identically to the unknowns. These were issued by the geological surveys of the United States and Japan, MINTEK (the South African minerals agency), Natural Resources Canada and other agencies. A complete list of standards can be obtained from the authors on request.

Bulk-rock trace-element analysis

A total of 10 representative samples from Camp Alpha dikes plus the SARM-39 standard, were analysed for their trace element compositions using a Thermo Fisher iCAP-RQ quadrupole ICP-MS, in the Department of Geological Sciences at the University of Cape Town. For analysis, 0.05 g of sample powder was weighed out into 3ml Teflon vials, to which 2ml of a 4:1 mixture of concentrated hydrofluoric (HF) and nitric acids (HNO_3) were added. The Teflon vial was capped and placed into a Teflon capsule of a steel Parr digestion vessel. In order to decrease the pressure difference between the outer Teflon and inner Teflon vials, 2ml of pure water was added to the outer vessel. The digestion vessels are firmly sealed and put into a 200° C oven for a period of 24 hours to allow for complete digestion. After 24 hours, the 3 ml Teflon vial was removed from the capsule and the cap was carefully removed. The vial was put on a hot plate at 100° C to allow the acid mixture to evaporate, followed by the addition and subsequent evaporation of 2ml of pure nitric acid (HNO_3). Samples were redissolved in 1.7 ml of 2M HNO_3 and then quantitatively split by weight into two aliquots: ±0.2 mL taken for elemental abundance analysis; and ±1.5 mL for radiogenic isotope analysis. The 0.2 mL aliquots were dried down again, after which they and taken up and diluted using a stock solution of 5% HNO_3. Indium, Re, Rh and Bi were used as internal standards for analysis. Calibration curves were obtained from standards made from synthetic solutions.

Bulk-rock Sr-Nd-Hf isotope analyses

The procedure for the Sr-Nd elemental separation and isotope analyses of the Camp Alpha samples was the same as per Howarth et al. (2019), with similar external precisions. The 1.5 mL aliquots prepared above were used for the elemental separation of Sr and Nd, following sequential column chemistry after Pin et al. (2014). The analyses were performed using the Nu Instruments NuPlasma HR Multicollector Inductively Coupled Plasma Mass Spectrometer (HR MC-ICP-MS) housed in the Department of Geological Sciences at the University of Cape Town. The Sr isotope ratios were analysed as 0.2% HNO_3 solutions containing ~200 ppb of Sr, using NIST SRM987 ($^{87}Sr/^{86}Sr = 0.710255$) as bracketing reference standard (Waight et al., 2002). All Sr isotope data were corrected for Rb interference using the measured ^{85}Rb signal and the natural $^{85}Rb/^{87}Rb$ ratio. The exponential law and an $^{86}Sr/^{88}Sr$ value of 0.1194 were used for the correction of instrumental mass fractionation. The Nd isotope ratios were analysed as 2% HNO_3 solutions containing ~50 ppb Nd, using JNdi-1 ($^{143}Nd/^{144}Nd = 0.512115$) as reference standard (Tanaka et al., 2000). All Nd isotope data were corrected for Sm and Ce isobaric interferences using the

natural Sm and Ce isotope abundances and measured signals for ^{147}Sm and ^{140}Ce. The exponential law and a $^{146}Nd/^{144}Nd$ value of 0.7219 were used for the correction of instrumental mass fractionation. ε_{Nd} values are calculated relative to the chondritic (CHUR) composition of Bouvier et al. (2008). Results for samples and reference materials are reported in the SOM Table.

Hafnium separation and measurement of Lu/Hf ratio and Hf isotopes were performed at the Institute of Geochemistry and Petrology, ETH Zurich. For each sample around 100 mg of powder was dissolved in 3:1 HF-HNO_3 for 48 hours on a hotplate. The resulting solutions were dried down and repeatedly attacked with concentrated HNO_3 and HCl, after which the samples were dissolved in ~7M HNO_3. The resulting solutions were clear and free of solid residue. A 10% fraction of the dissolved sample was set aside for trace element analysis to quantify Lu/Hf and dried down before dilution into 2% HNO_3 + 0.005 M HF. Lu and Hf trace element concentrations were obtained following the procedures of Eggins et al. (1997). A multi-element spike containing Be, In and Bi was added prior to analysis of the solutions, which was undertaken using an Element XR sector field ICP-MS. The isotopes ^{9}Be, ^{115}In and ^{209}Bi were used as internal standards, and the CRPG basalt reference material BE-N was used for calibration. Internal counting statistics for multiple runs of the same sample solutions show that uncertainties for all elements are less than 5% (%RSD). USGS basalt BCR-2 and BHVO-2 and kimberlite reference material SARM-39 were analysed as unknowns for quality control and yielded results consistent with published reference values. The remaining aliquots (around 90 mg) of each sample were dedicated to Hf isotope analysis. Hafnium was separated therefrom using ion-exchange column-chromatography methods adapted from Münker et al. (2001). Isotopic analyses of Hf were carried out using a Nu Plasma II multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS). Samples and standards were diluted to a Hf concentration of around ~65 ppb, corresponding to a total Hf signal between 10-15 V. Instrumental mass bias was corrected by normalization to $^{179}Hf/^{177}Hf = 0.7325$ using the exponential law. $^{176}Hf/^{177}Hf$ ratios for unknowns and secondary standards are normalized to JMC475 = 0.282160 (Vervoort and Blichert-Toft, 1999). External precision (2 s.d.) is ± 0.000012 for $^{176}Hf/^{177}Hf$, based on the long-term reproducibility of standard reference materials in this laboratory. Age corrections were calculated using $^{176}Lu/^{177}Hf$ ratios derived from trace element data for the same sample solutions. εHf values are calculated relative to the chondritic (CHUR) composition of Bouvier et al. (2008). Results for samples and reference materials are reported in the SOM Table.

Perovskite U-Pb dating and trace element analysis

Analyses of perovskite for trace element and $^{207}Pb/^{206}Pb$, and $^{238}U/^{206}Pb$ ratio determinations were carried out at ETH Zurich using an Australian Scientific Instruments (ASI) RESOlution 193 nm excimer laser ablation system coupled to a ThermoFisher Element XR ICP-MS. Ablation was performed in a He atmosphere (500 mL/min) with additional N_2 (2mL/min) to increase signal sensitivity. Instrument settings were optimized while ablating synthetic glass NIST612 to minimize the production of oxides (ThO/Th <0.2 wt.%) and doubly charged ions (Ba^{++}/Ba^{+} ≈ 5%). Analytical conditions for perovskite included use of a 29 µm spot size, a pulse rate of 5 Hz, and laser fluence of ≈3.5 J/cm^2. In addition, large grains (i.e., macrocrysts) of low U/Pb phlogopite mica were ablated using larger spot sizes of between 74 and 110 µm in order to constrain the perovskite's initial Pb isotopic composition. Each analysis included 30 s of ablation time and gas blank measurement. Dwell times were of 11 ms for every monitored isotope (e.g.,^{27}Al, ^{49}Ti, ^{139}La, ^{232}Th) except ^{206}Pb, ^{207}Pb (50 ms; 100 ms in mica) and ^{238}U (20 ms; 50 in mica). Trace element quantification was undertaken using ^{43}Ca as internal standard with a nominal Ca concentration of 26.8 wt.% in perovskite, and GSD-1G as calibration material. NIST610 was ablated as a secondary standard to assess data reproducibility and returned results generally consistent with published values (Jochum et al., 2005; SOM Table). Data reduction was performed using the Iolite 4 software (Paton et al., 2011).

$^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ were quantified using perovskite IR-6 from (355.8 Ma; Heaman, 2009; Burgess et al., 2023) and the UcomPbine data reduction scheme available in Iolite (Chew et al., 2014), which addresses variable common Pb contents in reference materials and unknowns while correcting for downhole fractionation. Perovskite 83P13 from the Tummatapalle P13 kimberlite (India; 1100 Ma; Paton et al., 2009) was analysed to monitor data quality and reproducibility (SOM Table) and returned an age of 1122 ± 11 Ma (2se; n = 12/14) assuming an initial $^{207}Pb/^{206}Pb$ of 0.917 (i.e., based on the crustal Pb evolution curve of Stacey and Kramers, 1975). For the mica analyses, $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ were quantified using the synthetic glass NIST614 as calibration material, and natural glass GOR128G (Gorgona Island) was employed as a low U-Pb secondary standard (SOM Table). U-Pb downhole fractionation in mica is small and not systematic compared to the NIST614 calibration material. We therefore did not apply a correction for U-Pb downhole fractionation.

Perovskite Sr isotope analysis

In situ Sr isotope analyses of perovskite in thin section were undertaken using an ASI RESOlution 193 nm excimer laser probe interfaced to a Nu Plasma II MC-ICP-MS at ETH Zurich. Prior to ablation of

perovskite unknowns and standards, the instrument was tuned for optimal Sr signal and peak shape using NIST610 and a fragment of modern marine carbonate. Oxide production rate based on measurement of ThO/Th in NIST610 was ≤0.3 wt.%. Analytical conditions for perovskite analyses included 38 or 50 µm spot size, a pulse rate of 5 Hz, and laser fluence of ~4 J/cm^2. Each analysis consisted of a sequence of 30 seconds of gas blank measurement, 45-50 seconds of ablation time and 30 seconds of washout. Total Sr signals varied between 1.0 and 3.5 volts for both reference materials (83P13 and Ice River IR-6; Paton et al., 2007; Heaman, 2009) and unknowns. Data reduction, including corrections for isobaric interferences (Ca dimers, Ca argides, Rb, doubly-charged REE) and instrumental mass bias was performed using the Iolite 4 software (Paton et al., 2007, 2011). Analytical accuracy and instrumental drift were evaluated by repeated ablation of 83P13 and Ice River IR-6 perovskite reference materials, which were measured once every block of 10-12 unknowns. All data are reported relative to IR-6 $^{87}Sr/^{86}Sr$ of 0.702858 (Pearson, D.G., unpublished data) via standard bracketing. Weighted mean $^{87}Sr/^{86}Sr$ for 83P13 (0.70244 ± 10, 2se; n = 14; SOM Table) is consistent with isotope dilution values of the same samples (Paton et al., 2007). Mean $^{84}Sr/^{86}Sr$ of both perovskite reference materials and unknowns are within uncertainty of the natural ratio (0.0565). $^{87}Rb/^{86}Sr$ ratios are negligible (i.e., <0.001), which makes corrections for $^{87}Sr/^{86}Sr$ ingrowth insignificant. Therefore, the reported Sr isotope ratios are considered to be equal to the initial Sr isotope ratios at time of emplacement.