

ELECTRONIC APPENDIX A

Major elements in the dykes (Table 2) were analysed by XRF, both at the Geological Survey of Namibia (GSN) at Windhoek and the University of Leicester. The latter data are used here. Cr and Ni were analysed (using pressed powder disks) by XRF at GSN; the remaining trace elements were analysed by ICP-MS at Durham University. Isotopes (Tables 3 and 4) were determined as follows: Sr and Nd, Durham, McMaster and Open Universities; Hf, Durham; Pb, Durham, McMaster; Os, Durham. Four mass-spectrometers were used, TIMS at Durham, McMaster and the Open University and PIMMS at Durham. As a result, the machine reproducibility data recorded here are complex. Long-term reproducibility data are given for the Durham and McMaster TIMS but not for the OU instrument because it was substantially modified during the days immediately before and after the Spitzkoppe run. Only short-term reproducibility data are appropriate for PIMMS results

Major elements were analysed on fused beads at Leicester University and the GSN, using a Philips PW1400 (Leicester) and 2404 (GSN) X-Ray-Fluorescence spectrometers with rhodium anodes, operating at 50Kv and 50mA and using international reference materials as calibration standards. The current Durham University technique for preparing and analysing samples by ICP-MS was described by Thompson *et al.* (2005).

McMaster: Sr, Nd and Pb in Spitzkoppe dykes and Damara crustal samples

Samples were leached with 6M HCl overnight and then rinsed twice with high-purity de-ionised water before dissolution. The residues were dissolved in concentrated HF and HNO₃ in Savillex “bomb” vessels at 125 °C for three days, before conversion to the chloride form for ion exchange. Standard cation and reverse phase column separation methods were used. Procedural blanks were less than 20pg for Nd (Sr not measured). Sr and Nd isotope ratios were measured on a VG isomass 354 Thermal Ionisation Mass Spectrometer (TIMS). Sr was loaded on single Ta filaments and analysed by dynamic multi-collection, using a 3-collector algorithm. Data were corrected for mass fractionation using an ⁸⁶Sr/⁸⁸Sr ratio of 0.1194 and the exponential law. Nd was run on double filaments using Ta for evaporation and Re for ionisation. Data were collected using a 4-collector peak switching algorithm. Within-run fractionation was corrected for using a ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219 and the

exponential law. During this work, the NBS 987 Sr and La Jolla Nd standards gave average values of 0.710287 ± 0.000035 (2SD; n=10) and 0.511860 ± 0.000015 (2SD; n=9) respectively. Long term values for La Jolla reproducibility at McMaster are 0.511860 ± 0.000020 (2 SD; n=27). Values for Sr in samples were normalised to NBS987 = 0.71024. Nd isotopes for samples were not normalised as the standard fell within error of recommended value.

Lead was separated using 0.2 ml anion exchange columns eluted with > 0.7 M HBr. Pb was loaded onto single Re filaments with silica gel and phosphoric acid, and analysed by static multi-collection at ca. > 1350° C. The Pb blank was 80 pg. During this work, the NBS 981 standard gave ratios averaging 16.900 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.443 for $^{207}\text{Pb}/^{204}\text{Pb}$ and 36.562 for $^{208}\text{Pb}/^{204}\text{Pb}$. All Pb samples were consequently corrected for mass fractionation of 0.1% per amu. Sample reproducibility is estimated at 0.02, 0.015 and 0.04 (2 sigma) for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, respectively.

Open University: Sr in Damara crustal samples

Strontium isotopes ratios for Damara crustal samples were analysed at the Open University. Samples were prepared using standard digestion techniques, followed by separation of Sr using small Sr Spec resin columns (Charlier *et al.*, 2006). Total procedural blanks were <10 pg, which is insignificant compared with the ca. 600 ng of Sr loaded. Sr was loaded on to Ta filaments and analysed for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on a ThermoElectron Triton TIMS instrument using a static multi-collection routine. Mass fractionation was corrected for using an $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 and an exponential law. During sample analysis the average $^{87}\text{Sr}/^{86}\text{Sr}$ value for 600ng loads of the NBS987 standard was 0.710263 ± 0.000028 (39.4ppm 2SD; n=9).

Arthur Holmes Isotope Geology Laboratory (AHIGL) Durham University: Sr, Nd, Hf, Pb and Os in Spitzkoppe dykes

Dyke samples were dissolved for Sr-Nd-Hf chemistry in Teflon beakers with 1ml 16N HNO₃ and 3mls 29N HF at 120°C for 48hrs. Damara crustal samples were dissolved at McMaster in Savillex teflon vessels for 4 days at > 125 C, using 1ml 16N HNO₃ and 12mls 29N HF, and the dried residues sent to Durham for further chemical processing. For Os, samples were digested in Carius tubes with 5mls 16N HNO₃ and 2mls 12N HCl at 230°C for 48hrs and were spiked for both Re and Os. After

dissolution Sr-Nd-Hf were separated using a combination of cation and anion exchange columns (Dowall *et al.*, 2003). Pb was separated using small Sr Spec resin columns (Charlier *et al.*, 2006). Os was separated using the method of Pearson & Woodland (2000). Total procedural blanks for Sr-Nd and Hf were all <100pg and approximately 0.5pg for Os.

Isotope ratios in the fractions for Sr, Nd and Hf were measured using the AHIGL ThermoElectron Neptune Multi-collector Plasma Mass Spectrometer (MC-ICP-MS). The basic analytical method used for each element on the Neptune comprises a static multi-collection routine of 1 block of 50 cycles with an integration time of 4sec per cycle; total analysis time 3.5mins. Os isotopes were measured by negative ion TIMS using the AHIGL ThermoElectron Triton using the secondary electron multiplier and a peak-hopping routine comprising 100 measurements of 7 cycles with integration times for each cycle varying between 2 and 8secs depending on the abundance of the isotope. Further element-specific analytical details are presented below.

After chemistry, Sr samples were taken up in 1ml of 3% HNO₃ and introduced into the Neptune using an ESI PFA50 nebuliser and a dual cyclonic–Scott Double Pass spraychamber. With this sample introduction set up, and the normal H skimmer cone, the sensitivity for Sr on the Neptune is typically ~60V total Sr ppm⁻¹ at an uptake rate of 90µl min⁻¹. Prior to analysis a small aliquot was first tested to establish the Sr concentration of each sample by monitoring the size of the ⁸⁴Sr beam (⁸⁸Sr was too high in non-diluted aliquot to measure directly) from which a dilution factor was calculated to yield a beam of approximately 20V ⁸⁸Sr. Instrumental mass bias was corrected for using a ⁸⁸Sr/⁸⁶Sr ratio of 8.375209 (the reciprocal of the ⁸⁶Sr/⁸⁸Sr ratio of 0.1194) and an exponential law. The dyke samples were analysed in a single session during which the average ⁸⁷Sr/⁸⁶Sr value for NBS987 was 0.710253±0.000012 (16.3ppm 2SD; n=9).

Following chemistry the REE cuts containing the Nd fraction were taken up in 1ml of 3% HNO₃ and introduced into the Neptune using an ESI PFA50 nebuliser and a dual cyclonic–Scott Double Pass spraychamber. With this sample introduction set up, and the normal H skimmer cone, the sensitivity for Nd on the Neptune is 60-80V total Nd ppm⁻¹ at an uptake rate of 90µl min⁻¹. Instrumental mass bias was corrected for using a ¹⁴⁶Nd/¹⁴⁵Nd ratio of 2.079143 (equivalent to the more commonly used

$^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219) and an exponential law. The $^{146}\text{Nd}/^{145}\text{Nd}$ ratio is used for correcting mass bias since at Durham Nd isotopes are measured on a total REE-cut from the 1st stage cation columns and this is the only Ce and Sm-free stable Nd isotope ratio. This approach requires a correction for isobaric interferences from Sm on ^{144}Nd , ^{148}Nd and ^{150}Nd . The average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios measured on the dyke and crustal samples during the Nd isotope ratio measurement was ~0.055 and ~0.015 respectively. The correction used is based on the method of Nowell & Parrish (2001). The accuracy of the Sm correction method during analysis of a total REE fraction is demonstrated by repeat analyses of BHVO-1, which gave an average $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512982 ± 0.000007 (13.5ppm 2SD, n=13) after Sm correction; identical to the TIMS ratio of 0.512986 ± 0.000009 (17.5ppm 2SD; n=19) obtained by Weis *et al.* (2005). The dyke samples were analysed in a single session during which the average $^{143}\text{Nd}/^{144}\text{Nd}$ value for pure and Sm-doped J&M standard was 0.511101 ± 0.000005 (10.1ppm 2SD; n=15). During analysis of the Damara crustal samples the pure and Sm-doped J&M standards gave an average $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511096 ± 0.000008 (15.5ppm 2SD; n=9).

For Hf isotopic analysis, samples were taken up in 0.5ml 3% HNO_3 – 1N HF and were introduced using an ESI PFA50 nebuliser together with a Cetac Aridus desolvator. With this sample introduction set up, and the high sensitivity X skimmer cone, the sensitivity for Hf on the Neptune was 400-450V total Hf ppm^{-1} at an uptake rate of $90\mu\text{l min}^{-1}$. Instrumental mass bias was corrected for using a $^{179}\text{Hf}/^{177}\text{Hf}$ ratio of 0.7325 and an exponential law. Corrections for isobaric interferences from Yb and Lu on ^{176}Hf were made by monitoring $^{172-173}\text{Yb}$ and ^{175}Lu and using the approach of Nowell & Parrish (2002), although in practice the average $^{176}\text{Yb}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios obtained on the samples were 0.0002 and 0.000005 and the corrections negligible. The dyke samples were analysed in a single session during which the JMC 475 standard gave an average value of 0.282147 ± 0.000003 (11.6ppm 2SD; n=8). The Damara crustal samples were analysed in a separate session during which the JMC 475 standard gave an average value of 0.282140 ± 0.000003 (11.6ppm 2SD; n=5).

Lead samples were taken up in 1ml of 3% HNO_3 . Prior to analysis each sample was tested on the Neptune to determine its Pb concentration and thereby calculate the appropriate amount of tantalum spike to add in order to obtain a Pb/Tl ratio of ~12. After spiking with Tl each sample was introduced into the Neptune using an ESI

PFA50 nebuliser and a dual cyclonic–Scott Double Pass spraychamber. With this set-up, and the normal H skimmer cone, the sensitivity for Pb on the Neptune is typically $\sim 100\text{V}$ total Pb ppm^{-1} at an uptake rate of $90\mu\text{l min}^{-1}$. Pb mass bias was corrected for externally using the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of the admixed Tl spike and an exponential law. The $^{205}\text{Tl}/^{203}\text{Tl}$ ratio used for correcting the Pb ratios is determined for each analytical session by minimising the difference in offset between the session average Pb ratios (all ratios) and the Galer & Abouchami (1998) values, *i.e.* it is the ratio that gives the best fit for all the Pb ratios to the values of Galer & Abouchami (1998) simultaneously that is used. Samples were analysed in a single analytical session during which the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio used for mass bias correction was 2.38835 and the average $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for the NBS981 Pb std were 16.9405 ± 0.0017 , 15.4966 ± 0.0012 , 36.7159 ± 0.0044 respectively (all 2SD; $n=10$).

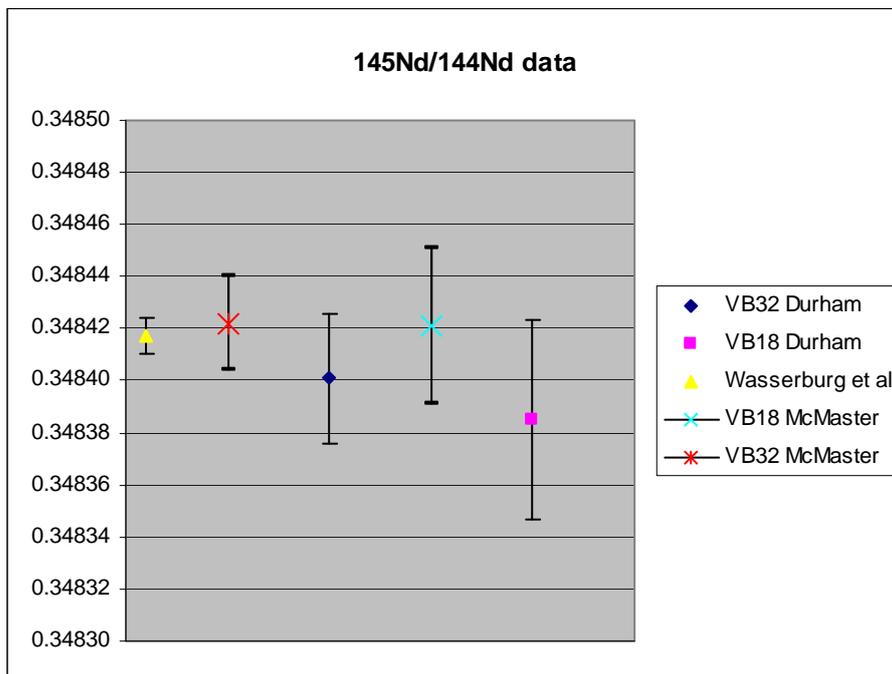
Osmium samples were loaded on Pt filaments with a $\text{Ba}(\text{OH})_2$ activator solution. Raw data were exported and corrected for oxygen isotope fractionation, Os mass fractionation (using a $^{192}\text{Os}/^{188}\text{Os}$ ratio of 3.08271) and an exponential law, and finally blank contribution. Using the peak-hopping routine, the long-term mean $^{187}\text{Os}/^{188}\text{Os}$ value for 161 runs of the University of Maryland College Park standard, at signal sizes equivalent to those of the samples, was 0.11383 ± 0.00032 (2 SD; 2.8‰). The mean $^{189}\text{Os}/^{188}\text{Os}$ over this period is 1.21976 ± 0.00192 (2 SD; 1.6‰). Re was analysed on Durham ThermoElectron Element 2 mass spectrometer by ion counting, in peak-hopping mode. The procedure uses a GE Conikal 1ml min^{-1} nebuliser and a dual cyclonic-Scott Double Pass spray chamber. Data quality are checked against the in-house GP-13 PGE standard, whose long-term “reference” values are reported in Pearson *et al.* (2004).

Comparison of Durham and McMaster Sr-Nd isotopic ratios for picrites VB18 and 32

As explained in the main text, the small differences in initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ between picrites VB18 and 32 measured at Durham and McMaster cannot be ascribed to post-crystallisation hydrothermal alteration. Before considering whether the cause might be very-small-scale isotopic variability in the two powders, it is essential to check the accuracy of the Nd isotopic ratios measured in the two laboratories. The table below shows values for three pairs of stable Nd isotope ratios in Durham samples VB18 and 32, compared with standard values (Wasserburg *et al.*, 1981).

		145Nd/144Nd	2SE _{lab}	2SE _{ppm}	146Nd/144Nd	2SE _{lab}	2SE _{ppm}	148Nd/144Nd	2SE _{lab}	2SE _{ppm}
Wasserburg et al	0.1	0.348417	0.000007		0.7219	0.000008		0.241578	0.000008	
VB32	1	0.348401	0.000025	71.76	0.721866	0.000052	72.04	0.241524	0.000029	121.73
$\Delta_{\text{Wasserburg}}$ ppm		-45.92			-47.10			-223.53		
VB18	2	0.348385	0.000038	109.65	0.721835	0.000079	110.00	0.241523	0.000066	272.44
$\Delta_{\text{Wasserburg}}$ ppm		-91.84			-90.04			-227.67		

Only $^{145}\text{Nd}/^{144}\text{Nd}$ is analysed at McMaster and so direct comparison between the laboratories for stable Nd-isotopic ratios is confined to this value. These differences may be expressed graphically:



The McMaster values for $^{145}\text{Nd}/^{144}\text{Nd}$ are as follow:

VB32 0.348422 ± 0.000030 (2SD)

VB18 0.348421 ± 0.00018 (2SD)

Clearly, analytical error is not the cause of the difference between the Durham and McMaster values for $^{145}\text{Nd}/^{144}\text{Nd}$ in sample VB18. Therefore we deduce that there is very-small-scale isotopic variability in picrites VB18 and 32 (see main text for discussion).

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