



## RE-OS ISOTOPE CONSTRAINTS ON THE AGES OF DIAMONDS FROM MWADUI, TANZANIA

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### INTRODUCTION

The ability to obtain Re-Os isotope data on single sulphides included in diamonds (Pearson et al., 1998) has provided important constraints on the timing of diamond formation beneath Archaean cratons worldwide (e.g., Aulbach et al., 2009a; Aulbach et al., 2009b; Pearson et al., 1999a; Pearson et al., 1999b; Richardson et al., 2001; Richardson et al., 2004; Westerlund et al., 2006). The majority of diamond inclusion isotope dating has been conducted on diamonds from Southern Africa and Canada (e.g. Gurney et al., 2010 and references therein). To date there are few temporal constraints about the evolution of the lithosphere beneath Eastern Africa and these are all derived from xenoliths studies (Chesley et al., 1999).

Here we analyse 24 diamonds from the Mwadui kimberlite (formerly known as the Williamson Mine) that is located within the Tanzanian Craton. The eruption age of the kimberlite is ~52 Ma (Davis, 1977; Gobba, 1989). The crystals were selected based on the presence of large sulphide inclusions allowing the first Re-Os age estimates for diamonds from the Tanzanian Craton. The ages are integrated with nitrogen aggregation data to erect a model for the thermal and tectono-magmatic evolution of the Tanzanian Craton.

### GEOLOGICAL SETTING

The Archaean Tanzanian Craton is underlain

by a thick lithospheric keel to depths of 150-200 km (Chesley et al., 1999; Weeraratne et al., 2003). Proterozoic mobile belts surround the craton on the South, East and West. The Mozambique Belt to the East is composed mainly of Archaean crust that has been reworked in two separate collisional events (Maboko, 2000; Möller et al., 1998). The Usagaran orogeny, occurred at the southeastern margin of the craton and includes 2.0 Ga eclogite facies rocks that have mid-ocean-ridge basalt (MORB)-like precursors, suggesting that subduction of oceanic lithosphere played a role in the formation of the belt (Collins et al., 2004). The Kibaran Fold Belt was formed west of Lake Victoria between 1.4 and 1.0 Ga. The East African orogeny (ca. 600 Ma) represents a major event that involved the collision of Eastern and Western Gondwana and is associated with westward emplacement of granulite-facies nappes (Fritz et al., 2009). The Mwadui diamonds were deposited as crater-infill in a kimberlite below palaeo Lake Victoria when it had ~ 50% larger aerial extent than today.

### METHODS

Single sulphides were extracted from the Mwadui diamonds by cracking. The sulphides were digested by micro-distillation at Durham University, UK, following the technique of Pearson et al (1998). The Os fractions recovered after micro-distillation were analysed with a



Thermo Finnigan Triton thermal ionisation mass spectrometer. The average total Os blank is  $5.0 \pm 1$  fg and the  $^{187}\text{Os}/^{188}\text{Os}$  blank isotopic composition is  $0.2398 \pm 0.0080$ . The Re fractions were separated with micro-column anion-exchange chemistry and analysed with a Thermo Finnigan Element2 high resolution mass spectrometer. Uncertainties for Re and Os data include full propagation of blank uncertainties ( $2\sigma$ ).

The major element (Fe, Ni and Cu) and Pb trace element compositions were determined with a Quadrupole Thermo X-Series II mass spectrometer at VU University Amsterdam, The Netherlands. The weight percentages of the sulphides were calculated following the method of Richardson et al. (2001).

Infrared absorption spectra of diamond rim fragments were collected using a *Nicolet Nexus* Fourier Transform Infra Red (FTIR) *Spectrometer* at The Research Department of HRD Antwerp in Lier, Belgium. The nitrogen content, nitrogen aggregation state and integrated mantle residence temperature were determined following the methods of Mendelsohn and Milledge (1995) and Taylor et al. (1990). The residence times that were used to calculate integrated mantle residence temperatures are based on the Re-Os isotope ages obtained in the current study. Because sulphides were extracted from specific regions within the diamond and the FTIR measurement represents an integrated signal from a diamond rim fragment, we may expect some degree of decoupling between information provided by the dating and nitrogen-based residence histories. The carbon isotope composition of the fragments studied by FTIR was determined using a Carlo Erba NC 2500 elemental analyser coupled to a Thermo Finnigan Delta Plus isotope ratio mass spectrometer at VU University Amsterdam, The Netherlands. The reproducibility of standard carbon isotope compositions is within  $\pm 0.3\%$ .

## RESULTS AND DISCUSSION

### Diamonds

The diamonds (Fig. 1) are resorbed with imperfect rounded dodecahedral morphologies for the majority of the crystals and boat-shaped features on their crystal faces. Additionally, the faces have lamination lines caused by plastic deformation. In an initial study, five diamonds, four E-type and one P-type, with up to three sulphide inclusions each were analysed. Nine sulphides were extracted in total with weights of 1.1–37.9  $\mu\text{g}$  (Table 1).

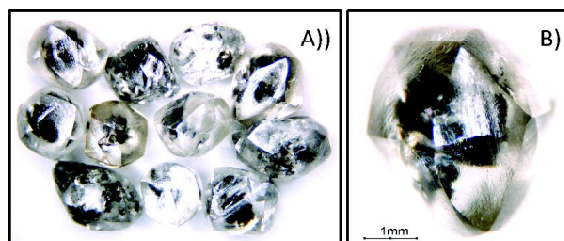


Fig. 1. A) Diamonds from Mwadui with large sulphide inclusions, B) Diamond MW07 with rounded dodecahedral morphology and micro-lamination.

Table 1. Paragenesis, weight, major element composition of the sulphides.

Sulphide	Type	E/P	weight ( $\mu\text{g}$ )	Fe (wt%)	Ni (wt%)	Cu (wt%)	Pb (ppm)
MW_S01a	po	E	7.5	54.9	2.8	3.9	5
MW_S01b	po	E	15.3	54.0	3.0	4.7	10
MW_S03a	po	E	3.8	59.8	0.5	0.4	14
MW_S03b	po	E	1.1	58.7	1.5	0.8	23
MW_S07	pn	P	6.8	29.8	37.0	0.6	382
MW_S13a	po	E	37.9	59.8	0.5	0.4	112
MW_S13b	po	E	12.2	59.2	0.9	0.8	12
MW_S13c	po	E	22.8	59.7	0.6	0.4	17
MW_S20	po	E	1.9	59.2	0.9	0.7	17

The concentrations of Fe+Ni+Cu are normalized to 100 weight percent. The total procedural blank is 18 ppm for Pb. po = pyrrhotite, pn = pentlandite, E = E-type, P = P-type

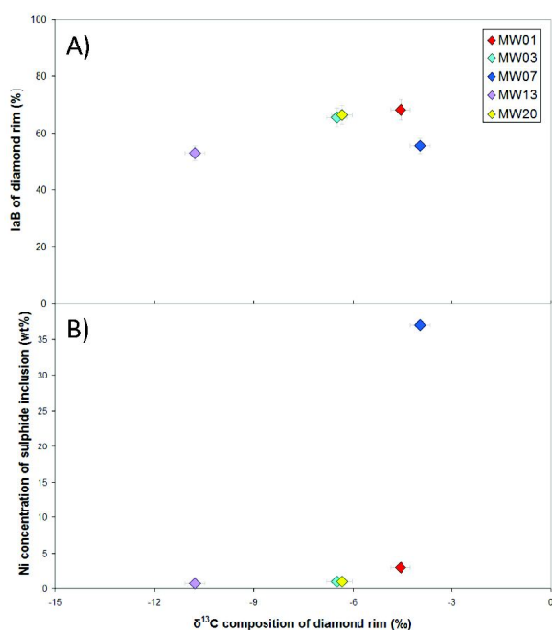
The rim fragments of the diamonds after sulphide extraction were subjected to carbon isotope analyses. The E-type diamonds have  $\delta^{13}\text{C}$  values between  $-4.5 \pm 0.3$  and  $-6.5 \pm 0.3\%$  with one more extreme composition of  $-10.8 \pm 0.3\%$



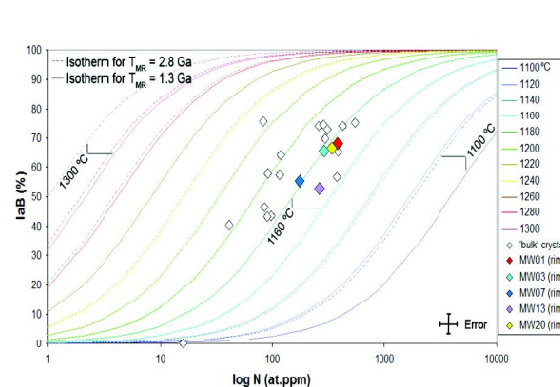
(diamond MW13; Fig. 2). The rim of the P-type diamond MW07, in contrast, records a heavier value with  $-3.9 \pm 0.3\text{‰}$  (Fig. 2).

The nitrogen contents of the rim fragments from the E-type diamonds are between 291-385 at. ppm with ~65% IaB aggregation, except for diamond MW13 that contains 266 at. ppm nitrogen with ~50% IaB aggregation (Figs. 2A, 3). The rim of the P-type diamond has 176 at. ppm nitrogen that is ~55% aggregated into the B form (Figs. 2A, 3).

Despite the differences in nitrogen concentration and aggregation states, the E-type diamond fragments approximate to a single isotherm (Fig. 3), except diamond MW13. Consequently, the rims of the E-type diamonds appear related and probably formed at similar times, or at least experienced similar time-temperature histories.



**Fig. 2.** A) Co-variation of the  $\delta^{13}\text{C}$  composition and nitrogen IaB aggregation state of the diamond rims. B) Co-variation of the  $\delta^{13}\text{C}$  composition of the diamond rims and Ni concentrations of included sulphides. Note that an average value for the Ni concentration is shown if the diamond contains multiple inclusions. Diamond MW13 (E-type) has a significant lighter  $\delta^{13}\text{C}$  composition in relation to the other E- and P-type diamonds, and diamond MW07 (P-type) demonstrates a higher Ni concentration.



**Fig. 3.** Theoretical isotherms based on mantle residence times that range between 1.3 and 2.8 Ga (i.e., the Re-Os isotope ages of the diamonds in this study). The rims of the diamonds approximate to integrated mantle residence temperatures of ~1150 °C, except for diamond MW13. Consequently, despite the presence of different diamonds populations as established by the different Re-Os isotope ages, the diamond rims appear related.

Additional bulk analyses of the rough diamonds in this collection demonstrate more variability in integrated mantle residence temperatures with 16-548 at. ppm with 40-76% of aggregation into the B form (Fig. 3). The majority of these sulphide-bearing diamonds indicate higher integrated mantle residence temperatures. These temperature estimates may indicate either that 1) there is another diamond population at Mwadui that are older, or resided at higher integrated temperatures than the diamonds selected for our detailed study, or that 2) the studied diamonds are zoned whereby the cores of the sulphide-bearing diamonds resided at higher integrated mantle residence temperatures and are significantly older than the rims. The second scenario also explains the scatter in the bulk data, as this may result from averaging different growth zones in diamonds if these diamonds have a multistage growth history. We therefore infer a multistage growth history for these sulphide-bearing diamonds from Mwadui.

## SULPHIDES

Eight of the E-type sulphides are pyrrhotites and the single P-type inclusion is pentlandite

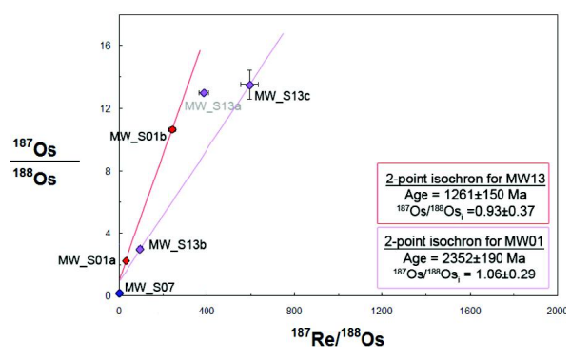


(Table 1). The Ni contents of the majority of pyrrhotites ranges between 0.5-1.5 wt.%, whereas the two sulphides extracted from diamond MW01 contain up to 3.0 wt.% Ni (Fig. 2B). The P-type sulphide contains 37.0 wt.% Ni (Fig. 2B).

The E-type sulphides are characterised by radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios (2.293-12.977) and the P-type is unradiogenic (0.108). The E-type sulphides have lower Os concentrations and higher  $^{187}\text{Re}/^{188}\text{Os}$  (4.0 to 25.2 ppb Os, and 30.77 to 1400  $^{187}\text{Re}/^{188}\text{Os}$ ) compared to the P-type sample (36.7 ppm Os, and 0.092  $^{187}\text{Re}/^{188}\text{Os}$ ).

### RE-OS ISOTOPE AGES

The different sulphides do not form a single coherent trend on a Re-Os isochron diagram (Fig. 4). However, when inclusions are regressed on the basis of inclusion chemistry and diamond characteristics the data provide clear evidence of multiple ages.



**Fig. 4.** Re-Os isochron diagram for the sulphides. The different sulphides do not form a single coherent trend, however, when inclusions are regressed on the basis of inclusion chemistry and diamond characteristics the data provide clear evidence of multiple ages. See text for explanations. The error bars include full propagation of blank uncertainties (2 $\sigma$ ).

The sulphide extracted from diamond MW07, the only P-type sample in this study, defines a Re depletion age (TRD) of ~2.8 Ga and a Re-Os mantle model age (TMA) of ~3.6 Ga (Table 2). In contrast, the E-type sulphides define multiple Re-Os isochron ages between 1.3 and

2.3 Ga with initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios between 0.9 and 1.1.

**Table 2.** Re-Os composition and age of the sulphides.

Sulphide	Re (ppb)	Os (fg)	Os (ppb)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	TMA (Ga)
MW_S01a	95.6	144	19.2	30.77	2.29	-
MW_S01b	528.6	385	25.2	239.9	10.65	-
MW_S03a*	559.8	19	5.1	1400	12.71	-
MW_S03b*	180.3	10	9.3	125.5	2.74	-
MW_S07	699.4	249331	36659.8	0.09	0.11	3.6***
MW_S13a**	167.1	212	5.6	385.6	12.98	-
MW_S13b	151.3	125	10.2	98.01	3.01	-
MW_S13c	177.6	90	4.0	593.1	13.52	-
MW_S20*	94.4	14	7.6	83.37	3.10	-

\* small sample (see Table 1) with Os contents approaching blank values

\*\* potentially metasomatised sample with high Pb contents (Table 1)

\*\*\* TRD of MW\_S07 is 2.8 Ga

The sulphides that were included in diamonds MW03 and MW20 are very small with weights <4  $\mu\text{g}$ . Consequently, the Re-Os data of these samples are likely subject to large errors, especially as extremely low Os concentrations (i.e., <20 fg) were obtained that are close to blank values of ~5 fg. Regression of the Re-Os isotope data of the three sulphides from E-type diamonds MW03 and MW20, which results in a correlation with an age of  $437 \pm 53$  Ma (2 $\sigma$ ) and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $2.48 \pm 0.43$  (MSWD=0.21), is not considered a reliable result. Additionally, this young age does not correlate with the relatively high aggregation states of the rims of these diamonds (Taylor et al., 1990).

The sulphides from diamond MW01, with similar major element compositions (Table 1), yield a two-point isochron age of  $2.3 \text{ Ga} \pm 0.2 \text{ Ga}$  (2 $\sigma$ ) and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $1.06 \pm 0.29$ .

The distinct chemical and isotope composition of diamond MW13 (Figs. 2-3) suggests a distinct history for this crystal. The sulphides S13b and S13c extracted from this diamond yield a two-point isochron age of  $1.3 \pm 0.2 \text{ Ga}$  (2 $\sigma$ ) and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.93 \pm$





0.37. Regression with sulphide S13a results in a negative Os initial. The major element composition of the large and unbroken sulphide S13a is not significantly different from the other two sulphides included in this diamonds. However, this sample has elevated Pb contents (112 ppm), whereas the other sulphides approximate to blank values of 18 ppm (Table 1). Increased Pb levels are regarded as interaction with a different melt/fluid (Bulanova et al., 1996). Consequently sulphide S13a appears to have experienced a different history compared to the other two sulphides extracted from the same diamond and excludes this sample from isochron correlation.

The TRD and TMA ages (2.8 to 3.6 Ga) for MW\_S07 bracket the likely minimum and maximum age of this diamond. P-type sulphide isochrons commonly have radiogenic initial Os isotope compositions (e.g., Aulbach et al., 2010; Westerlund et al., 2006) and so the Meso-Archaeon TMA age is probably an over-estimate. This is also supported by the elevated Pb content of this sulphide, suggesting the likelihood of incorporation of radiogenic Os during growth, increasing the TMA age. Taken at face value, the TRD age is within error of the 2.9 Ga lithosphere ages estimated by Chesley et al. (1999) for the lithosphere in this region.

### TEMPERATURE CONSTRAINTS

The ages of >1 Ga correlate with the relatively high aggregation states of the diamonds. Integrated residence temperatures of ~1160 °C (Fig. 3) are inferred for each diamond using mantle residence times of 1.3, 2.4 or 2.8 Ga (i.e., based on the Re-Os isotope ages). However, because the aggregation data of the rims of the diamonds do not necessarily correlate with the sulphide data, as the sulphides are extracted from the interiors of the diamond, the rims may have experienced shorter residence times.

### MULTISTAGE GROWTH HISTORY

The current data set does not allow full assessment of the exact variability in age and integrated mantle residence temperature of the potentially different growth zones of the individual diamonds, because of the complexities in their growth histories. Nonetheless, despite the similarity in nitrogen aggregation of the rims of the diamonds, the sulphides extracted from some of these diamonds may originate from core zones that appear to be significantly older (Fig. 3). Consequently, the nitrogen aggregation data suggest multistage growth of individual diamonds from Mwadui.

### CONCLUSIONS

The nitrogen aggregation data and Re-Os isotope constraints demonstrate the presence of different diamond populations at Mwadui, a feature of numerous other diamond suites worldwide (e.g., Pearson et al., 1998; Richardson et al., 1993 for South African diamonds). The isotope data do not form a single coherent trend on a Re-Os isochron diagram, but when regressed on the basis of inclusion chemistry and diamond characteristics the data provide clear evidence of multiple ages. Isochron ages of 1.3 and 2.4 Ga are obtained for the E-type diamonds and a model age of 2.8 Ga for the P-type diamond. Although uncertainties are large, these ages are consistent with diamond formation associated with the major tectono-magmatic events that have affected the Tanzanian Craton; Kibaran Fold Belt and Usagaran orogeny.

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