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SPECIAL

U–Pb zircon (SHRIMP) ages for the Lebombo rhyolites, South Africa: refining the duration of Karoo volcanism

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U–Pb SHRIMP ages are reported for three rhyolite flows from the Lebombo rift region of the Karoo volcanic province. Two flows are interbedded with the Sabie River Basalt Formation and a third sample is from the overlying rhyolitic Jozini Formation. The interbedded rhyolites yield ages of 182.0 ± 2.1 and 179.9 ± 1.8 Ma, whilst the overlying Jozini Formation rhyolite yields an age of 182.1 ± 2.9 Ma. Combined with existing $^{40}Ar/^{39}Ar$ geochronology, the new SHRIMP data fine-tunes the chronology of the Karoo volcanic province and indicates the 12 km succession of volcanic rocks in the Lebombo rift were erupted in 1–2 million years and lends considerable support to the links between the Pleinsbachian–Toarcian extinction event and the global environmental impact of Karoo volcanism.

Keywords: Lemombo rhyolites, U–Pb, flood basalts, rhyolites, Karoo.

The Karoo volcanic province of southern Africa and East Antarctica is one of the largest flood basalt provinces of the Phanerozoic, and may be contiguous with the Ferrar magmatic province of the Transantarctic Mountains. Radiometric dating of the Karoo volcanic province has led to widely distributed ages (*c.*150–200 Ma; Fitch & Miller 1984), particularly when the intrusive record is investigated. However, geochronology by Duncan *et al*. (1997) indicates a much more restricted age range (179–184 Ma) for the extrusive rocks of southern Africa and Antarctica, which form the most significant volume of the province.

Three rhyolite units from key positions in the Lebombo stratigraphic sequence have been dated using U–Pb (SHRIMP) techniques. SHRIMP dating is considered more robust than $^{40}Ar/^{39}Ar$ geochronology, particularly on rhyolites (e.g. Pankhurst *et al*. 2000) and the ages corroborate and further strengthen the chronology of the Lebombo stratigraphy. The rapid eruption of the Karoo succession is thought to have been responsible for triggering the early Toarcian extinction event (Hesselbo *et al*. 2000).

Geological setting. The Karoo Supergroup succession along the Lebombo monocline is highlighted in Figure 1. The oldest phase of Karoo volcanism is marked by the Mashikiri nephelinites, which unconformably overlie Jurassic Clarens Formation sandstones (Fig. 2). The nephelinites have been dated at 182.1 ± 1.6 Ma ($^{40}Ar/^{39}Ar$ plateau age; Duncan *et al*. 1997) and form a lava succession up to 170 m thick (Bristow 1984). These rocks are confined to the northern part of the Lebombo rift and are absent along the central and southern sections. The nephelinites are conformably overlain by picrites and picritic basalts of the Letaba Formation, although in the southern Lebombo the picrites directly overlie the Clarens Formation. The picrites overlap in age (182.7 ± 0.8 Ma; Duncan *et al*. 1997) with the Mashikiri nephelinites and are believed to form a succession up to 4 km in thickness.

The Letaba Formation picrites are in turn overlain by a major succession (4–5 km thick) of low-MgO basalts, termed the Sabie River Basalt Formation (Cleverly & Bristow 1979). These basalts are again similar in age to the underlying sequences, with Duncan *et al*. (1997) recording ages in the range 181.2 ± 1.0 to 184.2 ± 1.0 Ma. Duncan *et al*. (1997) interpreted the Sabie River Basalt Formation was erupted during a period of <0.5 million years, as the sequence lies within a single magnetic normal period. At least four lenticular rhyolite units are interbedded with the Sabie River Basalt Formation along the Olifants and Sabie rivers (Fig. 1). These are referred to as the Olifants River Beds and form part of the Sabie River Basalt Formation. The westernmost Olifants River Bed is intrusive, but the following unit to the east, is extrusive (SA.39.1). The second of the three extrusive rhyolite beds (SA.29.1) is a moderate–strongly welded ignimbrite with a pronounced eutaxitic texture, which is overlain by a flow-banded rhyolite lava characterized by chaotic flow folding. A further rhyolite crops out further south along the Sabie River gorge (SA.24.1; Fig. 1).

In the southern and central areas of the Lebombo, the voluminous Lebombo rhyolites, which are up to 5 km in thickness (Cleverly *et al*. 1984), overlie the Sabie River Basalt Formation with slight angular disconformity (Bristow 1982). The rhyolites are subdivided into the older Jozini Formation (called Mwenezi, previously Nuantesti rhyolites in Zimbabwe) and the younger Mbuluzi Formation (Fig. 1). The Jozini Formation crop out in a narrow belt (3–15 km wide) along the border with Mozambique (Fig. 1) and comprise a thick sequence of largely high-temperature, anhydrous ignimbrites, interbedded with rare rhyolite lava flows. The majority of the rhyolites are porphyritic and contain phenocrysts of one or more of the following: plagioclase, clinopyroxene, magnetite, quartz and sanidine, plus accessory apatite and zircon.

Sample descriptions. Samples for U–Pb SHRIMP dating were selected from the Olifants River Beds rhyolites (two samples: SA.24.1, SA.39.1; Fig. 1), which are interbedded with the upper part of the Sabie River Basalt Formation and a single sample (SA.42.1) from the central-upper part of the Jozini Formation rhyolites at the Mozambique border, along the Olifants River (Fig. 1).

SA.39.1 (24°00.2882′ S, 031°44.6986′ E; 179 m asl). The lowermost extrusive rhyolite unit in the Sabie River Basalt Formation crops out along the Olifants River below the Olifants Rest Camp (Fig. 1). The unit is composed of several massive lava flows, with a total thickness of

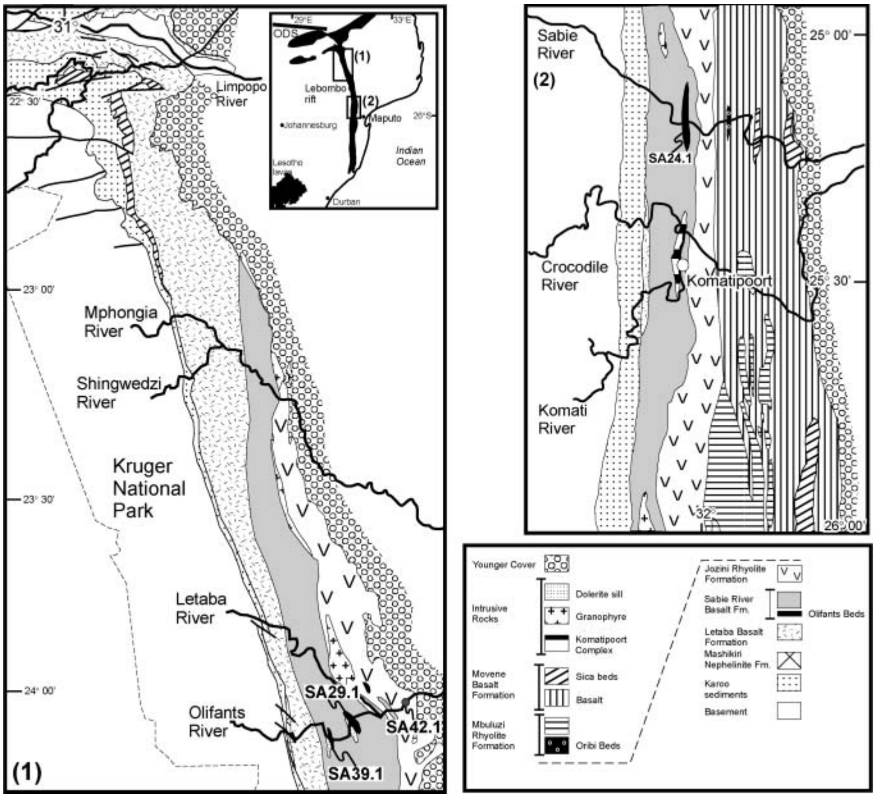

Fig. 1. Geological map of the northern and central Lebombo (Bristow 1982). Inset shows the distribution of the principal erosional remnants of the Karoo igneous province.

300 m. The unit lies conformably on the eastward dipping flows of the Sabie River Basalt Formation and its contact is extrusive, characterized by a thin palaeosol along the eastern contact. The flows are strongly feldspar-phyric and also contain clinopyroxene phenocrysts. Quartz appears to be absent. The feldspar is plagioclase and typically occurs as fragmented phenocrysts, which characteristically have a sieve texture. The clinopyroxene are typically subhedral and often associated with the plagioclase. They are pale green crystals and are interpreted to be ferroaugite. Magnetite and titanomagnetite are the dominant accessory phases, along with apatite and zircon.

SA.24.1 (25°09.6269′S, 031°59.9376′E; 124 m asl) crops out along the Sabie River (Fig. 1) and is interbedded with the upper part of the Sabie River Basalt Formation. It is the uppermost of the Olifants River Beds and is very similar in appearance to the lowermost unit, SA.39.1, although it is not as thick (230 m).

SA.42.1 (23°57.4240′S, 031°52.8369′E; 85 m asl) was sampled from the central to upper part of the rhyolitic Jozini Formation, overlying the Sabie River Basalt Formation. The sample was taken at the Mozambique border along the Olifants River (Fig. 1). The unit is an orange/red-weathered ignimbrite, which is generally massive and strongly feldspar-phyric. The unit is moderate to poorly welded, with oblate pumice clasts, up to 8 cm in diameter. Lithic fragments are absent or rare. The ignimbrite, which is at least 12 m in thickness, is overlain by a flow banded rhyolite unit. Petrographically, the ignimbrite is dominated by corroded and fragmented feldspar phenocrysts, clinopyroxene and magnetite, with accessory apatite and zircon. Quartz is rare, but was identified as a cluster of angular grains.

Geochronology.

Previous work. Allsopp *et al*. (1984) report a Rb–Sr whole rock isochron age of 179.1 ± 3.8 Ma for the ‘Jozini Rhyolites’ of the southern Lebombo and Swaziland. Rb–Sr data on Jozini rhyolites from central and northern Lebombo produced a similar isochron age of 176.7 ± 5.6 Ma, which included eight samples (of a total of 14) from a single granophyre dyke at Komatipoort (Fig. 1). Fitch & Miller (1984) dated (K–Ar whole rock) three samples from a Lebombo rhyolite of the Jozini Formation (Ngweni Quarry, Natal), which yielded repeat ages of 179 ± 3, 180 ± 3 and 182 ± 3 Ma. Duncan *et al*. (1997) undertook a detailed $^{40}Ar/^{39}Ar$ study on a diverse group of Karoo volcanic rocks, including two rhyolites from the lower part of the Jozini Formation (KVU-5, KSA-12). The two rhyolites produced ages of 178.1 ± 0.6 and 179.7 ± 0.7 Ma (plateau ages), with a mean of 178.9 ± 0.5 Ma, younger than the main basaltic units dated by Duncan *et al*. (1997).

This study. Zircons were analysed using a Sensitive High Resolution Ion Microprobe (SHRIMP) at the Australian National University (Williams 1998). Zircons were mounted in epoxy resin, polished to expose the centres of the grains, and gold-coated. Internal zoning and grain characteristics were mapped by microphotography and cathodoluminescence imaging. Clean areas, free of cracks, inclusions and radiation damage were analysed. Analysis was carried out with a primary O_2- beam; secondary ion beam intensities were measured using an ion-counting detector. Calibration was carried out using zircon standards mounted together with the samples (mostly AS-3; Paces & Miller 1993). Data were reduced for background, mass bias, calibration and common Pb corrections using SQUID (Ludwig 1999). All errors on ages are at the 2σ level. A summary of the SHRIMP U–Pb zircon results can be obtained from the Society Library or the British Library Document Supply Centre, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, UK as Supplementary Publication No. SUP 18208 (2 pages). It is also available online at http://www.geolsoc.org.uk/SUP18208.

All of the analysed grains are colourless, euhedral prisms. All had low U contents, leading to low concentrations of radiogenic Pb, and limiting the precision of the resulting analyses.

SA.39.1. Of 18 spots analysed using SHRIMP, one has high common Pb, and is excluded from the age calculations. The remaining 17 spots plot on a discordia, indicating an age of 180.2 ± 2.7 Ma (MSWD = 1.3; Fig. 3a). This is identical within

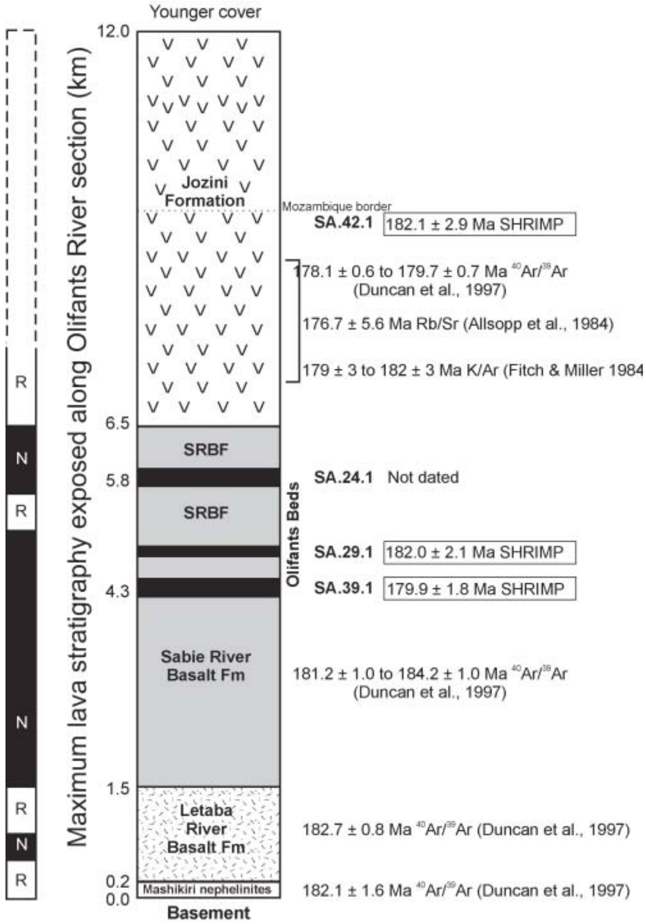

Fig. 2. Thickness of Karoo volcanic rocks along the Lebombo rifted volcanic margin and reported radiometric ages. Magnetostratigraphic information is from Hargreaves *et al.* (1997).

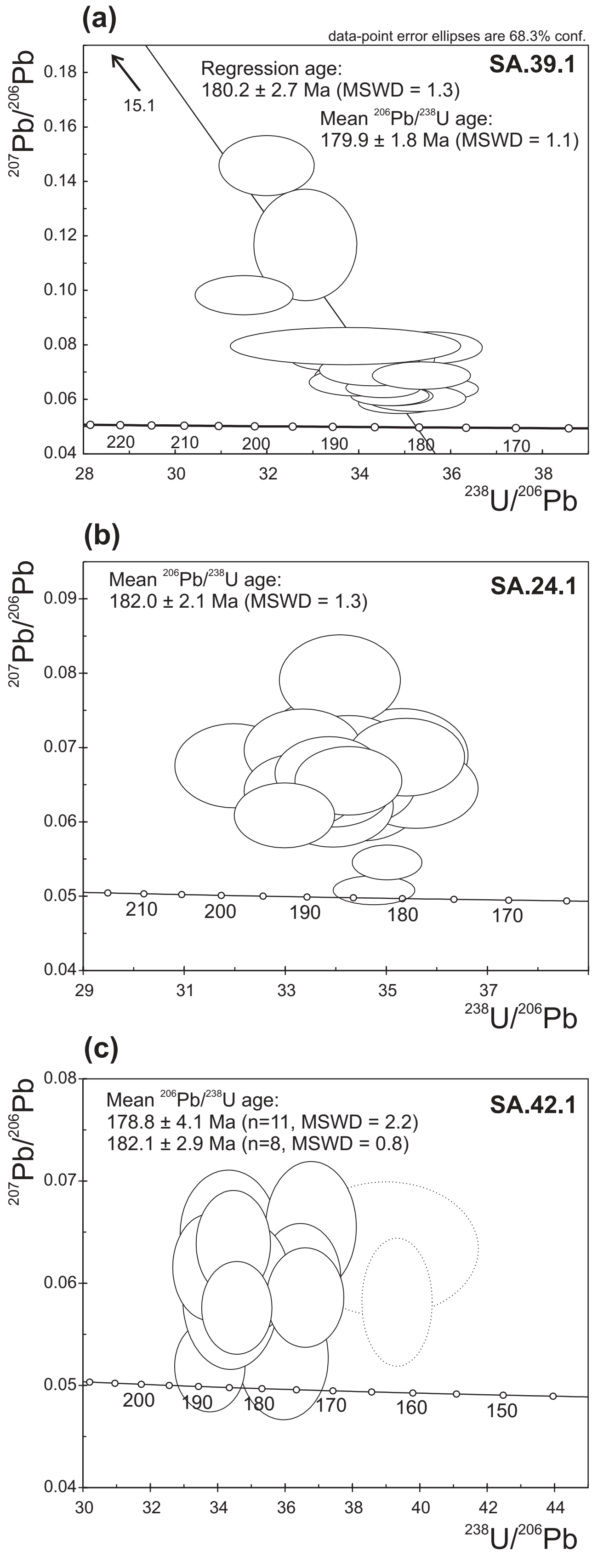

Fig. 3. U–Pb SHRIMP Tera–Wasserburg concordia plots for zircons from the Lebombo rhyolites. (**a**) SA.24.1, (**b**) SA.39.1, (**c**) SA.42.1.

error to the mean $^{206}Pb/^{238}U$ age of 179.9 ± 1.8 Ma (MSWD = 1.1), which is the preferred age for this sample.

SA.24.1 Twenty of the analysed grains plot close to Concordia, with a mean $^{206}Pb/^{238}U$ age of 182.0 ± 2.1 Ma (MSWD = 1.3; Fig. 2b). The spread in $^{238}U/^{206}Pb$ in Figure 3b may result from a combination of minor Pb loss with minor inheritance, or may simply reflect the low-U nature of the analysed grains. Inspection of linear probability plots suggests that 13 of the analysed spots form a single normally distributed population. However, the mean $^{206}Pb/^{238}U$ age of this population (182.1 ± 2.0, MSWD = 0.2) is indistinguishable from the mean age of the entire dataset.

One subhedral prism gave an Archaean $^{207}Pb/^{206}Pb$ age of 3119 ± 10 Ma and represents a xenocryst. This age is typical of the granitoids that post-date the Moodies Group of the Barberton greenstone belt and that predate the deposition of the Pongola Supergroup and Dominion Group Archaean cover sequences of the Kaapvaal craton (De Wit *et al*. 1992).

SA.42.1. Of 15 analysed grains, two have high common Pb contents, and are highly discordant. The remaining 13 analyses plot close to Concordia at *c.*180 Ma (Fig. 3c), but show a markedly skewed distribution on a probability plot, indicative of significant Pb loss. Removing two further points with significant Pb loss leaves a population with a mean $^{206}Pb/^{238}U$ age of 178.8 ± 4.1 Ma

(MSWD = 2.2). Three further points have minor Pb loss; discarding these analyses leaves a population of eight analyses with a mean $^{206}Pb/^{238}U$ age of 182.1 ± 2.9 Ma (MSWD = 0.8).

Interpretation. The two rhyolite units (Olifants River Beds), which are interbedded with the Sabie River Basalt Formation have ages of 179.9 ± 1.8 and 182.0 ± 2.1 Ma. The age range of the Sabie River Basalt Formation according to the $^{40}Ar/^{39}Ar$ data is not consistent with the geochronology of the underlying units: the Mashikiri nephelinites and Letaba picrites have been dated at 182.1 ± 1.6 and 182.7 ± 0.8 Ma respectively (Duncan *et al.* 1997), which would be consistent with a 182 Ma age for the overlying Sabie River Basalt Formation, even though the nephelinite age is based on a two-step plateau. A 182 Ma age for the Sabie River Basalt Formation is clearly consistent with the U–Pb age of one of the Olifants River Beds rhyolites (182.0 ± 2.1 Ma) and marginally within error for the other Olifants River Beds rhyolite (SA.39.1; 179.9 ± 1.8 Ma).

The age of the Jozini Formation rhyolites using U–Pb SHRIMP is 182.1 ± 2.9 Ma, which is within error of the Duncan *et al.* (1997) age of 178.9 ± 0.5 Ma. Nevertheless, the new age suggests that the rhyolites are closer in age to the underlying basaltic formations.

The new rhyolite ages from the Karoo succession tighten up the chronology of the volcanic sequences of the Lebombo. Combined with the $^{40}Ar/^{39}Ar$ geochronology of Duncan *et al.* (1997) there is considerable evidence that the most voluminous extrusive phase of the Karoo succession was emplaced during a period of 1–2 million years at *c.*182 Ma, with a major part erupted in less than 0.5 Ma (single magnetic period; Duncan *et al.* 1997). The $^{40}Ar/^{39}Ar$ ages of Duncan *et al.* (1997) combined with the SHRIMP ages from this study provide a more robust chronostratigraphy for the Lebombo succession, however the ages are not entirely consistent with the stratigraphy, e.g. the stratigraphically oldest Olifants Bed (SA.39.1) yields the youngest age, 179.9 ± 0.5 Ma. The contrast between $^{40}Ar/^{39}Ar$ and U–Pb ages in the Jozini Formation rhyolites maybe attributed to hydrothermal alteration preventing closure of the Ar–Ar geochronometer (Riley & Knight 2000). The $^{40}Ar/^{39}Ar$ age of the rhyolites (178.1 ± 0.6 to 179.7 ± 0.7 Ma) may represent a cooling age, whilst the U–Pb age (182.1 ± 2.9 Ma) represents a crystallization age.

The mafic/felsic succession of lavas and pyroclastic rocks is estimated to be at least 12 km in thickness and their eruption in a very short time period (1–2 million years) suggests more intense environmental impacts than hitherto supposed. The rapid emplacement of the basaltic and rhyolitic successions in the Karoo province indicates average eruption rates of 1–2 $km^3\ a^1$. These high levels of eruption are thought to have been responsible for triggering the end Pliensbachian extinction event (Hesselbo *et al.* 2000), which although not a major event, still led to the extinction of approximately 5% of marine animal families and genera (Pálfy & Smith 2000). The end-Pliensbachian event is also associated with a major inflection in the $^{87}Sr/^{86}Sr$ seawater curve. The subsequent rise of the curve in the Toarcian is thought to reflect increased humidity and continental weathering triggered by global warming associated with the increased volcanic emissions (Pálfy & Smith 2000; Cohen *et al.* 2004).

The revised age for the Jozini Formation rhyolites is also of significance for petrogenetic models proposed for the Karoo silicic magmatism. Bryan *et al.* (2002) reviewed the proposed models for the Lebombo rhyolites and favoured partial melting of recently underplated mafic magma, following crustal thinning. Such a model is supported by the overlap in age between the basaltic successions and the Jozini Formation rhyolites confirmed by U–Pb data, whereas previous data (Duncan *et al.* 1997) suggested a significant hiatus between the rhyolites and basalts.

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