Earth and Planetary Science Letters 302 (2011) 147–153

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

The onset of flood basalt volcanism, Northern Paraná Basin, Brazil: A precise U–Pb baddeleyite/zircon age for a Chapecó-type dacite

Valdecir de Assis Janasi [a,*], Vivian Azor de Freitas [a], Larry H. Heaman [b]

[a] Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, São Paulo, SP, 05508-080, Brazil
[b] Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, Alberta, T6G 2E3, Canada

ARTICLE INFO

Article history:
Received 17 August 2010
Received in revised form 23 November 2010
Accepted 1 December 2010
Available online 28 December 2010

Editor: R.W. Carlson

Keywords:
basalt
dacite
Large Igneous Province
U–Pb dating
Paraná–Etendeka Province

ABSTRACT

We report the first U–Pb baddeleyite/zircon date for a felsic volcanic rock from the Paraná Large Igneous Province in south Brazil. The new date of 134.3 ± 0.8 Ma for a hypocrystalline Chapecó-type dacite from Ourinhos (northern Paraná basin) is an important regional time marker for the onset of flood basalt volcanism in the northern and western portion of the province. The dated dacite was erupted onto basement rocks and is overlain by a high-Ti basalt sequence, interpreted to be correlative with Pitanga basalts elsewhere. This new U–Pb date for the Ourinhos dacite is consistent with the local stratigraphy being slightly older than the few reliable step-heating $^{40}Ar/^{39}Ar$ dates currently available for overlying high-Ti basalts (133.6–131.5 Ma). This indicates an ~3 Ma time span for the building of the voluminous high-Ti lava sequence of the Paraná basin. On the other hand, it overlaps the $^{40}Ar/^{39}Ar$ dates (134.8–134.1 Ma) available for the stratigraphically older low-Ti basalt (Gramado + Esmeralda types) and dacite–rhyolite (Palmas type) sequences from South Brazil, which is consistent with the short-lived character of this volcanism and its rapid succession by the high-Ti sequence.

1. Introduction

The Paraná–Etendeka Magmatic Province in southern South America and Southwest Africa is one of the largest continental flood basalt provinces preserved on Earth, with an estimated exposed area of ~1.0 million km². The origin of the Paraná and other Mesozoic flood basalt provinces have been central to evaluating models of the Large Igneous Province formation and evolution; however, there has been considerable debate over its exact timing, duration, stratigraphy and petrogenetic significance. Absolute dating of the dominantly basaltic magmatism within the Paraná flood basalts with sufficient precision (e.g., better than ± 1.0 Ma; 2σ) has been largely achieved using the $^{40}Ar/^{39}Ar$ method. By far the majority of the dates for the Paraná–Etendeka lava pile were obtained by the $^{40}Ar/^{39}Ar$ laser total fusion technique (Stewart et al., 1996; Turner et al., 1994), which was shown by more recent studies to yield misleading results (Kirstein et al., 2001; Thiede and Vasconcelos, 2010). As a result, currently less than a dozen published dates, obtained by the $^{40}Ar/^{39}Ar$ step heating technique (Ernesto et al., 1999; Renne et al., 1992; Thiede and Vasconcelos, 2010), can be considered “reliable” for the entire lava pile in Brazil.

U–Pb dating by isotope dilution thermal ionization mass spectrometry (ID-TIMS) is a robust technique for dating mafic rocks (e.g., Heaman and LeCheminant, 1993), yielding precise age determinations. However, aphanitic basalts are often devoid of U-bearing minerals suitable for U–Pb dating, such as zircon or baddeleyite. Using backscatter electron (BSE) imaging combined with Energy Dispersive Spectrometry semi-quantitative analyses we identified for the first time very small (<20 μm) baddeleyite (plus some zircon) crystals in silicic volcanics which, although volumetrically subordinate constituents of the Paraná–Etendeka Magmatic Province in Brazil (~2.5 vol.%; Bellieni et al., 1986; Garland et al., 1995), occur at key stratigraphic positions within the lava pile and are thus important regional time markers. Additionally, since it has been recognized that a systematic bias exists in previous $^{40}Ar/^{39}Ar$ dates, requiring an adjustment in the age of the flux-monitor (Kuiper et al., 2008; Min et al., 2000), the new ID-TIMS U–Pb age result obtained here allows a test for accuracy of the Paraná-Etendeka dating, as has been done in other Large Igneous Provinces, such as the Siberian Traps (Kamo et al., 2003; Reichow et al., 2009) and the Karoo (Riley et al., 2004).

2. Stratigraphy, timing and duration of the Paraná–Etendeka volcanism

Knowledge of the Paraná–Etendeka Magmatic Province stratigraphy in Brazil is still unsatisfactory, in part because apart from the well-exposed coastal Serra Geral escarpment, erosion levels are not deep enough to expose the lower levels of the lava pile inland. However, a relative stratigraphy has been constructed from province-wide magma-type correlations based on geochemical information from regional sections and a few deep oil drilling boreholes (Peate, 1997;

* Corresponding author. Tel.: +55 11 30913994; fax: +55 11 30914258.
E-mail address: vajanasi@usp.br (V.A. Janasi).

0012-821X © 2010 Elsevier B.V. Open access under the Elsevier OA license.
doi:10.1016/j.epsl.2010.12.005

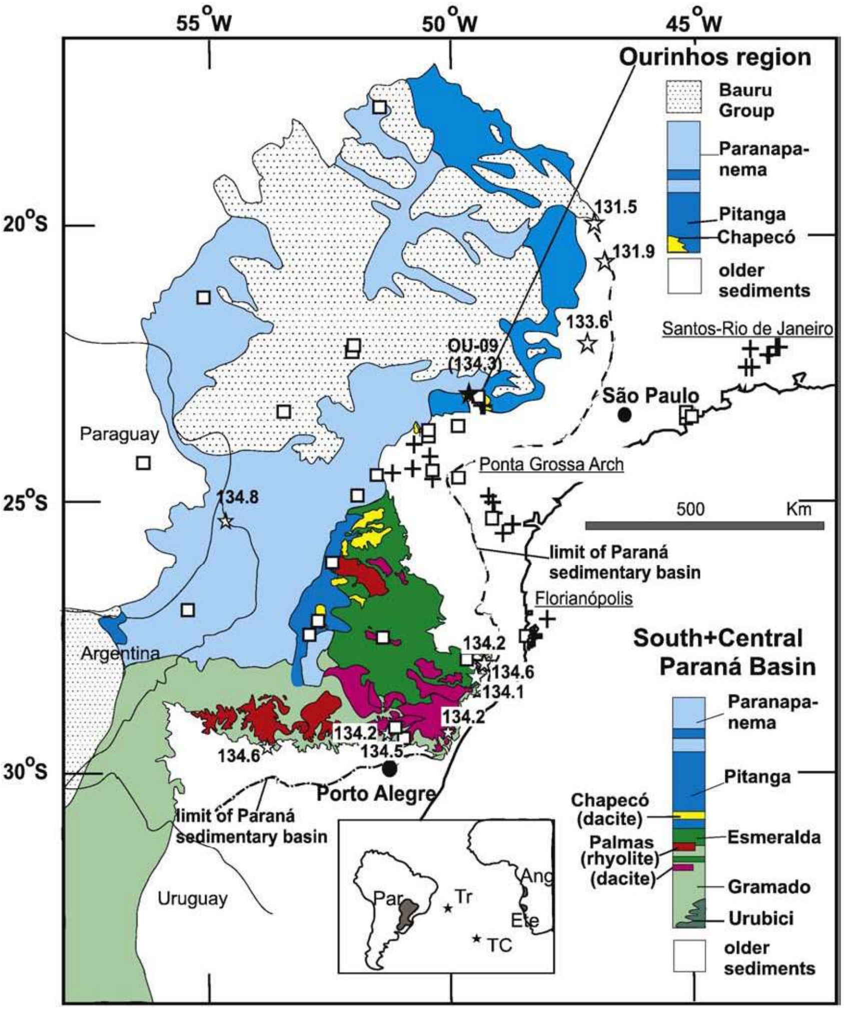

Fig. 1. Sketch map showing the distribution of the main basalt and dacite–rhyolite types in the Paraná sedimentary basin. Stratigraphic columns based on Nardy (1996) and Peate et al. (1992) (south-central portion of the Paraná basin) and Janasi et al. (2007) (Ourinhos region). Gramado, Esmeralda, Pitanga and Paranapanema are Paraná basalt magma-types after Peate et al. (1992). Chapecó and Palmas are high-Ti and low-Ti silicic magma-types. Open stars: sites of $^{40}Ar/^{39}Ar$ dating of lava flows and associated sills by stepped heating; all ages in Ma, recalculated to a 28.201 Ma for Fish Canyon Sanidine. Closed star: location of dated sample OU-09. Open squares: sites of $^{40}Ar/^{39}Ar$ dating of lava flows and dykes by total fusion (Stewart et al., 1996; Turner et al., 1994), presently considered to be unreliable; crosses: sites of $^{40}Ar/^{39}Ar$ dating of dykes by stepped heating (see text for age ranges). Inset at lower center shows the position of the Paraná (Par), Etendeka (Ete) and Angola (Ang) lavas within South America and Africa; Tr and TC are the location of Trindade and Tristán da Cunha, respectively.
Modified from Peate et al., 1992 and Stewart et al., 1996.

Peate et al., 1990, 1992). These studies indicated that the early volcanics, preserved at the southeastern portion of the Paraná basin, erupted as a sequence of "low-Ti" basalts (Gramado and Esmeralda magma-types) topped by genetically related low-Ti dacites and rhyolites (Palmas-type volcanics). A younger sequence of "high-Ti" basalts (Pitanga and Paranapanema magma types) makes up the northern and western portion of the Paraná basin (Fig. 1), overlying the low-Ti sequence, which extends as far as 300 km west of its outcrop area, as shown in the borehole sections (Peate, 1997; Peate et al., 1992). Felsic volcanics associated with the high-Ti basalts (Chapecó-type dacites) are volumetrically minor, and were shown to occur at the lower portion of this sequence, resting directly over the basement in the north (Janasi et al., 2007; Piccirillo et al., 1987) and overlying the upper flows of the low-Ti sequence (Esmeralda basalts or Palmas rhyolites) in the center of the Paraná basin (Nardy, 1996; Peate et al., 1990).

As mentioned above, estimates of timing and duration of the Paraná–Etendeka magmatism are largely based on $^{40}Ar/^{39}Ar$ dating. The studies by Stewart et al. (1996) and Turner et al. (1994) reported a large number of age determinations ($N = 42$) for lava flows from most of the exposed area of the Province in Brazil and from the over 1000-m-thick unexposed lava sequences in the central portion of the province (recovered as chips from boreholes). The total fusion technique used by these authors, however, was later shown in the works by the same research group to yield misleading results in similar rocks (Kirstein et al., 2001, p. 587). The suspicion that these results might be unreliable was recently confirmed by re-analysis of the exact same hand samples for which the oldest (~138 Ma) and youngest (~128 Ma) dates were obtained by Stewart et al. (1996); these new $^{40}Ar/^{39}Ar$ step-wise heating dates ($N = 3$) were shown to be identical at 134.2–134.8 Ma (Thiede and Vasconcelos, 2010).

Fig. 1 shows the distribution of the meagre 11 published $^{40}Ar/^{39}Ar$ dates by step-wise heating currently available in the literature for the Paraná–Etendeka lavas in Brazil: five from Renne et al. (1992), three from Ernesto et al. (1999), plus the three re-analysed samples by Thiede and Vasconcelos (2010)[1]. It is clear from Fig. 1 that the dataset

[1] All $^{40}Ar/^{39}Ar$ dates reported here were re-calculated to the currently used 28.201 Ma age for the Fish Canyon sanidine (FCs) flux monitor (Kuiper et al., 2008) and are presented in Table A; Supplementary Data. A paper by Renne et al. (2010) published while this article was under review proposes a slightly older $^{40}Ar/^{39}Ar$ age for the FCs (24.305 Ma); the use of this value would increase the ages reported here by ~0.4 Ma.

is concentrated on the stratigraphically oldest low-Ti basalt types (Gramado and Esmeralda), so claims for an ~1 Ma duration (134.6 ± 0.6 Ma) for the building of the whole lava pile (Thiede and Vasconcelos, 2010) must be taken with caution. The slightly younger ages reported for the northern high-Ti basalt types by Ernesto et al. (1999) (133.6–131.5 Ma) instead suggest a duration of ~3 Ma (134.8–131.5 Ma), and are consistent with the northward progression from "low-Ti" to "high-Ti" magmatism as deduced from the regional stratigraphic correlation (Peate et al., 1990).

Also shown in Fig. 1 is the *location* of $^{40}Ar/^{39}Ar$ step-wise heating dates obtained for dykes from the three main dyke swarms of the Paraná–Etendeka (Santos–Rio de Janeiro, Ponta Grossa and Florianópolis; Deckart et al., 1998; Guedes et al., 2005; Raposo et al., 1998; Renne et al., 1996a,b). Most of the dyke dates overlap with the lavas (23 out of 34 dates are within the 130–136 Ma range), but younger dates (128–121 Ma) were found in Ponta Grossa (3 out of 17) and especially in Florianópolis, where the bulk of the samples with "accepted" ages (Raposo et al., 1998) tends to yield younger dates (130–121 Ma). Accurate dating of the dyke swarms is further complicated by the common existence of older dates (146–140 Ma) that were attributed to excess Ar (Raposo et al., 1998). In the Santos–Rio de Janeiro Dyke Swarm, Deckart et al. (1998) analysed plagioclase crystals from four diabase samples and obtained in all cases complex patterns with a younger "mini-plateaux" (~132 Ma) at lower temperature and an older one (135–136 Ma) at high temperature. The authors attributed the older ages to excess argon, and assumed that the lower temperature plateaux represent the magmatic age, but later work by Guedes et al. (2005) in the same region yielded plagioclase and whole-rock step-wise heating $^{40}Ar/^{39}Ar$ dates of 134–135 Ma.

In summary, although a comparatively large number of step-wise heating $^{40}Ar/^{39}Ar$ analyses exists for the Paraná dyke swarms, some of these results may be spurious, owing to problems with Ar excess and/or loss. The time span reported in the literature for dyke emplacement within a single swarm in the Paraná–Etendeka Magmatic Province appears to be larger than what is currently indicated for the entire lava pile (e.g., up to 11 Ma in Ponta Grossa). At least in the Florianópolis swarm, the majority of the 'accepted' ages (including dykes which chemically appear to correspond to feeders of the Urubici magma-type; Marques, 2001; Peate et al., 1999) are younger than the lavas.

Regarding the duration of the Paraná–Etendeka magmatism, it is also relevant to observe that alkaline magmatism at the western border of the Paraná basin in Paraguay, considered as genetically related to the province, is represented by two distinct associations, one predating the tholeiitic basalts at ~145 Ma and the immediately post-dating the basalts at 128–126 Ma (step-wise heating $^{40}Ar/^{39}Ar$ dates from Comin-Chiaramonti et al., 2007; Gibson et al., 2006). Persistence of small-volume magmatism after building of the main lava pile is also revealed by the ages of felsic volcanic rocks in the southern border of the Paraná–Etendeka Province in Uruguay (most $^{40}Ar/^{39}Ar$ dates are 130–126 Ma; Kirstein et al., 2001). In Etendeka, where the ages of felsic volcanic rocks and related intrusive complexes typically overlap the eruptive basalts (average age of 134 Ma; Renne et al., 1996a,b), consistent with a coeval origin based on field relations, small-volume alkaline rocks dated at ~131–130 Ma are locally present (Renne et al., 1996a,b; Wigand et al., 2004).

3. Local geology and sampling for U–Pb dating

BSE imaging combined with semi-quantitative EDS analyses revealed the presence of small amounts of U-bearing accessory minerals, such as titanite, baddeleyite, monazite, zircon and zirconolite in hypocrystalline felsic volcanic rocks from the Paraná–Etendeka Province in Brazil (Fig. 2). Baddeleyite occurs as 0.5 to 20 μm grains associated with matrix micrographic intergrowths of alkali feldspar and quartz or included in Fe–Ti oxides. Whereas other recent studies were successful in extracting magmatic zircon from Paraná–Etendeka felsic volcanic rocks (e.g., Pinto, 2010), we notice that baddeleyite is

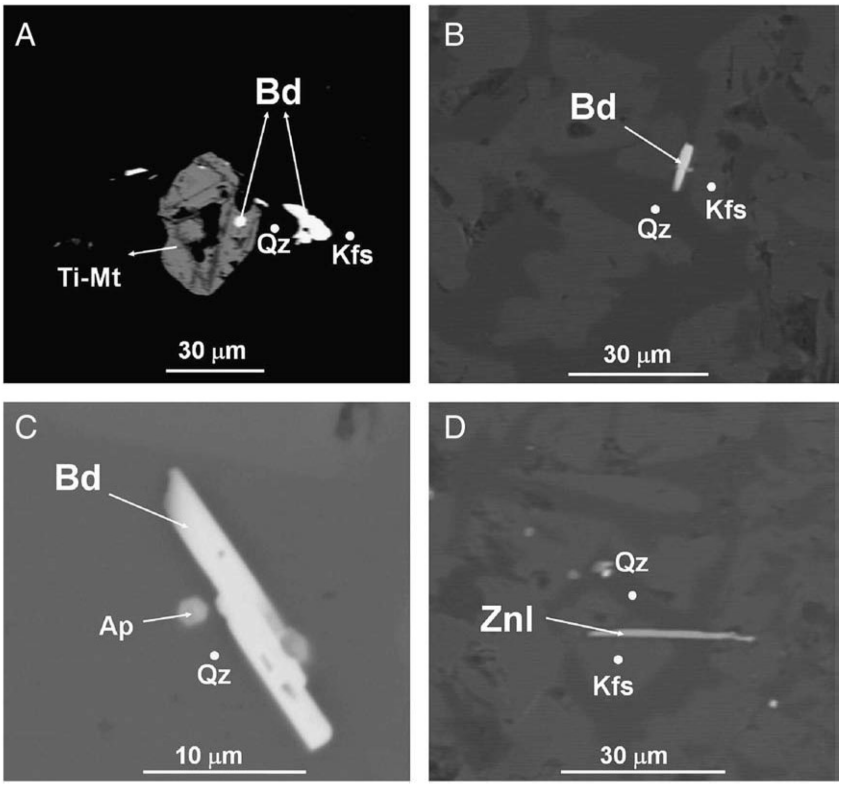

Fig. 2. BSE images of baddeleyite and zirconolite and their textural relationships. (A) baddeleyite (Bd) crystals included in Ti-magnetite (Mt) and associated with matrix quartz (Qz) + alkali feldspar (Kfs); (B) baddeleyite associated with matrix intergrowth of alkali feldspar + quartz; (C) detail of two blade-shaped baddeleyite crystals associated with quartz; (D) acicular zirconolite (Znl) crystal associated with quartz + alkali feldspar.

the main, and in some cases, the only Zr-bearing accessory mineral in many of the silica-supersaturated rocks in this study. This is somewhat surprising, but stable baddeleyite plus quartz assemblages have been known for some time (e.g., Heaman and LeCheminant, 1993), and have been reported in high-silica rhyolites from Yellowstone (Bindeman and Valley, 2001).

Although baddeleyite was identified in several samples from both "low-Ti" Palmas and "high-Ti" Chapecó felsic volcanics, due to its very small size (typically <10 μm) sufficient amounts for U–Pb dating were only recovered from a sample of Chapecó-type dacite from the Ourinhos region. Recovering baddeleyite from Palmas-type volcanics has proven particularly difficult given the usually glassy texture of these rocks and their lower Zr contents (<300 ppm, nearly half the contents in the Chapecó-type).

The Ourinhos dacites are the northernmost occurrences of Paraná–Etendeka felsic volcanic rocks in Brazil, and are exposed as a ~65×20 km elongated strip trending 320° (Janasi et al., 2007). They were emplaced directly over a very irregular dune field (the Botucatu Formation sandstones) and are overlain by high-Ti basalts (Piccirillo et al., 1987; see Fig. 1). Locally, the first basalt flows geochemically correspond to the Pitanga magma-type of Peate et al. (1992) and are in turn overlain by Paranapanema-type basalts (Janasi et al., 2007; Peate, 1997).

The eruption mechanism of the high-temperature (~1000 °C) Chapecó-type silicic volcanics is controversial. Marsh et al. (2001) suggested that the Ourinhos dacites are part of a single rheoignimbrite unit extending for some 650 km, by correlating it with the chemically and stratigraphically equivalent Khoraseb acid volcanics in Etendeka. This concept was further explored by Bryan et al. (2010), who identified the Ourinhos–Khoraseb unit as one of a series of at least nine large magnitude silicic eruptions that would have occurred within a short period (~1 Ma) in the Paraná–Etendeka Province. On the other hand, extrusion as lava flows or lava-domes was admitted by Garland et al. (1995) as the more likely emplacement mechanism for the Chapecó-type volcanics, and detailed examination of field structures and petrographic features in the Ourinhos dacites showed no signs of pyroclastic emplacement (Luchetti, 2010). There is also no evidence that the Ourinhos dacites extend very far to the west beneath the younger basalts.

Our detailed field work over the whole area of occurrence of the Ourinhos dacites identified at least three flow units. The lower unit has a thick (>50 m) vesicular chocolate-brown lower portion when filling previous depressions (valleys in the dune field), but the other flows have a typical zoning (Janasi et al., 2007; Nardy et al., 2008): a thick central portion of vesicle-poor, hypocrystalline dacite with diffuse vertical jointing and "salt and pepper" texture is bordered by vesicular glassy top and basal portions. The glassy borders show different jointing patterns, a closely spaced horizontal jointing being typical of the lower portions. The lower flows are occasionally brecciated and intruded by mm–cm clastic dykes derived from underlying sandstones that can occur as interflow sediments. The thickness of individual dacite flows is variable but may reach up to 100 m.

The Ourinhos dacites are porphyritic with 10–15 vol.% phenocrysts of calcic andesine ($An_{47–40}$), augite, pigeonite, Fe–Ti oxides and apatite set in a rhyolitic matrix (70–78 wt.% SiO_2; 7–11 wt.% Na_2O+K_2O); see Janasi et al. (2007) for further details.

4. Analytical techniques

In view of the small size of the Zr-rich minerals that were the target of this study, sample preparation was a critical step, and was performed at the Radiogenic Isotope Facility, University of Alberta. Based on the petrographic observations from the most crystalline samples, dacite OU-09 (from the upper flow unit), which contains the least amount of glassy material, was the only sample that yielded a sufficient amount of zircon and baddeleyite for U–Pb dating (~50 crystals). A slice (12×5×1.5 cm) of the sample was pulverized in a tungsten carbide shatter box to produce a powder with grain size smaller than 100 mesh. The powder was mixed with water and detergent and then slowly poured by hand (~100 g/h) on a Wilfley Table to obtain a heavy mineral concentrate that was then passed through disposable nylon sieves; most of the Zr-bearing minerals were identified in the <74 μm fraction. These minerals were further segregated using a variety of magnetic (Frantz Isodynamic Separator) and density (methylene iodide) separation techniques. Baddeleyite and zircon crystals present in the non-magnetic fraction were hand-picked using a binocular microscope.

Cleaning of the selected crystals was carefully done with acetone and 4N HNO_3 in custom-built Teflon pipettes; fraction weights were estimated from the number, size and density of grains. The fractions were loaded into TFE Teflon bombs with 48% HF:7N HNO_3 (10:1) plus a measured amount of a $^{205}Pb–^{235}U$ spike solution, then placed in an oven for approximately 100 h at a temperature of 215 °C. Uranium and lead were purified from the sample solution using anion exchange chromatography. Custom built Teflon micro-columns were loaded with Dowex AG1 X8, 200–400 mesh, chloride form resin. After an initial elution with 3.1N HCl, U and Pb were collected with the addition of 6.2N HCl and H_2O, respectively. Isotopic analyses were performed using a VG354 thermal ionization mass spectrometer operating in single collector Daly photomultiplier detector mode. Total analytical blanks obtained during this study were 1 pg Pb and 0.5 pg U. The isotopic composition of the Pb blank used in this study ($^{206}Pb/^{204}Pb=18.24$; $^{207}Pb/^{206}Pb=0.85757$; $^{208}Pb/^{206}Pb=2.056$; 1σ uncertainty is ~2%) is the average composition determined over a two year period. The total amount of common lead present in the analysed zircon and baddeleyite fractions were between 5 and 14 pg, an exception being one baddeleyite fraction with 164 pg Pb. The source of this common Pb in excess of the estimated analytical blank is unknown but is likely related to Pb residing along fractures and in tiny mineral inclusions (Fig. 2) that was not removed during acid cleaning. To constrain the initial Pb isotopic composition of the dacite magma and to provide an estimate for the appropriate common Pb correction for the baddeleyite and zircon analyses, a total of 160 clinopyroxene crystals were selected from sample OU-07. The results are presented in Table 1: clinopyroxene has moderate $^{238}U/^{204}Pb$ (78.7) and initial $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ isotopic compositions of 18.55 and 15.57, respectively; assuming a crystallization age of 135 Ma. These compositions are very similar to the values estimated using 135 Ma Stacey and Kramers (1975) average crustal Pb of 18.50 and 15.62 and provide independent evidence that these are the appropriate initial Pb isotopic compositions of the dacite magma. One sigma uncertainties in the initial Pb isotopic compositions ($^{206}Pb/^{204}Pb=2\%$; $^{207}Pb/^{204}Pb=0.5\%$; $^{208}Pb/^{204}Pb=2\%$) are numerically propagated in calculating the total uncertainty in these analyses. Therefore, isotopic ratios were corrected for the common Pb in excess of this blank using the two-stage model of Stacey and Kramers (1975). Ages were calculated using the ISOPLOT software (Ludwig, 1992). Decay constants ($^{235}U=0.98485\times10^{-9}$ $year^{-1}$), ^{238}U (0.155125×10^{-9} $year^{-1}$) and U isotopic composition ($^{238}U/^{235}U=137.88$) are those determined by Jaffey et al. (1971) and recommended by Steiger and Jäger (1977).

5. Results of U–Pb dating

Three baddeleyite fractions each consisting of between 6–21 crystals and one zircon fraction (5 crystals) from dacite OU-09, the most crystalline textural variety from the Ourinhos occurrence, were analysed. The U–Pb results are presented in Table 1 and on a concordia diagram in Fig. 3. The zircon crystals are anhedral, colorless, small (50–70 μm), and have high Th/U (1.5) and U (~1000 ppm). As shown by Pinto (2010), high Th/U seems typical of zircon from the Paraná silicic rocks; their SHRIMP analyses of two samples from Chapecó-type dacites have shown even higher Th/U (2.9) at similar U (1000–

Table 1
U–Pb TIMS results for baddeleyite, zircon and clinopyroxene from Chapecó-type dacites, northern Parana Basin, Brazil.

Description	Weight (µg)	U (ppm)	Th (ppm)	Pb (ppm)	Th/U	TCPb (pg)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{238}U$	1s error	$^{207}Pb/^{235}U$	1s error	$^{207}Pb/^{206}Pb$	1s error	Model ages (Ma) $^{206}Pb/^{238}U$	1s error	$^{207}Pb/^{235}U$	1s error	$^{207}Pb/^{206}Pb$	1s error	%Disc
OU-09-1 Baddeleyite																				
6 tan frags	2.0	348	65	91	0.19	164	26	0.02649	0.00146	0.2986	0.0493	0.08174	0.01401	168.6	9.2	265.3	37.8	1239.3	303.6	−5.4
OU-09-2 Baddeleyite																				
13 tan frags, −325, FF0.4(NM)	1.0	751	802	35	1.07	14	100	0.02413	0.00014	0.1727	0.0062	0.05190	0.00178	153.7	0.9	161.7	5.3	280.9	76.4	−2.5
OU-09-3 Zircon																				
5 anhedral colorless grains	2.0	999	1509	34	1.51	14	209	0.02104	0.00007	0.1391	0.0040	0.04793	0.00130	134.2	0.4	132.2	3.5	96.0	63.0	−0.6
OU-09-4 Baddeleyite																				
21 tan frags, −325, FF0.4(NM)	1.0	263	19	9	0.07	5	91	0.02113	0.00014	0.1416	0.0083	0.04861	0.00272	134.8	0.9	134.5	7.3	129.0	126.5	−0.1
OU-07-1 Clinopyroxene																				
160 black, −325, FF0.2(M)	68.6	0.2	1.1	0.2	4.22	19	19	0.02180	0.01147	0.1427	2.8699	0.04748	0.95317	139.0	72.0	135.4	1275.4	73.3	5165.0	−90.6

Atomic ratios corrected for blank (1.0 pg Pb; 0.5 pg U), fractionation and initial common Pb (Stacey and Kramers, 1975). TCPb refers to the total amount of common lead present in the analyses in picograms. Th concentration estimated from the amount of ^{208}Pb present in the analysis and the $^{207}Pb/^{206}Pb$ age. %Disc refers to the amount of discordance along a reference line to zero age. All errors in this table are reported at 1 sigma. −325 = less than 325 mesh, FF0.4(NM) = non-magnetic split at 0.4 A on a Frantz Isodynamic Separator. Sample location: OU-07: 23.161 S; 49.509 W; OU-09: 23.181 S; 49.559 W. Clinopyroxene fraction was analysed in order to estimate the Pb isotope composition.

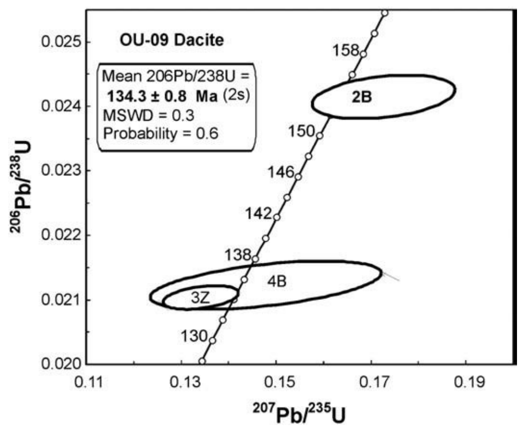

Fig. 3. Concordia diagram showing U–Pb results for two baddeleyite and one zircon fraction from Ourinhos dacite OU-09. 2B and 4B correspond to baddeleyite analyses OU-09-2 and OU-09-4 respectively, and 3Z corresponds to zircon analysis OU-09-3 in Table 1. The mean $^{206}Pb/^{238}U$ date of 134.3 ± 0.8 Ma interpreted as the magmatic age corresponds to the weighted average of 4B and 3Z.

1100 ppm). The recovered baddeleyite crystals are yellow to tan in color, small (10–40 µm), subhedral, with a blade-like habit. Fractions #1 and 3 have low Th/U (0.09–0.19) and U (263–348 ppm), typical for magmatic baddeleyite whereas fraction #2 has much higher Th/U (1.07) and U (751 ppm).

Baddeleyite fraction #4 and zircon fraction #3 yielded consistent $^{206}Pb/^{238}U$ ages of 134.8 ± 0.9 and 134.2 ± 0.4 Ma (1σ), respectively. The weighted average $^{206}Pb/^{238}U$ date for these two fractions of 134.3 ± 0.8 Ma (2σ) is considered the best estimate for the age of magmatic crystallization of dacite OU-09.

The other analyses did not provide meaningful U–Pb results for constraining the timing of dacite crystallization. Baddeleyite fractions #1 and 2 yield older $^{206}Pb/^{238}U$ ages of 168.7 ± 9.2 and 153.7 ± 0.9 Ma (1σ) respectively, but are not considered good estimates for the time of dacite crystallization. Fraction #1 has a high total common lead content (164 pg) and is extremely sensitive to the common Pb correction used, as indicated by the high associated error (not shown on concordia diagram). Fraction #2 has an unusually high Th/U for baddeleyite (usually <0.2), which could indicate that some mineral fragments other than baddeleyite were accidentally included in this fraction (e.g., a tiny fragment of a xenocrystic zircon crystal).

6. Discussion

The Chapecó-type dacites from the Ourinhos region dated in this study were erupted directly onto basement and are overlain by the main package of high-Ti basalts from the northern Paraná basin (Janasi et al., 2007; Peate, 1997; Piccirillo et al., 1987). Along their wide area of exposure the Chapecó-type dacites show some important geochemical variations, but their stratigraphic position does not appear to change; the volumetrically more abundant Guarapuava subtype that occurs at the central portion of the Paraná basin is consistently positioned immediately above the low-Ti basalt sequence, and predates or is interleaved with the first high-Ti basalts (e.g., the "RS" borehole, Peate et al., 1992). Therefore, the weighted average $^{206}Pb/^{238}U$ zircon/baddeleyite date of 134.3 ± 0.8 Ma (2σ) obtained for the Ourinhos dacite provides a new age constraint for the onset of high-Ti basalt volcanism in the northern portion of the basin. This is consistent with the slightly younger $^{40}Ar/^{39}Ar$ ages obtained by Ernesto et al. (1999) for one flow and two associated sills of overlying high-Ti basalt in the northern portion of the Province (133.6–131.5 Ma).

Previous ages available for the Ourinhos dacites by the K–Ar method are in agreement with the results presented here, but much less precise (133 ± 6 and 134 ± 6 Ma; Piccirillo et al., 1987). The $^{40}Ar/^{39}Ar$ stepped-heating age reported for a 50-m-wide "rhyolite" dyke from this region by Renne et al. (1996a,b) (132.9 ± 0.5 Ma; sample PR93-17B in Supplementary Table A) appears slightly younger but nearly overlaps our U–Pb date.

Other ages are reported in literature for Chapecó-type dacites from the central portion of the Paraná basin (the Guarapuava subtype, which as discussed is in an equivalent stratigraphic position). Mantovani et al. (1985) reported a Rb–Sr isochron date of 135.5 ± 3.2 Ma for three samples from this region. Pinto (2010) reported SHRIMP U–Pb zircon ages for two Chapecó-type dacites from the central Paraná basin which, although less precise (134.8 ± 1.4 Ma and 135.6 ± 1.8 Ma), are within error with the ID-TIMS U–Pb age reported here.

Based on province-wide stratigraphic relationships, the "southern" low-Ti (Gramado and Esmeralda type) basalts are expected to be older than the Chapecó-type acid volcanics. In the central Paraná–Etendeka Province, the latter can be shown to cap Palmas-type rhyolites (Nardy, 1996) which in turn were emplaced at the top of the low-Ti basalts (Garland et al., 1995). $^{40}Ar/^{39}Ar$ dates for the low-Ti Gramado and Esmeralda basalts in the type-area located in the southern Brazil escarpment by Renne et al. (1992) and Thiede and Vasconcelos (2010) are clustered at 134.1–134.8 Ma. The overlap between the $^{40}Ar/^{39}Ar$ stepped-heating dates of the low-Ti basalt magmatism from south Brazil and the ID-TIMS U–Pb age obtained here for the Ourinhos dacite is consistent with the idea that these basalts (and overlying Palmas-type felsic volcanics) were emplaced over a very short period of ~1 Ma (as also supported by the paleomagnetic data; cf. Renne et al., 1992; Thiede and Vasconcelos, 2010).

In our view, the picture that emerges from the evaluation of the current geochronological dataset for the entire Paraná–Etendeka lava pile in Brazil and neighboring areas in Paraguay and Argentina is consistent with a short duration of ~3 Ma for the building of the full lava pile. The emplacement of the main high-Ti basalt sequence (Pitanga and Paranapanema types), inferred from known stratigraphic relations to be younger than the Ourinhos dacites, may have spanned some 3 Ma (~134.5–131.5 Ma), judging from our new data and the previous $^{40}Ar/^{39}Ar$ stepped-heating dates from Ernesto et al. (1999). The few precise U–Pb TIMS zircon dates for felsic volcanic rocks available in the literature reinforce the view that the Paraná–Etendeka basalt–rhyolite magmatism largely occurred during this 3 Ma period. For example, a precise TIMS $^{206}Pb/^{238}U$ zircon date of 133.1 ± 0.3 Ma recently presented by Renne et al. (2010) for a rhyolite from Uruguay is in excellent agreement with this conclusion. Less precise U–Pb SIMS zircon dates hint that the duration of volcanism could be slightly longer (135–130 Ma; Pinto, 2010; Wigand et al., 2004) but confirmation of the accuracy of these rhyolite dates requires additional high-precision study. Likewise, the "old" $^{40}Ar/^{39}Ar$ dates obtained by the total fusion technique by Stewart et al. (1996) and Turner et al. (1994) were used by these authors to infer that the magmatism commenced at the northern and western portion of the Paraná basin, but these are now considered misleading (e.g., sample PAR-1, dated at ~138 Ma was re-analysed by Thiede and Vasconcelos, 2010, yielding 134.8 ± 0.7 Ma). However, there are clearly too few age determinations for basalts from the northwestern part of the basin; more analyses are needed to confirm their chronology.

We finish by observing that there is excellent agreement between our new 134.3 Ma U–Pb age for the Ourinhos dacite and revised $^{40}Ar/^{39}Ar$ dates for basalts that are only slightly stratigraphically higher in the section, reinforcing the suggestion that a revision in the published $^{40}Ar/^{39}Ar$ dates using the slightly older ages proposed recently for the Fish Canyon sanidine (Kuiper et al., 2008; Renne et al., 2010) may indeed reconcile the U–Pb and Ar/Ar clocks. This allows both methods to be used in conjunction not only for estimating the duration but also for absolute timing of magmatism in the Paraná–Etendeka. Felsic volcanic rocks are more common in the Paraná–Etendeka Province than in most continental basalt provinces and occur at key stratigraphic positions within the lava pile. We conclude therefore that a combination of high-precision U–Pb baddeleyite/zircon and $^{40}Ar/^{39}Ar$ step-heating techniques can be successfully applied to unravel the detailed volcanic history of the province.

Supplementary materials related to this article can be found online at doi:10.1016/j.epsl.2010.12.005.

Acknowledgements

Tarcisio Montanheiro and Francisco Negri are thanked for the collaboration in the field work that was critical for the establishment of stratigraphic relationships. Judy Schultz and Gayle Hatchard were of invaluable help with the heavy mineral extraction and mass spectrometer analyses, respectively, at the University of Alberta. We appreciate financial support for the U–Pb geochronology from NSERC (Discovery and Major Resources Support Grants) and for field and laboratory work from the Brazilian funding agencies Fapesp and CNPq. Paulo Vasconcelos is thanked for sharing a copy of his spreadsheet used to recalculate $^{40}Ar/^{39}Ar$ ages with a change in flux monitor age. David Peate, an anonymous referee, and the editor, Richard Carlson, provided very helpful comments.

References

Bellieni, G., Comin-Chiaramonti, P., Marques, L.S., Melfi, A.J., Nardy, A.J.R., Papatrechas, C., Piccirillo, E.M., Roisenberg, A., Stolfa, D., 1986. Petrogenetic aspects of acid and basaltic lavas from the Paraná Plateau (Brazil): geological, mineralogical and petrochemical relationships. J. Petrol. 27, 915–944.

Bindeman, I.N., Valley, J.W., 2001. Low-δ18O rhyolites from Yellowstone: magmatic evolution based on analyses of zircons and individual phenocrysts. J. Petrol. 42, 1491–1517.

Bryan, S.E., Peate, I.U., Peate, D.W., Self, S., Jerram, D.A., Mawby, M.R., Marsh, J.S., Miller, J.A., 2010. The largest volcanic eruptions on Earth. Earth Sci. Rev. 102, 207–229.

Comin-Chiaramonti, P., Marzoli, A., de Barros Gomes, C., Milan, A., Riccomini, C., Velázquez, V.F., Mantovani, M.M.S., Renne, P., Tassinari, C.C.G., Vasconcelos, P.M., 2007. The origin of post-Paleozoic magmatism in eastern Paraguay. Geol. Soc. Am. Spec. Pap. 430, 603–633.

Deckart, K., Féraud, G., S. Marques, L., Bertrand, H., 1998. New time constraints on dyke swarms related to the Paraná-Etendeka magmatic province, and subsequent South Atlantic opening, southeastern Brazil. J. Volcanol. Geotherm. Res. 80, 67–83.

Ernesto, M., Raposo, M.I.B., Marques, L.S., Renne, P.R., Diogo, L.A., de Min, A., 1999. Paleomagnetism, geochemistry and $^{40}Ar/^{39}Ar$ dating of the North-eastern Paraná Magmatic Province: tectonic implications. J. Geodyn. 28, 321–340.

Garland, F., Hawkesworth, C.J., Mantovani, M.S.M., 1995. Description and petrogenesis of the Paraná rhyolites, Southern Brazil. J. Petrol. 36, 1193–1227.

Gibson, S.A., Thompson, R.N., Day, J.A., 2006. Timescales and mechanisms of plume–lithosphere interactions: $^{40}Ar/^{39}Ar$ geochronology and geochemistry of alkaline igneous rocks from the Paraná–Etendeka large igneous province. Earth Planet. Sci. Lett. 251, 1–17.

Guedes, E., Heilbron, M., Vasconcelos, P.M., Valeriano, C.M., Almeida, J.C.H., Teixeira, W., Thomaz Filho, A., 2005. K–Ar and $^{40}Ar/^{39}Ar$ ages of dykes emplaced in the onshore basement of the Santos Basin, Resende area, SE Brazil: implications for the south Atlantic opening and tertiary reactivation. J. S. Am. Earth Sci. 18, 371–382.

Heaman, L.M., LeCheminant, A.N., 1993. Paragenesis and U–Pb systematics of baddeleyite (ZrO2). Chem. Geol. 110, 95–126.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M., 1971. Precision measurements of half-lives and specific activities of 235U and 238U. Phys. Rev. C4, 1889–1906.

Janasi, V.A., Montanheiro, T.J., Freitas, V.A., Reis, P.M., Negri, F.A., Dantas, F.A., 2007. Geology, petrography and geochemistry of the acid volcanism of the Paraná Magmatic Province in the Piraju–Ourinhos region, SE Brazil. Rev. Bras. Geocienc. 37, 745–759.

Kamo, S.L., Czamanske, G.K., Amelin, Y., Fedorenko, V.A., Davis, D.W., Trofimov, V.R., 2003. Rapid eruption of Siberian flood–volcanic rocks and evidence for coincidence with the Permian–Triassic boundary and mass extinction at 251 Ma. Earth Planet. Sci. Lett. 214, 75–91.

Kirstein, L.A., Kelley, S., Hawkesworth, C., Turner, S., Mantovani, M., Wijbrans, J., 2001. Protracted felsic magmatic activity associated with the opening of the South Atlantic. J. Geol. Soc. 158, 583–592.

Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R., Wijbrans, J.R., 2008. Synchronizing rock clocks of earth history. Science 320, 500–504.

Luchetti, A.C.F. 2010. Aspectos vulcanológicos dos traquidacitos da região de Piraju–Ourinhos (SP) [Master Dissertation]. São Paulo, SP, Brazil, Universidade de São Paulo, 92 pp.

Ludwig, K.R., 1992. ISOPLOT—a plotting and regression program for radiogenic isotope data, version 2.57. U.S. Geological Survey Open File Report 91. . 445 pp.

Mantovani, M.S.M., Cordani, U.G., Roisenberg, A., 1985. Geoquímica isotópica em vulcânicas ácidas da Bacia do Paraná, e implicações genéticas associadas. Rev. Bras. Geocienc. 15, 61–65.

Marques, L.S., 2001. Geoquímica dos diques toleíticos da costa sul-sudeste do Brasil: contribuição ao conhecimento da Província Magmática do Paraná. [Livre-Docência Thesis]. São Paulo, SP, Brazil, Universidade de São Paulo.
Marsh, J.S., Ewart, A., Milner, S.C., Duncan, A.R., Miller, R.M., 2001. The Etendeka Igneous Province: magma types and their stratigraphic distribution with implications for the evolution of the Paraná–Etendeka flood basalt province. Bull. Volcanol. 62, 464–486.
Min, K., Mundil, R., Renne, P.R., Ludwig, K.R., 2000. A test for systematic errors in $^{40}Ar/^{39}Ar$ geochronology through comparison with U/Pb analysis of a 1.1-Ga rhyolite. Geochim. Cosmochim. Acta 64, 73–98.
Nardy, A.J.R., 1996. Geologia e petrologia das rochas vulcânicas mesozóicas da região central da Bacia do Paraná [Doctoral thesis]. Rio Claro, SP, Brazil, Universidade Estadual Paulista
Nardy, A.J.R., Machado, F.B., Oliveira, M.A.F., 2008. As rochas vulcânicas mesozóicas ácidas da Bacia do Paraná: litoestratigrafia e considerações geoquímico-estratigráficas. Rev. Bras. Geocienc. 38, 178–195.
Peate, D.W., 1997. The Paraná–Etendeka Province. In: Mahoney, J.J., Coffin, M.F. (Eds.), Large Igneous Provinces: Continental, Oceanic, and Planetary Flood Volcanism, Volume 100. American Geophysical Union, pp. 217–245.
Peate, D.W., Hawkesworth, C.J., Mantovani, M.S.M., Rogers, N.W., Turner, S.P., 1999. Petrogenesis and stratigraphy of the high-Ti/Y Urubici magma type in the Paraná Flood Basalt Province and implications for the nature of 'Dupal'-type mantle in the South Atlantic Region. J. Petrol. 40 (3), 451–473.
Peate, D.W., Hawkesworth, C.J., Mantovani, M.S.M., Shukowsky, W., 1990. Mantle plumes and flood-basalt stratigraphy in the Parana, South America. Geology 18, 1223–1226.
Peate, D.W., Hawkesworth, C.J., Mantovani, M.S.M., 1992. Chemical stratigraphy of the Parana lavas (South America): classification of magma types and their spatial distribution. Bull. Volcanol. 55, 119–139.
Piccirillo, E.M., Raposo, M.I.B., Melfi, A.J., Comin-Chiaramonti, P., Cordani, U., Kawashita, K., 1987. Bimodal fissural volcanic suites from the Paraná Basin (Brazil): K–Ar ages, Sr-isotopes and geochemistry. Geochim. Brasiliensis 1, 55–69.
Pinto, V.M., 2010. Condições de formação do cobre nativo, estratigrafia de derrames e geocronologia de basaltos da região de Vista Alegre, Província Magmática Paraná, Sul do Brasil. Doctoral Thesis, Universidade Federal do Rio Grande do Sul, Brazil, 116 pp.
Raposo, M.I.B., Ernesto, M., Renne, P.R., 1998. Paleomagnetism and dating of the early Cretaceous Florianópolis dyke swarm (Santa Catarina Island), Southern Brazil. Phys. Earth Planet. Inter. 108, 275–290.
Reichow, M.K., Pringle, M.S., Al'Mukhamedov, A.I., Allen, M.B., Andreichev, V.L., Buslov, M.M., Davies, C.E., Fedoseev, G.S., Fitton, J.G., Inger, S., Medvedev, A.Y., Mitchell, C., Puchkov, V.N., Safonova, I.Y., Scott, R.A., Saunders, A.D., 2009. The timing and extent of the eruption of the Siberian Traps large igneous province: implications for the end-Permian environmental crisis. Earth Planet. Sci. Lett. 277, 9–20.
Renne, P.R., Ernesto, M., Pacca, I.G., Coe, R.S., Glen, J.M., Prévot, M., Perrin, M., 1992. The age of Parana flood volcanism, rifting of Gondwanaland, and the Jurassic–Cretaceous boundary. Science 258, 975–979.
Renne, P.R., Deckart, K., Ernesto, M., Féraud, G., Piccirillo, E.M., 1996a. Age of the Ponta Grossa dyke swarm (Brazil), and implications to Parana flood volcanism. Earth Planet. Sci. Lett. 144, 199–211.
Renne, P.R., Glen, J.M., Milner, S.C., Duncan, A.R., 1996b. Age of Etendeka flood volcanism and associated intrusions in southwestern Africa. Geology 24, 659–662.
Renne, P.R., Mundil, R., Balco, G., Min, K., Ludwig, K.R., 2010. Joint determination of ^{40}K decay constants and $^{40}Ar^{*}/^{40}K$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}Ar/^{39}Ar$ geochronology. Geochim. Cosmochim. Acta 74, 5349–5367.
Riley, T.R., Millar, I.L., Watkeys, M.K., Curtis, M.L., Leat, P.T., Klausen, M.B., Fanning, C.M., 2004. U–Pb zircon (SHRIMP) ages for the Lebombo rhyolites, South Africa: refining the duration of Karoo volcanism. J. Geol. Soc. Lond. 161, 547–550.
Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet. Sci. Lett. 26, 207–221.
Steiger, R.H., Jäger, E., 1977. Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. Earth Planet. Sci. Lett. 36, 359–362.
Stewart, K., Turner, S., Kelley, S., Hawkesworth, C., Kirstein, L., Mantovani, M., 1996. 3-D, $^{40}Ar–^{39}Ar$ geochronology in the Parana continental flood basalt province. Earth Planet. Sci. Lett. 143, 95–109.
Thiede, D.S., Vasconcelos, P.M., 2010. Parana flood basalts: rapid extrusion hypothesis confirmed by new 40Ar/39Ar results. Geology 38, 747–750.
Turner, S., Regelous, M., Kelley, S., Hawkesworth, C., Mantovani, M., 1994. Magmatism and continental break-up in the South Atlantic: high precision $^{40}Ar–^{39}Ar$ geochronology. Earth Planet. Sci. Lett. 121, 333–348.
Wigand, M., Schmitt, A.K., Trumbull, R.B., Villa, I.M., Emmermann, R., 2004. Short-lived magmatic activity in an anorogenic subvolcanic complex: 40Ar/39Ar and ion microprobe U–Pb zircon dating of the Erongo, Damaraland, Namibia. J. Volcanol. Geoth. Res. 130, 285–305.